Engineering Materials

Akhina H
Thomas Sabu *Editors*

Poly(Vinyl Chloride) Based Composites and Nanocomposites

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Engineering Materials

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Contents

Fabrication of PVC Based Composites and Nanocomposites by Mechanical Mixing

Jiao Zhiwei and He Wei

Abstract Mechanical mixing is a relatively simple technique and operation to physically modify PVC to produce PVC composites with better processing or use properties. In this chapter, the structure, principles, characteristics and applications of the various types of mechanical equipment used in the premixing and blending process in mechanical mixing will be described.

1 Introduction

Polyvinyl chloride (PVC) is widely used in various fields because of its excellent chemical stability, good mechanical properties, excellent electrical insulation and low cost. However, PVC has defects such as poor thermal stability, which starts to decompose when the temperature reaches about 100 °C without heat stabilizers and decomposes faster at higher temperatures; poor photo-stability, which can be caused by UV light and oxygen in the environment; poor toughness and lack of impact resistance. Therefore, PVC must be modified by a variety of additives such as stabilizers, plasticizers, fillers, nanoparticles, colorants or other polymers to obtain better processing performance or use performance of PVC composites.

There are many ways to modify PVC for processing, which can be generally divided into two main categories: chemical and physical methods. Chemical methods are straightforward and effective, and are based on the principle of improving the properties of PVC at the molecular chain structure level. The physical method is a more convenient and effective way to improve the overall performance of PVC without changing its molecular structure by adding various additives or modified substances to the PVC matrix, and then co-blending, filling, and reinforcing them through mechanical equipment. The physical modification process is simple, easy to

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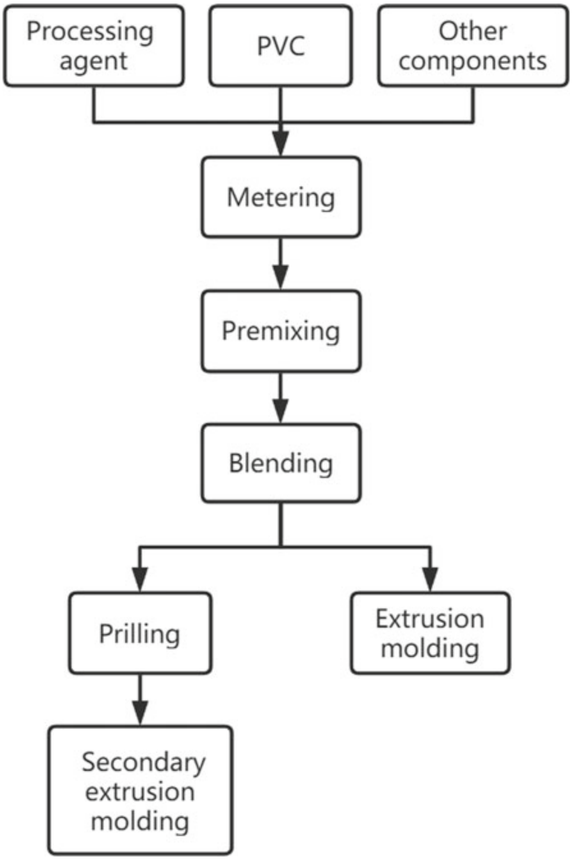
operate, and has outstanding advantages in production applications, and is currently a common processing method. Physical modification is carried out by mechanical mixing.

The process of processing PVC by mechanical mixing method (physical method) is shown in Fig. 1. It mainly includes: metering, premixing, blending, direct extrusion molding or prilling followed by extrusion molding. Common premixing equipment include: screw belt mixer, kneader and high-speed mixer. Common co-blending equipment include: parallel twin-screw extruder, conical twin-screw extruder and planetary screw extruder, etc. In addition, adding layer multiplication units to the mixing equipment can well improve the performance of PVC composites.

Fig. 1 Flow chart of PVC composites prepared by mechanical mixing



2 Premixing and Its Equipment

The first step in the PVC processing is premixing: mixing the PVC raw materials and various modified materials after batching. The process of premixing is not only a simple mechanical mixing between the components, but also the process of mutual friction and collision between the components, and the continuous warming and uniform dispersion of the materials. Premixing, although simple, has a great positive effect on the subsequent processing of PVC, and the quality of premixing directly affects the quality of PVC products. Whether it is a test or industrial production, premixing is indispensable.

2.1 Premixing Principle

Premixing is done in order to mix the ingredients of the components of a defined formulation so that they are uniformly distributed to form a dry mix with high apparent density, good flow-ability, and looseness and dryness. Premixing relies mainly on compression, shear, distribution and displacement [1] and can be understood as two steps: distribution mixing and dispersion mixing.

Distribution mixing: makes the spatial distribution of two or more components change. As shown in Fig. 2.

Dispersion mixing: the physical properties of one or more components are changed during the mixing process, including particle size reduction or dissolution in other components (Fig. 3).

In the premixing process, the two mixes are generally carried out and completed simultaneously, and the change process of PVC and other components of raw

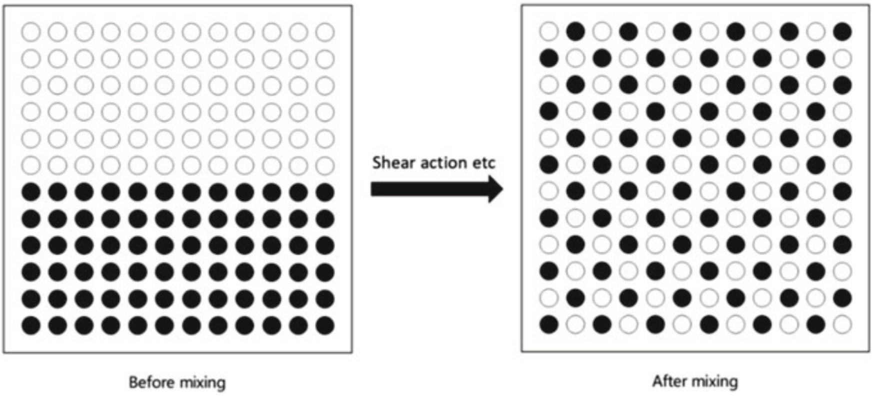


Fig. 2 Schematic diagram of the change in spatial position of the two components before and after distribution mixing

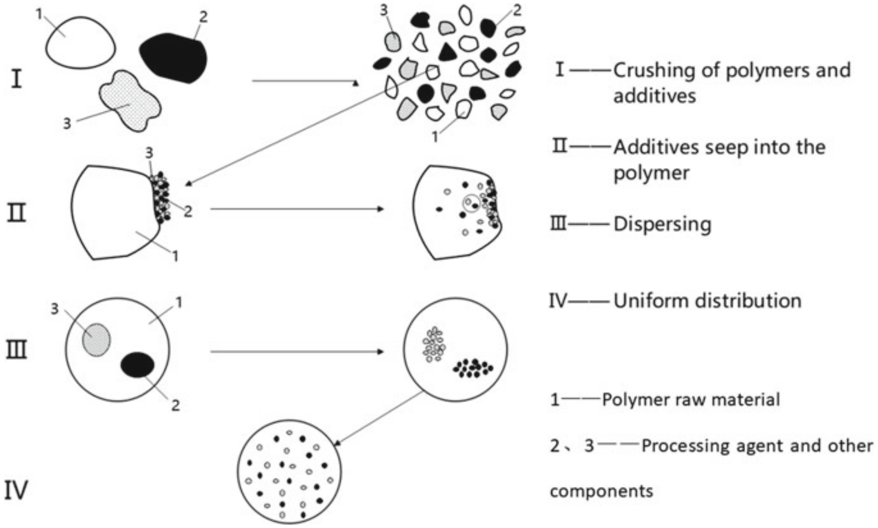


Fig. 3 Dispersion mixing diagram

materials is: particle refinement—recombination—particle size increase—additives absorption—dispersion uniformity [2].

2.2 Premixing Process

The main steps of premixing can be divided into: batching, hot mixing, and cold mixing.

2.2.1 Batching

Batching is strictly according to the requirements of formula components and dosage, using different precision measuring instruments, accurate weighing and proportioning of the various raw materials required for production. The ingredients and dosage of the formula are obtained after many strict tests, too much dosage will increase the cost, too little dosage will affect the performance of PVC products, so if there is a mistake in the dosage process, it will have a great impact on the quality of PVC composites.

2.2.2 Hot Mixing

Hot mixing, refers to the mixture through high-speed stirring friction heat, so that the temperature reaches the PVC softening temperature (about 75 °C) above the mixing process. In the hot mix, the relative changes in the spatial position of the components, and the particles also undergo the process of breaking the particle size decreases and then gradually increases. In order to ensure that the quality of PVC dry mix qualified, the hot mix process must be strictly in accordance with the specified amount of material, the order of material, mixing time and temperature implementation.

After all the raw materials are added to the mixer according to the recipe, the mixer is gradually increased from low speed to high speed. With the rotation of the stirring paddles at high speed, the dry mixer material is sharply dispersed along the inner wall of the machine and moves upward along the inner wall of the mixing chamber, reaching a certain height and then falling back to the center of the impeller due to gravity [3], thus forming a vortex-like motion process. The high speed rotation of the impeller drives the material and material, material and impeller and mixing chamber wall collision, friction and a certain shear effect, the material in this process, the temperature is also increasing, PVC particles gradually become soft expansion, and a certain degree of preplasticization, many components with low melting point (such as lubricants, etc.) will melt and penetrate or adhere to the surface layer of PVC. Under high speed shear, various particles are broken up and refined, and the energy of the surface is rapidly increased and adsorbed on the PVC surface, making the particle size of PVC particles gradually increase, and the material obtains better dispersion and preplasticization. At this time, the material is transformed from solid, single-phase, uneven state to multi-phase, homogeneous state and partial plasticized state. High-speed mixing of conventional PVC materials need to reach the temperature between 110 °C and 120 °C, more than 100 °C is conducive to the drying of materials, too low will affect the uniformity of premixing, too high will lead to the decomposition of the PVC matrix. At the same time to ensure a reasonable hot mixing time, and the material must be cold mixed immediately after the hot mixing.

2.2.3 Cold Mixing

After the end of the hot mixing, the material is quickly put into the cold mixer, through the slow stirring of the mixer and the role of the cooling system inside the cold mixer pot, the material is fully dispersed to cool down, which is cold mixing. The volume of the cold mixer is several times larger than the volume of the hot mixer, and the mixing blades rotate at a lower speed, which can largely improve the cooling efficiency of the material. General cold mix set temperature of about 40 °C, the cooling water temperature setting value will be lower. In actual production, in order to reduce premixing time and increase premixing efficiency, the use of more hot mixer and cooling mixer combination of machines.

2.3 Premixing Effect

(1) So that the components of the raw material can be evenly distributed in space, which is conducive to each component to give full play to their role.
(2) Through hot mixing, the PVC particles undergo a process from the original state to breaking and micro-melting to coagulation and aggregation, thus making the dry mixes obtain a certain preplasticization effect and dispersion.
(3) By hot mixing, the influence of moisture and volatile components in the raw material on the product quality can be excluded to a great extent.
(4) Through the cold mix, on the one hand, can prevent the hot mix after a long time in the case of high temperature storage degradation; on the other hand, can also prevent the material in the cooling process of water absorption and moisture; can also eliminate the impact of static electricity on the dry mix, reduce the "bridge".
(5) After premixing, the overall particle size of the dry mix is large and uniform, which facilitates its stable delivery and yield improvement.

2.4 Premixing Equipment

At present, the commonly used premixing equipment are screw belt mixer, kneader and high-speed mixer, etc. High-speed mixer is commonly used for premixing of PVC materials.

The high-speed mixer is divided into two stages: hot mixing and cold mixing. The materials should be discharged to the cold mixer for cooling, after hot mixing.

The high-speed mixer for hot mixing (Fig. 4) consists of six parts: mixing pot, rotating blades, transmission, spraying device, unloading device and heating device. Its working principle is: the motor through the pulley, reducer box directly driven by the spindle rotation, installed in the spindle with a special shape of the rotating blade followed by rotation, under the action of centrifugal force, the material along the inner wall of the fixed mixing tank rise, in a state of return motion, forming a kind of cyclonic movement, for different density of materials easy to mix uniformly in a short time. The mixing efficiency is twice as high as the general mixing machine. The solid raw materials and processing aids involved in the mixing are put in by the upper inlet, and for the liquid processing aids are sprayed in through the spray head under the pot cover. The mixed materials are discharged from the side discharge port of the mixing tank. In order to adapt to the mixing requirements of certain materials, the equipment is equipped with a heat preservation set, which can heat and keep warm the materials.

The cold mixer (Fig. 5) consists of five parts: mixing pot, rotating blades, transmission device, discharge device and cooling device. It is different from the principle of hot mixing. The hot material entering the cold mixer is gradually cooled by the

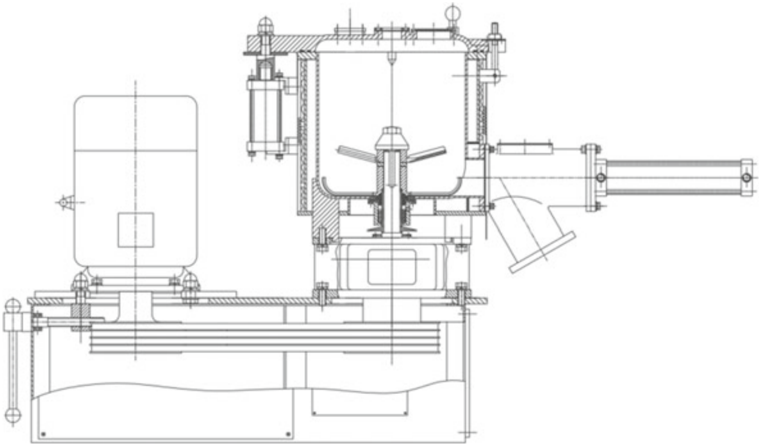


Fig. 4 Structure of hot-mix high-speed mixer

heat absorbed by the cooling water in the wall sandwich of the pot in a more spacious environment and the slow stirring of the rotating blades.

The new high-speed mixer for premixing of PVC composites for industrial use contains the following trends:

(1) Fully automatic operation, hot and cold mixing one high-speed mixer, hot and cold mixing switch promptly and quickly.
(2) Large throughput of PVC dry mix premix can be achieved.
(3) The hot mixer contains a multi-stage mixing tool for frictional heating of the material, which distributes all formulation components and materials uniformly on the PVC substrate.
(4) Cold mixer for high performance cooling. Large cooling area and water circulation system in the tank and lid.

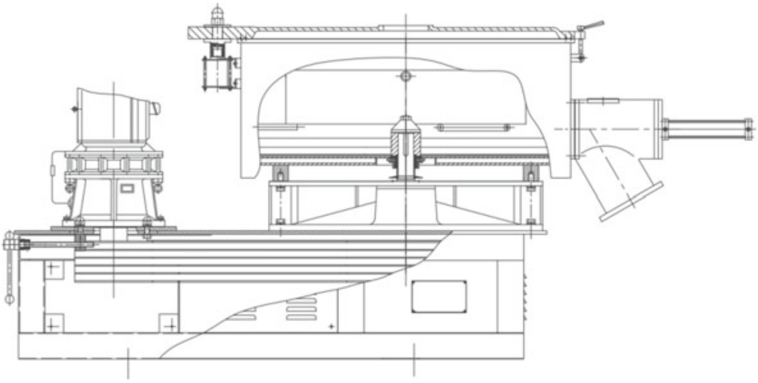


Fig. 5 Structure of cold mixer

(5) Easy to open, easy to clean.
(6) A variety of optional accessories can be adapted to different installation space requirements.
(7) Optimized hybrid tools and drives for energy efficiency.

3 Blending and Its Equipment

PVC raw materials, processing aids and other components are premixed to obtain a uniform distribution, forming dry mixes with high apparent density, good flowability and loose dryness, followed by blending and extrusion pelletizing of the dry mixes. Commonly used screw-type blending equipment is twin-screw extruder and planetary screw extruder, and they will be introduced next.

3.1 Twin-Screw Extruder Introduction

Twin-screw extruder is a polymer processing equipment that can integrate the functions of mixing, melting, conveying and extruding, which is being used more and more widely in the fields of polymer processing and food processing. Its main features include: easy to add material; stable conveying and short residence time; excellent self-cleaning and exhaust performance; excellent blending and plasticizing effect; with forced conveying and calendering effect; low energy consumption and high volumetric efficiency, etc.

3.1.1 Development and Classification of Twin-Screw Extruders

1. Development

As the requirements for polymer processing became more and more demanding, the single-screw extruders initially used for polymer processing were no longer able to meet these requirements, leading to the birth of the twin-screw extruder based on the single-screw extruder. It is not known when and where the first twin-screw extruders were born, but in the 1930s, Roberto Colombo and Carlo Pasquetti in Italy developed a co-rotating twin-screw extruder and a counter-rotating twin-screw extruder for polymer processing, respectively. In 1960, the Austrian company ANGER achieved great success in the extrusion of UPVC with a counter-rotating twin-screw extruder, and since then the counter-rotating meshing twin-screw extruder has become an important part of the extrusion machine field. A few years later, ANGER invented the world's first conical twin-screw extruder. In the late 1960s, modern twin-screw extruders in the true sense of the word began to emerge [4]. For the development of twin-screw extruders, modern meshing co-rotating twin-screw extruders were developed with the polymer processing industry, and modern meshing counter-rotating twin-screw extruders were developed with in the plastic products industry [5].

The twin-screw extrusion process is more complex because of the complex interactions between variables such as fluid flow, heat transfer and chemical reactions, leading to a very difficult study of the extrusion process [6]. In order to solve these problems, a large number of mathematical descriptions and numerical simulations of the extrusion process have been carried out based on experimental studies. Previously, researchers have analyzed both the screw structure and fluid flow by laying the barrel flat. For example, Zimmermann [7] analyzed the geometry of the screw. Armstroff and Zettler [8] published a flow model for the threaded element of a co-rotating twin-screw extruder. Werner [9] published a flow model in the pinch element. Booy [10] first proposed the geometric relationship between the depth of the screw groove and other screw parameters seen when the two screws are fully engaged, which provided a direct and effective theoretical basis for the design of future twin-screw extruders. Later, with the rapid development of computers, numerical simulation analysis became more and more popular in the study of twin-screws. Tadmor [11] studied the effect of non-Newtonian fluids on flow by using the finite element method (FEM) and the flow analysis network method. Lawal [12] and others continued the development by using a more sophisticated finite element method to analyze the effect of factors such as curvature on flow and to obtain the three-dimensional velocity field distribution of the fluid during screw engagement. Since the 1990s, numerous practical and efficient methodological techniques applied to numerical simulation and analysis have facilitated the optimal design of numerous twin-screw extruders.

2. Classification

There are many ways to classify twin-screw extruders [13], mainly by the relationship between screw steering and engagement (Fig. 6).

(1) According to the engagement method

Engaging twin-screw extruder: The distance between the two screw axes is less than the sum of the outer radius of the two screws, because the screw prongs of one screw are inserted into the screw groove of the other screw, so it is called the engaging type. And the engagement is divided into full engagement type and partial engagement (incomplete engagement), the difference between them is whether the top of the screw prongs of one screw and the other screw groove root does not leave any gap (refers to the geometric design, not manufacturing assembly). In addition, the engaging twin-screw extruder is divided into conjugate and non-conjugate. Conjugate means that the screw prongs of one screw and the screw groove of the other screw have similar geometry, and the two are closely matched together, leaving only a small manufacturing and assembly gap, while non-conjugate means that there is a large gap around the screw prongs.

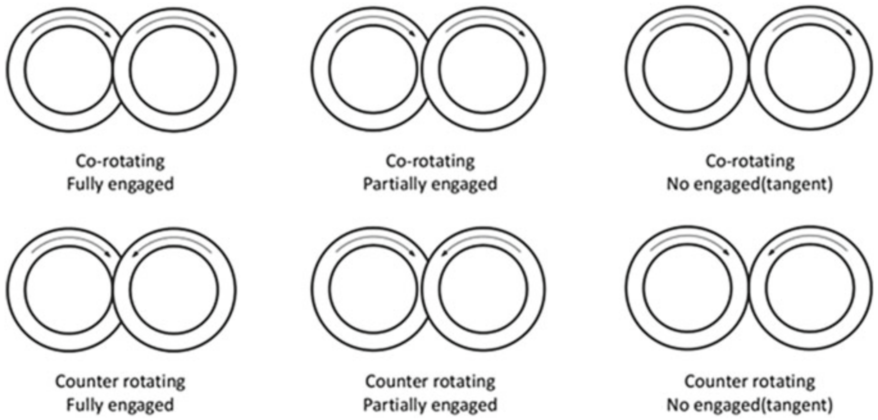


Fig. 6 The relationship between screw steering and engagement of twin-screw extruders

Non-engaging twin-screw extruder: the geometry is characterized by the fact that the distance between the axes of its two screws is at least equal to the sum of the outer radii of the two screws.

(2) According to the engagement zone is open or closed

Open and closed means whether there is a possible passage of the material along or across the screw groove in the screw groove in the engagement area (excluding the clearance left for manufacturing assembly). This can be classified as longitudinal open or closed, transverse open or closed, etc. If the material can flow from one screw to another (there is flow along the screw groove) during the process of conveying in the extruder, it is longitudinal open, and vice versa, it is longitudinal closed. In the engagement area of two screws, if the material can flow from one screw groove of the same screw to another screw groove or from one screw groove of one screw to two adjacent screw grooves of another screw, it is transversely open, and vice versa for transversely closed.

(3) According to the two screw rotation direction

Two screws with the same direction of rotation are the co-rotating twin-screw extruder, while the opposite direction of rotation is the counter-rotating twin-screw extruder.

(4) According to the two screw axis intersection or parallel

If the axes of the two screws are parallel to each other, it is a parallel twin-screw extruder, and if the axes intersect, it is a conical twin-screw extruder.

3.1.2 Structure of Twin-Screw Extruder

1. Overall Structure

   The three major components of the twin-screw extruder are the main machine, the auxiliary machine and the control system [14].

   (1) The main machine includes: (a) Extrusion system, mainly consisting of barrel and screw, which is the key component of the extruder. (b) Transmission system, consisting of electric motor and reduction box, etc., used to drive the screw and provide the necessary torque. (c) The heating and cooling system, which is used to meet the temperature requirements of the material in the molding process.

   (2) The auxiliary machine is composed of head, traction device, shaping device, cooling device, cutting device, winding device, etc.

   (3) The control system includes various electrical components, instruments and actuators, etc., which can realize the automatic control of the extruder for product quality.

2. Screw structure

   The screw is the most important part of the twin-screw extruder, and the screw can be divided into combined type and integral type.

   (1) The combination type is a single unit consisting of several individual spiral elements mounted on a single mandrel through certain design guidelines. The various spiral elements are interchangeable and can be freely combined according to the polymer product process being processed. Screw elements include: shear elements, compression elements, conveying elements, kneading elements, and blending elements. Parallel twin screws are generally used in combination. In Fig. 7, a: threaded element, which is a conveying element; b: kneading block (disc), which is a kneading element; c: toothed disc; d: counter-threaded element, which is a blending element.

   (2) Integral screws, which are machined on the entire metal raw material, directly machine each basic structure. The monolithic type cannot be interchanged between components according to the requirements of the polymer processing process, no adjustments can be made, and the screw is very difficult to machine. Conical twin screws are generally of the integral type.

Fig. 7 Spiral element

3. Main structural parameters

Screw L/D ratio: the ratio of the effective length of the screw to the outer diameter. The larger the L/D ratio the longer the material travels in the barrel, making the blending and plasticizing effect more adequate, the process, the temperature rise can also be more moderate, also provides certain conditions for increasing the screw speed and output.

Drive power: Larger drive power can provide greater torque and speed, giving the material greater shear deformation and extrusion pressure, while generating more shear friction.

Screw speed: The speed of the screw has a direct impact on extruder output, drive power, product quality and machine construction. Increased speed can increase the output, improve the denseness of the extrudate, and enhance the shear blending effect.

Screw torque: high torque is also a major trend in the development of twin-screw extruders, but high torque is limited by the strength of the screw mandrel, the strength of the gearbox and bearing life.

Production capacity: related to the size shape and combination form of the screw, speed, processing technology, material characteristics, head, screw prong clearance, etc.

Twin-screw extruders with high blending performance include: engaging co-rotating parallel twin-screw extruders, engaging counter-rotating parallel twin-screw extruders and engaging counter-rotating conical twin-screw extruders. The next three aspects will be introduced from their screw configuration, working principle and characteristics and applications.

3.2 Engaging Co-rotating Parallel Twin-Screw Extruder

3.2.1 Screw Configuration

The screw of an engaging co-rotating parallel twin-screw extruder is divided into the following zones according to their different functions: solids conveying section, melt mixing section, melt conveying section, exhausting section, homogenizing section and metering section, as shown in Fig. 8. Different functional zones require different screw elements to be combined to achieve the function of each zone. According to the material to be processed and the process requirements, the combination of screw elements is reasonably configured to achieve the optimal design of the screw configuration.

Solids conveying section: a functional area of the twin-screw extruder used to add materials and realize the conveying of materials along the extruding direction while carrying out a certain mixing effect. This section of the screw groove is not completely filled, the material is solid state, the screw is generally configured from large to small lead positive threaded elements (role: conveying materials and axial pressure), to improve the fullness of the screw groove.

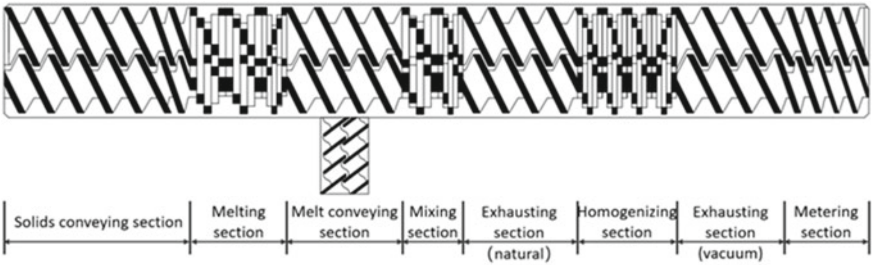


Fig. 8 Screw functional section

Melt mixing section: the functional area of the twin-screw extruder in which the melting of the material occurs by means of external heating and the mechanical energy provided by the internal screws, with the aim of making the material completely molten and homogeneously mixed. In this section the material is melted by the heat generated by the barrel heating, the extrusion and shearing of the kneading block elements and the friction. At the end of the melt mixing section, flow restricting elements, such as reverse threaded elements, are required to increase axial mixing and improve melt quality.

Melt conveying section: The solid phase remaining in the front enters this section and is completely melted into melt. The screw configuration in this section is mainly a positively threaded element with a large lead, a low degree of filling and no pressure build-up, so that additional materials can be added in this section by side or vertical feeding. Afterwards, they are fed together into the mixing section consisting of kneading blocks for dispersion and distribution mixing.

Exhausting section: This section of the screw configuration also has several positively threaded elements with large leads, less fullness, and a large free surface area to remove gases from the melt and mixing of the material, as well as gases brought in by the side feed, which facilitates the installation of exhaust ports for venting/de-volatilization. The gases are separated from the polymer melt by diffusion, and the separated gases are removed only when they are in the outer surface layer of the melt.

Homogenizing section: the mixture in the section of the kneading block shear action of the components for homogenization, so that the components are mixed evenly.

Metering section: the material in this area is completely filled, build pressure at the same time to consider reducing the temperature rise, in addition, the screw configuration in this area will affect the stability of the discharge, need to be considered comprehensively, generally using positive threaded elements, the thread lead and the number of heads will affect the ability to build pressure.

3.2.2 Working Principle

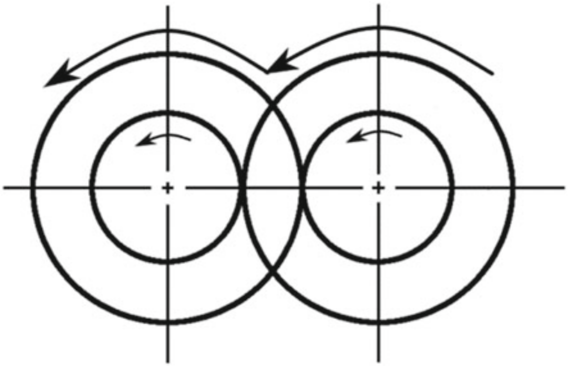
1. Conveying principle

In the process of blending and processing, the material is added from the charging port. Inside the barrel, the material is conveyed by the shearing and compression of the screw with "∞" shaped holes, melting and homogenizing the material, and finally the extrusion and pelletizing or molding process of the composite material is realized. The flow of material is shown in Fig. 9.The twin screws rotating in the same direction have opposite velocities in the engagement position. One screw has to pull the material into the engagement gap, while the other screw pushes the material out of the gap, so that the material is transferred from one screw to the other. This change in speed and the larger relative speed in the engagement area is very beneficial to the blending and homogenization of the material.

2. Blending principle

The polymer melt has an "∞" shaped flow process as it flows and advances through the screw, and this shear flow is the main mode of distribution mixing. Bigio and Erwin [15, 16] found experimentally that the blending efficiency of twin-screw extruders is not only related to the shear flow but also to the surface renewal, which is extremely low if there is only shear flow but no surface renewal. The main place where surface renewal occurs is the engagement zone between the two screws. Relying solely on common threaded elements to provide mixing is inadequate for most mixing processes, and the kneading section, consisting of kneading blocks, plays a major mixing role in an engaging co-rotating twin-screw extruder. When the melt enters the kneading section, the flow channel narrows so that the kneading section is completely filled, and the frequent surface renewal of the kneading section in the engagement area between the left and right screws greatly promotes the blending effect. Kneading element top and barrel wall clearance between the small, shear strength is very large, is the main place of dispersion mixing. Kneading element of the pinch piece between the staggered arrangement and reverse threaded section can change the fluid flow direction to increase the blending effect.

Fig. 9 Schematic diagram of material flow in a engaging co-rotating parallel twin-screw extruder



Based on conventional kneading block elements, new blending elements have also made some progress in recent years. The emergence of new screw elements has largely improved the blending quality and extrusion performance of twin-screw extruders. Examples include hexagonal elements [17], VCR elements [18], toothed disc elements [19], shear ring elements [20], and corrugated thread elements [21].

2. Melting principle

The melting process includes material warming, phase change, flow and blending, and may also be accompanied by complex chemical reactions. The complexity of its process and the uncertainty of its study have been the difficulties of research in the field of polymer processing: first, it is difficult to model the melting process; second, it is difficult to grasp the melting law; third, it is difficult to solve the melting process. Chang [22] studied the melting process of screw by numerical simulation to reveal the melting principle of engaging co-rotating parallel twin-screw extruder.

(1) Melting process: The melting of solid particles starts near the inner wall of the barrel, and the particles away from the barrel are melted last. On the screw, the particles on the thrust surface of the screw prongs are the first to melt, while the particles in the middle of the screw groove and at the drag of the screw prongs are the last to melt. The melt temperature has the greatest influence on the time required for melting and the displacement of the melt. The melt time and displacement are shorter in the engagement zone compared to the inside of the screw groove.
(2) Energy source: In the conventional threaded component area, the energy is mainly generated by thermal convection between the melt and the barrel and viscous dissipative heat generation. The latter accounts for 10–30% and is related to the screw speed and melt density. The heat increases with increasing speed. The heat decreases slightly with increasing density.
(3) Screw element structure influence: Knead block element compared to conventional threaded elements, it can make the material temperature rise more rapidly and more melting ability. The thicker the kneading plate and the larger the misalignment angle, the more beneficial to the melting of materials, but this will increase the power of the extruder.

3.2.3 Extrusion Characteristics and Applications

1. Extrusion characteristics

    (1) Good blending effect. In the threaded element (including the screw groove and engagement area) shear rate distribution is more uniform, by facilitating the distribution mixing. In the kneading section shear rate is high and blending is strong, which is conducive to dispersion mixing. However, the higher shear will be accompanied by a large amount of heat, so for the blending and processing of such heat-sensitive plastics as PVC, the requirements for heat stabilizers are higher.

(2) Good self-cleaning performance. Due to the small gap in the engagement area, the threads and grooves at the engagement have opposite velocity directions. Therefore, has a high shear speed and good self-cleaning effect, can scrape off any accumulated material adhering to the screw, so that the residence time of the material is very short.
(3) High speed operation. Its speed can reach up to 300–600r/min, with higher output.
(4) With lower conveying characteristics and general conveying efficiency, its pressure building capacity is relatively low and cannot be used for direct extrusion of products, so it is mainly used for material blending and granulation.

2. Applications

(1) Direct cleaning, coagulation, extrusion, dewatering drying and granulation of materials containing certain moisture, solvents and other monomers.
(2) Filling, co-blending, reinforcing, venting, coloring, homogenizing and granulating of polymers containing various additives.
(3) Dispersion mixing for powder coatings, masterbatches, catalysts, paints, food, pulp, etc.
(4) Blending and forming of special materials.

3.3 Engaging Counter-Rotating Parallel Twin-Screw Extruder

3.3.1 Screw Configuration

The engaging counter-rotating parallel twin-screw extruder has the same configuration as the co-rotating screw: a conveying zone, a melt zone and a metering and homogenization zone, and the screw elements on the constituent screws are basically the same in shape and function. The difference is that the screws turn in opposite directions when the two screws are properly engaged (Fig. 10).

Fig. 10 Engaged counter-rotating parallel twin screws

3.3.2 Working Principle

1. Conveying principle

The two screws are symmetrical but rotate in different directions, and because they are theoretically fully meshed, the path of the material spiral forward on one screw is blocked by the screw prongs of the other screw. In the solids conveying area, it is not possible to form a "∞" type movement similar to that of the co-rotating twin screws, but the material is conveyed forward in the form of a nearly closed "C" shaped chamber (Fig. 11). With the continuous rotation of the screw, the material from one "C"-shaped chamber axially into another "C"-shaped chamber, the material for positive displacement conveying, the mechanism is also known as the pumping mechanism. However, usually in order to blend the material, the design leaves a certain amount of clearance between the outer diameter of one screw and the root diameter of the other screw, so that the material can pass through. When the material passes through the radial gap between the two screws, it is subjected to strong shearing, stirring and calendering action.

2. Blending principle

First of all, assuming that the counter-rotating meshing is complete and closed both longitudinally and horizontally, then according to the conveying principle described above, the material is enclosed in each "C" shaped chamber and conveyed forward by a positive displacement mechanism. There is no material exchange between each "C" shaped chamber, and the residence time is short, thus the blending effect is not good. However, in actual production, the screws of the engaging counter-rotating parallel twin-screw extruder are modified and there are assembly errors, so gaps exist. The existence of the gap increases the material leakage to a certain extent and reduces the positive displacement conveying capacity, but this increases the blending capacity.

For a partially engaging counter-rotating parallel twin-screw extruder with a larger gap, the screw is not completely closed to each other, and the leakage flow is larger

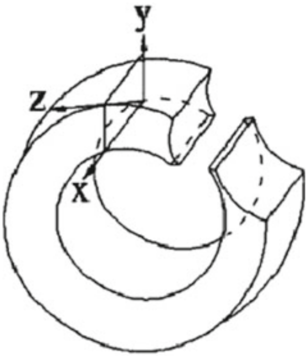


Fig. 11 "C" shaped chamber

and the pressure building capacity is weaker, so that it can work at a higher speed. When such an extruder works, most of the material is dragged through the screw engagement area to form the calendaring gap, which improves the shearing and stretching of the material and makes the material fully blended, but reduces the forward conveying capacity and pressure building capacity. Therefore, by changing the screw geometry parameters to adjust the shape and size of the gap, the balance between conveying and blending of the extruder can be adjusted.

3. Melting principle

Screw rotation in different directions is similar to the melting principle in the same direction. The material is firstly heated by the hot barrel, and as the temperature rises, the friction factor between the material and the surface of the screw increases, and when it increases to a certain degree the material is dragged into the gaps. In the gap, the particles are sheared, compressed and stretched, resulting in plastic deformation, so that the mechanical energy is highly dissipated, and the heat generated to melt the material quickly. After passing through these gaps, the material that has become molten will rotate with the screw. Due to the dragging force, other residual solids are also brought into the melt zone by the melt.

3.3.3 Extrusion Characteristics and Applications

Compared with the same direction extruder, the engaging counter-rotating parallel twin-screw extruder has insufficient blending effect, self-cleaning ability and uses a lower speed due to its conveying principle. However, it is used for direct extrusion of products because of its good forward conveying ability, strong pressure building ability and high pumping pressure, which is suitable for powder processing. Because of the deficiency compared with the same direction, it makes it more suitable for extrusion molding of heat-sensitive plastics like PVC.

Compared to full meshing, partial meshing extruder can also be used for blending and extruding pelletizing PVC composites because of its good blending performance. It is not suitable for the production of PVC profiles due to its large intermittency, poor self-cleaning performance and weak pressure building ability.

3.4 Engaging Counter-Rotating Conical Twin-Screw Extruder

3.4.1 Screw Configuration

The basic structure of the engaging counter-rotating conical twin-screw extruder (hereinafter referred to as conical twin-screw extruder) is the same as the common parallel twin-screw, the main difference lies in the screw and the matching barrel,

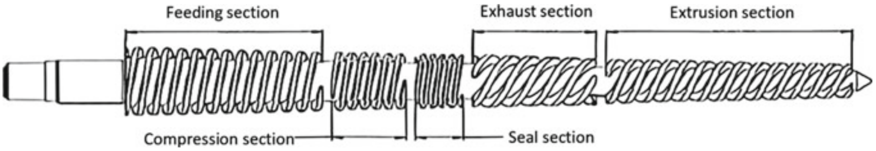


Fig. 12 Common conical twin screw

where the two axes intersect when the conical twin-screw is meshed. The screw can be divided into several segments according to different functions. The screw configuration is shown in Fig. 12. In the picture, we can see a very obvious exhaust section compared with the parallel twin-screw. The design of this section is mainly through the increase of the volume of the screw trough, which can discharge the gas generated during the blending of materials, so as not to affect the quality of extrusion granulation or products.

3.4.2 Working Principle

The conical twin-screw extruder is also a type of engaging counter-rotating twin-screw extruder, so it works on the same principle as the engaging counter-rotating parallel twin-screw extruder, forming a “C”-shaped chamber for forward conveying, as well as shearing, stirring and calendering at the meshing gap. The blending and melting principles are also basically the same, so we won’t introduce them too much here.

The biggest difference between the conical twin-screw extruder and the engaging counter-rotating parallel twin-screw extruder is that the volume of the “C” shaped chamber decreases from the charging section to the discharge section. In the charging section, a larger volume of powdered material can be added, and as the screw becomes smaller, the material is compressed and melted. In the discharge section, because the screw diameter is small, the screw circumferential speed is small, so the shear rate of the material here is lower, and the frictional heat generated is also small, which is very suitable for processing heat-sensitive materials.

3.4.3 Extrusion Characteristics and Applications

The conical twin-screw extruder not only has the advantages of closed screw groove cavity, forced material conveying, narrow material residence time distribution, better self-cleaning, and suitable for powder processing, but also has the following unique advantages:

(1) The large diameter of the charging section and the large volume of the screw groove make it easy to process a larger volume of loose density powder. High

screw strength and high system stiffness are conducive to the arrangement of thrust bearings and gears.

(2) The barrel and screw area of the charging section is large, which is conducive to heat transfer and easier to achieve heating and melting of materials.
(3) The diameter of the screw gradually decreases along the extrusion direction, and the material gradually gets compressed, so that the screw groove fills the material faster and ensures continuous and gentle plasticization of the material.
(4) Discharge section screw diameter is small, the circumferential speed is smaller, resulting in lower shear and less frictional heat.
(5) The smaller diameter of the screw in the discharge section results in less torque being applied to the screw under the same pressure and frictional resistance. The screw is also subjected to less back pressure at the same production capacity.

Due to the above characteristics, the conical twin-screw extruder is particularly suitable for the processing of powdered PVC, especially for the direct extrusion of UPVC dry-mixed powder into plastic products such as pipes, plates, sheets, rods, films and profiles. It is also suitable for the extrusion and granulation process of modified composite materials of PVC.

3.5 Planetary Screw Extruder

Extrusion equipment for polymer processing mainly includes single-screw extruders and twin-screw extruders. However, it has been continuously found that conventional single and twin-screw extruders have insurmountable disadvantages: Conventional single-screw extruders have weak blending function and poor ability to process powders. Twin-screw extruders are more difficult to overcome the low back pressure of the screw. Due to the poor thermal conductivity of the polymer, the material in each screw groove of a large diameter single or twin screw extruder is not heated evenly, thus resulting in less uniform plasticization. Therefore, the continuous improvement of single and twin-screw extruders has been accompanied by the development of new multi-screw extruders, of which the planetary-screw extruder is one of the most successful. The concept of planetary screw extruders has been developed for more than four decades and has become increasingly important in hybrid processing processes, as it rationalizes the production sequence by saving critical processes [23].

3.5.1 Structure of Planetary Screw Extruder

The planetary screw extruder is composed of four parts: the charging system, the temperature control system, the plasticizing and melting system and the mechanical drive system (Fig. 13). In contrast to conventional single-screw extruders and twin-screw extruders, planetary-screw extruders have a planetary section, which

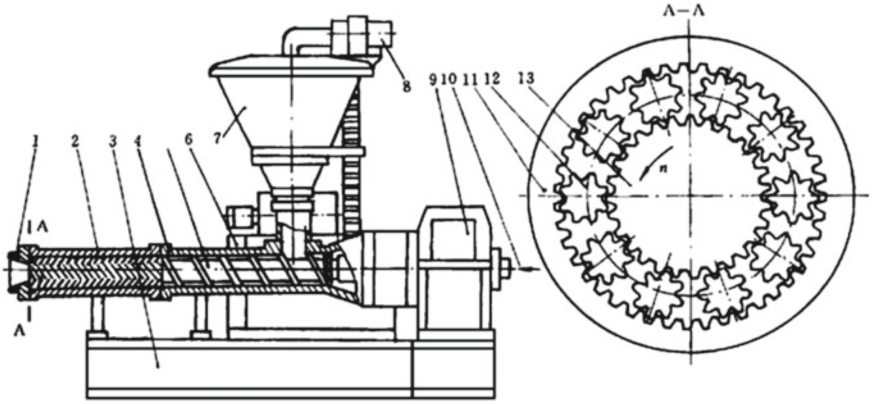


Fig. 13 Planetary screw extruder

allows efficient plasticization with melting and blending functions [24]. The planetary section consists of a main screw, several planetary screws (ranging from 7 to 18, depending on the screw diameter and application), and a barrel with open teeth on the inner wall. The mechanical strength requirements of this section are very high due to the meshing action of the planetary screw systems with each other. Therefore, the planetary section is generally made of high-strength alloy steel. Due to the axial force during operation, the planetary section barrel end is equipped with a thrust ring.

The plasticizing system of a planetary screw extruder consists of a charging section and a planetary section. The charging section is the same as the charging section of a single screw extruder. The single screw of the charging section is connected to the main screw of the planetary section and driven by the same power. Generally, the main screw of the planetary section is connected to the single screw by spline. When the main screw rotates, it drives the planetary screw, which not only rotates around the main screw, but also rotates around its own geometric center. The clearance between the planetary screw and the main screw and barrel is generally 0.2–0.8 mm, and the material enters this clearance during the operation of the planetary section, which also reduces the wear caused by the contact between the planetary screw and the main screw and barrel.

The charging system of the planetary screw extruder is usually a forced feeding device or a quantitative feeding device, thus achieving starvation feeding and at the same time preventing the material from bridging in the hopper.

The temperature control system of the planetary screw extruder includes the water cooling circulation system of the barrel in the charging section and the oil heating circulation system in the planetary section. They work together to ensure excellent temperature control performance. The planetary section can be set into multiple oil circulation circuits, which are heated by separate oil heaters, so that different planetary sections can be realized with different temperatures.

3.5.2 Working Principle

Firstly, the material is added to the charging device, and usually a metal detector and a metal separator are installed above the hopper to remove the metal impurities from the material. This is because the spiral teeth in the planetary section are very easy to be damaged by metal impurities. After entering the feed section of the planetary screw extruder, the material is conveyed to the planetary section, where it is compacted and preheated. The material is transported forward by the screw teeth with a helix angle of 45° in the planetary section, while the material is rapidly melted by heat transfer and by the heat generated by the extrusion, kneading and shearing of the screw teeth. The material is extruded into thin layers in the planetary section, so that the planetary screw extruder has a large heat exchange area. The spiral angle of 45° of the spiral teeth can force the material to flow forward, thus the self-cleaning performance of the planetary section is good. The number of spiral teeth engaged in the planetary section is quite large and proportional to the main screw speed and the number of planetary screws, which shows the great strength of various effects in the planetary section.

When a planetary screw extruder is operating, periodic disturbances are introduced into the screw groove of the main screw of the planetary segment by means of the planetary screw motion boundary conditions. This can be achieved: In the homogenization section, so that the fluid interface to achieve stretching, folding, re-stretching effect, so that the material in the process of advancing to the mouth mold cross, overlap, dispersion, and chaotic convection, to promote the fluid local re-circulation, so that the material particles produce an irregular trajectory, improve the polymer dispersion, distribution mixing. In the melting section, the relative motion between the planetary screw and the main screw is used to break the solid bed and further utilize the chaotic reinforcement of solid particles to achieve dispersed melting and enhanced heat transfer, thus saving energy and reducing consumption [25].

3.5.3 Extrusion Characteristics and Applications

1. Extrusion characteristics

    (1) The flow channel has no dead angle and strong self-cleaning effect. The self-sweeping action between the planetary screw, main screw and barrel makes it have good self-cleaning ability, and the material will not stagnate and decompose. It is easy to change materials, which is very beneficial to PVC processing.

    (2) Large heat exchange area. The main screw of the planetary section and the inner meshing sleeve are heated by oil, and this part is in direct contact with the material. The heat exchange area of the machine is the sum of the surface area of the main screw and the inner surface area of the inner sleeve, so the heat exchange efficiency is very high.

(3) The material is exchanged in the form of a thin film for heat exchange. This method also allows for high heat transfer efficiency and precise control of the material temperature by adjusting the heat medium temperature.
(4) High number of engagements. The meshing effect is usually proportional to the rotational speed of the screw. The high number of meshes results in a high number of shears, extrusions and stirring of the material, which in turn improves the blending effect of the material. This model has good dispersion mixing and distribution mixing ability, and can be used for co-blending and filling modification.
(5) Short material residence time. The residence time of the material in the planetary screw extruder is shorter than that of the single screw and twin screw extruders for the same extrusion volume. This can largely reduce the decomposition of the material.
(6) Good exhaust performance. The planetary screw extruder usually works in the state of full material, the free surface area of the material is large and frequently renewed, which facilitates the exhaust of gas. For two-stage machine, the extrusion volume of two-stage machine can be adjusted by adjusting the screw rotation of two-stage extruder to achieve stable extrusion. It is also possible to set up an exhaust chamber, which can reduce the material bubbling or lack of material caused by exhaust.
(7) Low production energy consumption, good economic efficiency, high yield and high applicability.

2. Applications

By far the most used applications of planetary screw extruders are still various PVC blending and granulation, calender feeding, calendering and coating. For the blending and processing of PVC composites, the extruder is required to be able to extrude a melt with high plasticization quality and homogeneous blending, and to ensure a short melt residence time and effective venting, and the planetary extruder is well suited to meet these requirements. Therefore, planetary screw extruders are particularly suitable for extrusion pelletizing or molding of PVC composites.

In addition to this, planetary screw extruders can be used for:

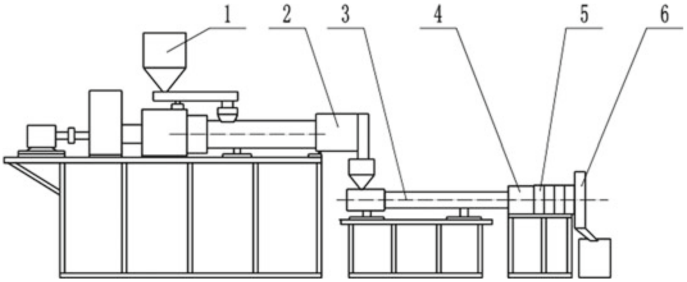
(1) Homogenization of polymer melts and dispersion and distribution mixing of reinforcing components.
(2) Wood plastic composites, including the production of wood fiber filled materials and wood fiber reinforced materials.
(3) Rubber products industry, widely used for rubber compounding, desulfurization and processing of scrap.
(4) PET extrusion processing, good exhaust and degassing properties make it possible to use it for drying and extrusion processing of PET products.
(5) It can also be applied to the production of adhesives, color masterbatches, powder coatings, etc.

4 PVC High-Performance Regulation Technology

PVC powders microscopically exhibit primary particles (about 1 micron) and aggregation of primary particles (secondary particles, about 3–10 microns). During the processing of PVC composites, it is necessary to add a quantitative amount of plasticizers to the system in order to improve the toughness and elasticity of the products. On the one hand, plasticizers can reduce the inter-molecular forces of PVC, improve the mobility of PVC molecular chains, reduce its glass transition temperature, and improve the deficiencies of toughness and elasticity [26]. On the other hand, PVC products containing plasticizers will undergo a certain degree of migration and volatilization of the plasticizers in the process of use, which will have a greater impact on the performance and lifetime of the products [27] and, more seriously, will cause damage to humans [28]. This has become one of the major factors limiting the application of PVC composites.

In order to solve the above defects of PVC products, Beijing University of Chemical Technology has proposed a high-performance preparation method of PVC based on the regulation of processing. By using a special flow field generated by special proprietary equipment during processing to open and conformationally regulate the primary particles of PVC, the action of "ball-like" primary particles evolves into the intertwining and physical cross-linking of extended molecular chains, thus achieving the purpose of strengthening the properties of PVC resin. It is also because of the dense and orderly molecular chain arrangement of the regulated PVC that the migration of plasticizers can be inhibited to a large extent. The schematic diagram of the equipment used for PVC high-performance regulation is shown in Fig. 14, including the extruder, micro-nano layer multiplier unit, extrusion exit die and other auxiliary devices, the key to which is the micro-nano layer multiplication unit. The principle of micro and nano layer multiplication [29] is shown in Fig. 15.

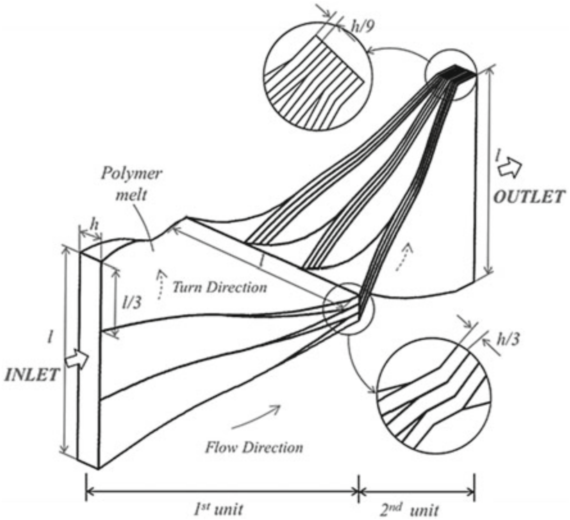
Micro-nano-layer extrusion technology is a new processing method. This technology uses layer multiplication units to divide the material into hundreds or thousands of micro-layer structures, and the melt is subjected to repeated shear and tensile stresses, and the number of layers of micro-layers is continuously increased and the



1-Planetary screw extruder 2-Converter 3-Melt pump 4-Transition block 5-layer multiplier 6-Cutter

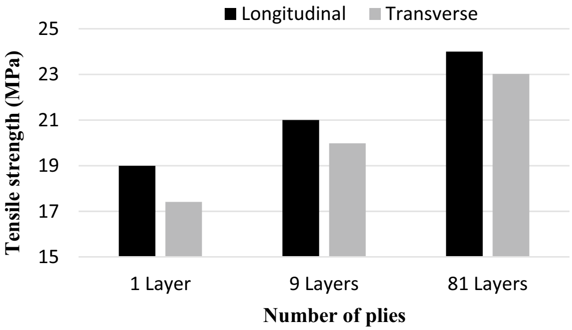
Fig. 14 Micro-nano layer multiplication extrusion device

Fig. 15 Schematic diagram of the layer multiplication unit



thickness of a single layer is continuously reduced through the process of layering and stacking. Eventually, PVC materials with alternating arrangements of up to thousands of layers and thicknesses of micrometers or even nanometers per layer can be prepared [30]. In Fig. 15 we can see two layer multiplication units in series. The polymer melt, which starts as n layers, enters the layer multiplication unit from the inlet, divides into 3 equal parts perpendicular to the flow direction, and each part continues to flow forward and rotates by 90°, becoming thinner and wider. At the interface, the melt converges into n × 3 layers with the same thickness and width as at the inlet. Each time the melt passes through a layer multiplication unit its layer number increases by a factor of 3. When the melt passes through k units, its layer number becomes n × 3^k layers. The melt is subjected to strong shear along the flow direction in the process of diversion → torsion → dilation → convergence cycle. The multiple shearing effects further improve the blending effect and high performance of the polymer.

Fig. 16 Tensile strength of PVC specimens with different number of layers in longitudinal and transverse directions



Figures 16 and 17 show the results of tensile testing and elongation at break testing of 1 layer (without layer multiplier), 9 layers (by two-section layer multiplier), and 81 layers (by four-section layer multiplier) PVC specimens for parallel to the extrusion direction (Longitudinal) and perpendicular to the extrusion direction (Transversal), respectively. It can be seen from the figure that as the number of layer multipliers increases and the number of layers of PVC specimens increases, the changes in tensile strength and elongation at break in both longitudinal and transverse directions are consistent and are increasing, and the longitudinal properties are better than those in transverse directions. Figure 18 shows the test results of water vapor transmission rate of PVC specimens with different number of layers. The higher the number of layers in the figure, the lower the water vapor transmission rate.

Figure 19 shows the results of plasticizer volatilization stability test in hot air in PVC specimens with different number of layers. From the figure, it can be found that the higher the number of layers of PVC specimens, the lower the volatilization loss rate under certain temperature conditions.

Combining the above experimental results, it is possible to verify the enhancement of PVC materials by the micro-nano-layering technology. The crystalline properties of PVC are improved and the tensile strength and elongation at break are increased. It is also because continuous shear improves the arrangement of PVC chains and the

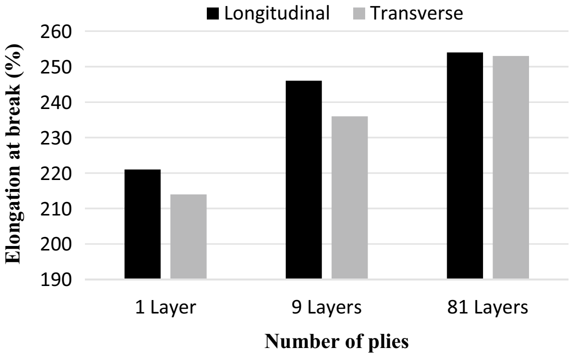


Fig. 17 Elongation at break of PVC specimens with different number of layers in longitudinal and transverse directions

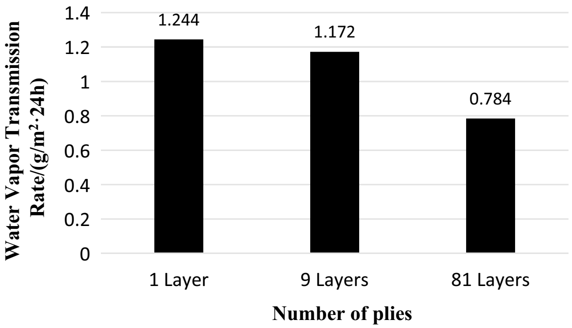
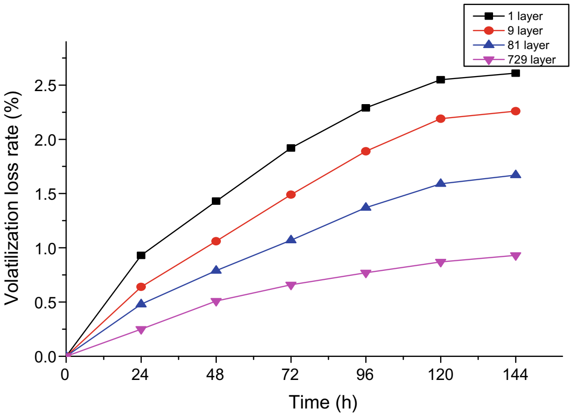


Fig. 18 Water vapor transmission rate of PVC specimens with different number of layers

Fig. 19 Volatilization loss rate of plasticizer in PVC specimens of different layers at different temperatures in hot air



distribution of plasticizers, and the compact and dense molecular chains limit the migration and precipitation of plasticizers to a large extent.

5 Conclusion and Outlook

The molecular structure of PVC resin is such that it has poor heat stability and high viscosity in the molten state when processed. Therefore, when processing PVC resins, processing aids or other polymers and nanoparticles must be added accordingly to make PVC composites. In order to reasonably control the melt viscosity, processing temperature, blending time, plasticization quality, product performance, etc., and to meet the production and processing process. This is the mechanical mixing method for the preparation of PVC composites, which in short means that PVC and other modified materials are co-blended or filled by specific machinery to obtain the desired good processing and material properties of PVC.

The first step of mechanical mixing method is premixing, including batching, hot mixing and cold mixing. Premixing to get a uniform distribution, high apparent density, good fluidity, loose and dry mixes. Commonly used equipment for high-speed mixer.

The dry mixes obtained by premixing needs to be further heated by (screw type) blending equipment, melt blending, extrusion pelletizing or extrusion molding. The machinery and equipment used in this process include: engaging co-rotating parallel twin-screw extruder (mainly for PVC composite extrusion and granulation), engaging counter-rotating parallel twin-screw extruder (mainly for PVC composite extrusion and molding), conical twin-screw extruder and planetary screw extruder (extrusion and molding are available).

This chapter also introduces a preparation method for high performance of PVC, which achieves a significant improvement of mechanical properties and plasticizer migration inhibition properties of PVC products.

With the development of processing technology, there will be more PVC mechanical mixing preparation methods, through which the composite material properties will be well improved.

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Fabrication of PVC-Based Composites by Freeze-Drying and Their Reinforcement Using Nanomaterials

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1 Introduction

Commercially manufactured in 1933 and patented in 1913, polyvinyl chloride (PVC) with chemical formula of $(C_2H_3Cl)_n$ became one of the most commonly used vinyl polymers on globe. Thanks to its durability, competitive chemical and mechanical properties, and flame retardancy, this polymer had a wide spectrum of potential additives that can change its features due to its high polarity. Of all manufactured plastics, PVC accounts for 12–25% that is only preceded in rank by polyethylene and polypropylene (PP). Table 1 presents the key specifications of commercial PVC.

PVC resins can be classified into two groups: unplasticized rigid which are produced by molding or extrusion, and plasticized flexible which are added generously (up to 50%) to enhance elasticity and softness of products. Non-plasticized PVC is widely utilized in plumbing, construction, fencing, automotive parts, and seating. The plasticized PVC is widely applied in electrical cables insulation, medical devices, waterproof clothing and in flooring. Nanocomposites belong to a class of materials where structure falls under at least one dimension at the nanometer scale,

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Table 1 Main properties of PVC [1]

Specifications	
CAS number	9002-86-2
Molecular weight of repeat unit	62.5 gr/mol
Mass percentage of CI	56.7
Glass transition temperature	70.8–114.8 °C
Tensile strength	56.6 MPa
Density@ 20 °C	1.391–1.431 gr/cm^3

defined as less than 100nm. Nanocomposites provide premium features in terms of heat retardancy, mechanical tolerance, and barrier resistance against CO_2, N_2 and O_2 as well as premium UV stability due to their anisotropic layered silicate structure [2]. Example, adding a scant amount of clay minerals portion (10% in mass) can enhance features of the polymer matrix and maintain silicate layers at even dispersion within it. The clay also optimizes the interface interaction that occurs between silicates and PVC.

In power cable industry, plasticized PVC provides a suitable electrical insulator for medium- and low-voltage power cables. However, PVC has many disadvantages such as poor durability, brittleness and low thermal stability that can be overcome by adding heat stabilizers. In addition, PVC-based cables were reported to show varying degrees of deteriorated insulation and degradation caused by repetitive stress during operation. To avoid these pitfalls and enhance its performance, nanosized materials are introduced to produce nanocomposites or nanodielectrics. The solid or liquid nanodielectrics have been widely searched lately with the main concern being the interface that connects impeded nanoparticles with the polymer matrix. There are different types of additives that can be integrated through preparation of PVC-based nanocomposites:

I. Clay minerals montmorillonite (MMT)

This clay is a key component of Bentonite and belongs to the Smectite group with a distinguished layered structure with the following formula $\{(Al_{1,67}Mg_{0,33})Si_4O_{10}(OH)_2\}Na_{0,33}.\ nH_2O$ with a negative charge on the clay's layers that attracts alkaline earth cations present in the inter-layer vicinity. Each single MMT layer comes at 200-600nm of length.

II. Organic modification of MMT

MMT is usually processed separately prior to addition to thermoplastics. This modification involves replacement of interlayer cations by a cationic surfactant to reduce surface energy of the layers and enhance its wettability. These features improve MMT's capability with the PVCs matrix as the interlayer area is increased by the organic tails of Al ions.

III. Layered silicate nanocomposites

One method to produce layered silicates as a filler in PVC nanocomposites involves using ε-caprolactam to intercalate MMT after polymerizing it to poly-caprolactam along with the addition of phosphoric acid and 6-aminocaproic acid.

Freeze-drying, also known as lyophilization, is a drying process where the polymer is first frozen to be solidified. Afterwards, upon heating, the solvent that is mixed with the polymer is evaporated by sublimation. During sublimation, the liquid state is not passed by present water and/or solvent. Therefore, 90% of the product's water content is lost. Freeze-drying is unique as a drying process because dehydration occurs when the product is frozen and less active under vacuum thus limiting oxidation effects. Another advantage of freeze-drying is that the product maintains its original morphology and texture via immobilizing the polymer after adding the appropriate amount of water as a common solvent. This step prevents denaturation of morphology caused by heating processes usually used in drying.

Many polymers have been composited including graphene. In deep freezing process, graphene oxide (GO) nanocomposites, for example, are mixed immediately with liquid nitrogen (N_2) and kept at 0.02 mbar vacuum at −70 °C [3].

2 Effects of Freeze-Drying on PVC Structures

The processing technique and conditions govern how nanoparticles are dispersed in the nanocomposite film. Freeze-drying is a reliable technique that produces uniformly grained powders which can be later processed to very high densities. This method has been widely applied in preparing reactive Al_2O_3, Fe_2O_3, and hydroxyapatite powders. In comparing evaporated and freeze-dried hot processed-composites based on poly (S-co-butyl acrylate) strengthened by nanocrystals prepared from wheat straws, showed that these composites were less homogenous and displayed variation in the concentration of nanoparticles between the lower and upper sides of the nanocomposite film [4].

Recent studies conducted on freeze-dried cellulose nanocomposites (CNCs) as a filler to polymer matrices showed, using Fourier transform infrared spectroscopy (FTIR), that CNCs are similar to nanocomposites prepared originally from cellulose nanocrystals and natural rubber (NR) latex [5]. The FRIR spectra showing the structure of the NR matrix and for the CNCs (Fig. 1) mixed with CNC_{SH} (NR5% weight).

Nanoparticles have received a great deal of attention recently thanks to their unique properties in terms of catalytic activity strength, sensing ability and good charge mobility. Noble Pt and Pd have been lately researched as metal nanocomposites due to their excellent catalytic activity and stability and with unique selectivity to hydrogen gas. To overcome their low conductivity, gas sensors based on reduced GO (rGO) reinforced with Pt or Pd nanoparticles are fabricated. These nanocomposites enjoy a high conductivity large, surface area, and they are specifically selective

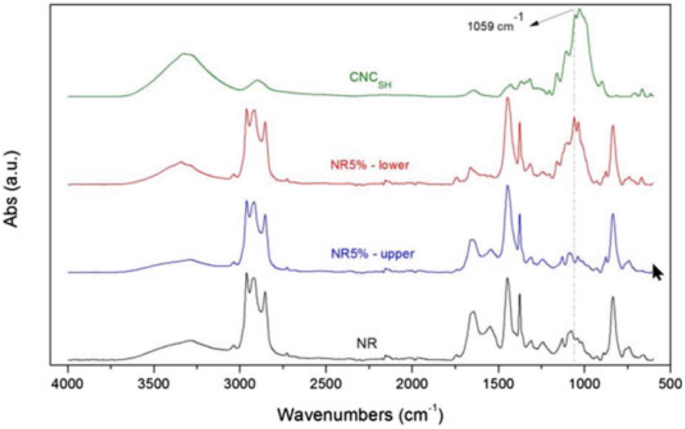


Fig. 1 FRIR spectra showing CNC$_{SH}$, neat NR, and upper and lower NR5% (Adopted from [5])

for Pd and Pt toward hydrogen. The structure of Pt-rGO nanocomposites prior and after freeze drying shows excellent sensing performance towards hydrogen at low temperature.

To produce polymers' nanocomposites using freeze drying, the polymer's aqueous suspension (i.e. dried cellulose nanocrystals) is subjected to solvent exchange (i.e. 85vol% in DI water), frozen at −32 °C. Afterwards, the polymer is freeze dried at −20°C [6]. Indeed, freeze-drying changes the morphology (Fig. 2) of many mixed polymers such as polylactic acid cellulose nanocrystal nanocomposites.

The morphology and structure of Pt-rGO nanocomposites are assessed using SEM. The images in Fig. 3a, b clearly shows that freeze-dried nanocrystals, using a temperature of −50 °C for 48 h, are dispersed evenly on the rGO surface.

In the case of prevulcanized Na$^+$-MMT aerogels by adding natural rubber (PNR), the impact of freeze-drying process on the final composites is reflected in terms of

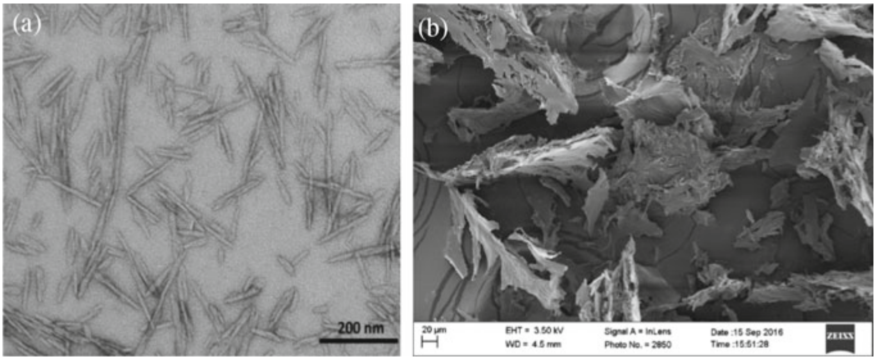


Fig. 2 **a** Scanning electron microscope (SEM) image of pure CNCs and **b** CNCs produced from 10% suspension solution followed by freeze-drying (Adopted from [6])

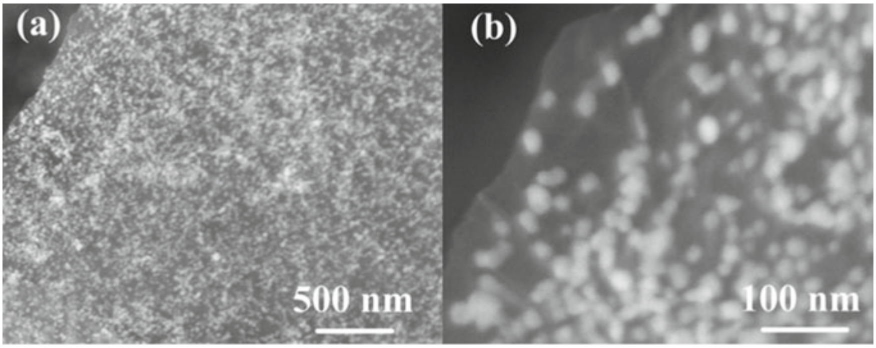


Fig. 3 SEM (**a**, **b**) and TEM (**c**, **d**) images of the Pt@rGO nanocomposite [7]

XRD-images (Fig. 4). The polymer chains intercalation into the interlayer space was examined at the range of 2θ = 1–10°. At 2θ = 7°, the Na$^+$-MMT product showed a well-defined 001 reflection. This reflection, corresponding to a basal spacing of 1.25 nm, is expectedly distinct from the PNR composites where the 001 reflection was reduced due to the dilution impact.

However, the basal spacing recorded for PNR/M1, PNR/M2, PNR/M3, PNR/M5, and PNR/M7 were 4.30, 4.19, 4.76, and 4.88, respectively reflecting an increment in the basal spacing. This increment is attributed to the high intercalation displayed by the polymer chains where the dispersion technique used caused silicate layers to be uniformly distributed within the rubber matrix. In the case of SEM images, Fig. 5, the Na$^+$- MMT aerogel showed a unique lamellar structure that resembles ice crystal morphology.

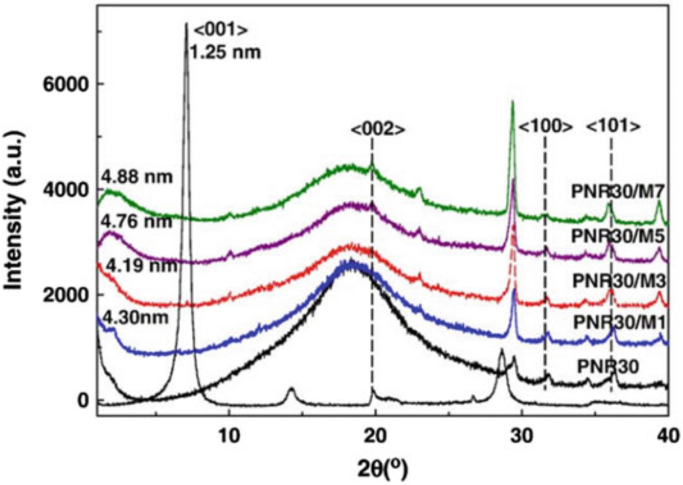


Fig. 4 X-ray diffraction patterns of freeze-dried Na$^+$-MMT composites [8]

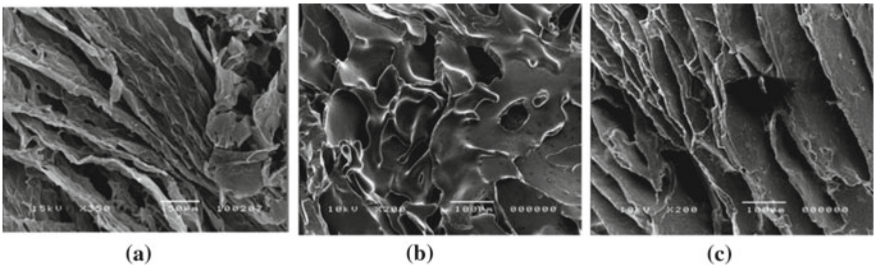


Fig. 5 SEM images of **a** freeze-dired Na^+- MMT, **b** PNR/M1, and **c** PNR/M5 [8]

In the case of the composite where 1 part per hundred of rubber (1phr) to the Na^+-MMT, the lamellar morphology was not achieved. However, when the concentration of rubber was increased to 5 phr, a regular layered morphology was observed with clear layers of NR. The morphology of nanocrystals prepared from CNCs is largely dependent on the drying method used in manufacture. The CNCs are usually obtained by oxidizing cellulose fibers or mixing with strong acids. Not only the CNCs are biocompatible for health puposes (i.e. surgeries to replace broken structures), but they are also biodegradable and highly advantegeuos for maintaining a sustainable envirnment.

In an experiment to study the impact of freeze-drying on the structure of CNCs, the CNCs nanoparticles were prepared and later frozen at −50 °C overnight. Afterwards, the frozen polymer aerogel was then subjected to freeze-drying using a special freeze-dryer (i.e. −52 °C, 0.05 mbar) for 2–3 days.

The CNC large flake morphology (N100μm) formed by slow cooling is shown (Fig. 6). The freeze-drying technique, unlike spray drying, caused ice crystals to grow and lead to CNC aggregation. The water is crystallized slowly, and the nucleates of ice crystals dominated the sample's bulk. Thus, is becomes easy for the CNC nanoparticles to be pushed away from the region where the ice crystals are dominant. Therefore, CNC nanocomposites, processed by freeze-drying become dense and agglomerated and they start to collide with each other.

3 Changes in Characteristic Properties of Freeze-Dried Structures

Since nanocomposites provide the advantages of lightness and smaller space storage in addition to durability, research has much been directed towards enhancing these features using freeze drying. For instance, MMT can be prepared in the form of aerogels with bulk densities that do not exceed 0.01–0.1 g cm^{-3}. The freeze-dried Na^+-MMT particles are easily aligned and sheared producing distinguished lamellar structures. In addition, after subjecting to vacuum sublimation, these structures become

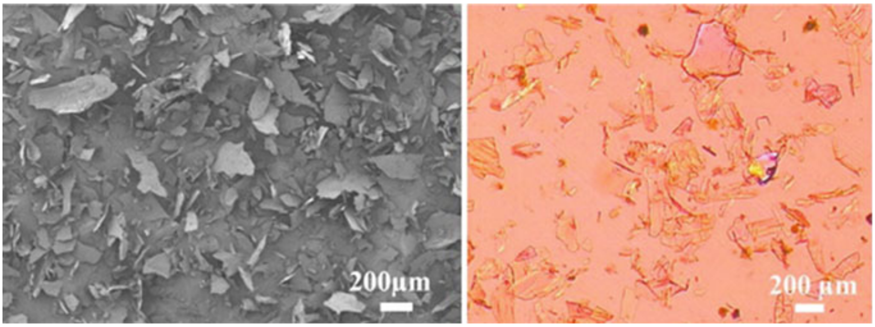


Fig. 6 Images of the freeze-dried CNC SEM (left) and PLM (right) [9]

very light in terms of density. However, Na^+-MMT aerogels tolerateless mechanical stress and are relatively fragile, therefore, the addition of a polymers into the aerogel improves its mechanical strength and enhances its foam-forming structures that are even more tolerant to heat and mechanical stress. Many organic polymers were mixed with the aqueous suspensions first, followed by gel formation and freeze drying. These include case in, poly(vinyl alcohol) and poly(ethylene imine) that resulted in lighter densities (0.05–0.15 gr/cm).

Na^+-MMT aerogel composites can be prepared with a polymer component, prevulcanized natural rubber (PNR), and then be subjected to freeze-drying to produce Na^+-MMT aerogel/PNR that is lighter than rubber itself due to their lighter densities (Fig. 7). Na^+-MMT dispersion was vigorously mixed with latex that was prevulcanized at 70 °C for 30 min. Aqueous dispersions were frozen at − 80 °C freezersubjected to freeze-drying at −108 °C and vacuumed (b0.1 mbar) to sublime the ice.

As shown in Fig. 8, the addition of Na^+-MMT dispersion to the polymer (PNR), increased the maximum torque (Dmax), significantly at 5 and 7 phr loading. However, only a minor effect was observed in regard to the optimum cure time (t90) compared to original PNR.

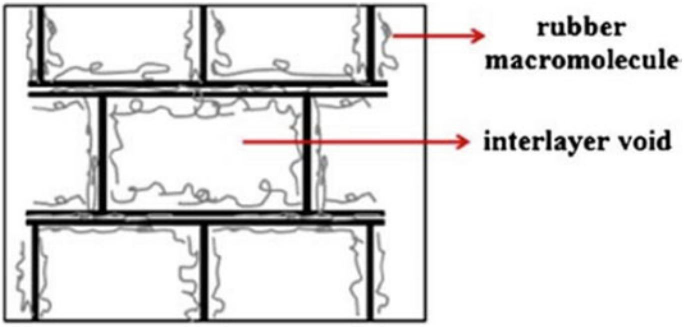


Fig. 7 Na^+-MMT aerogel/PNR composites [8]

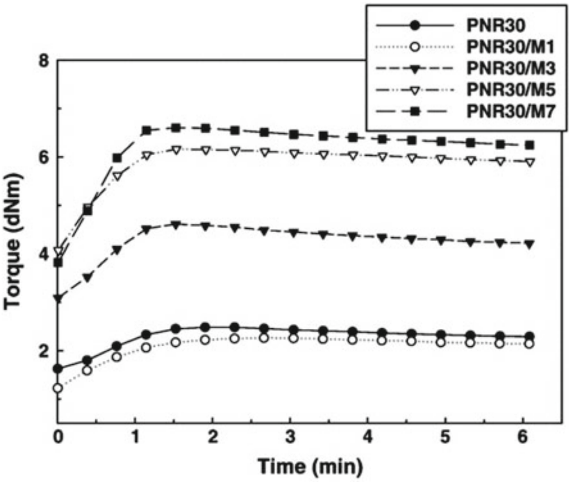


Fig. 8 The rheological profile of PNR and its nanocomposites obtained at 150 °C [8]

The rheometric data were used to extract the kinetics parameters including activation energy (Ea) and specific rate constant (K). To understand the rheometric data and the kinetics of polymers, the following equations are explained:

$$\ln(D_{max} - D_t) = -kt + \ln(D_{max} - D_{min}) \tag{1}$$

$$K(T) = K_0 \exp(-E_a/RT) \tag{2}$$

where E_a is the activation energy, K(T) is the first order rate constant at a given temperature T, D_t and D_{min} are the torque values at a given time and time zero, respectively. At 150 °C, the PNR shows a linear ln (($D_{max} - D_{min}$). When the Na^+-MMT freeze-dried dispersion is added to create Na^+-MMT/PNR nanocomposites, the K value in increased by the thermal energy abundance for the cure effect. Further, the Na^+-MMT addition to the polymer increased E_a value from 46.9 to 76.8 kJ mol^{-1}. This reflected that a larger quantity of E_a was necessary to cure nanocomposites. The Na^+-MMT addition caused the adsorption of the curing agents and blocked the PNR chains movement (Fig. 9).

When polyelectrolyte hydrogels are and compared to chitosan-poly(ɤ-glutamic acid) porous hydrogels that own the same composition are freeze-dried, the value of applying additive manufacturing principles to hydrogels.

The chitosan-polyɤ-glutamic acid (CS-ɤPGA) hydrogel was freeze dried at −20 °C for 24 h and then kept at 50 °C, 0.04 Torr for 72 h. As shown in Figure (dd), the swelling properties of the polymer that was freeze-dried show similar swelling degree curves characterized by achieving the maximal value within 30 min of immersion. This curve also shows a persistent plateau for 20 days later [10].

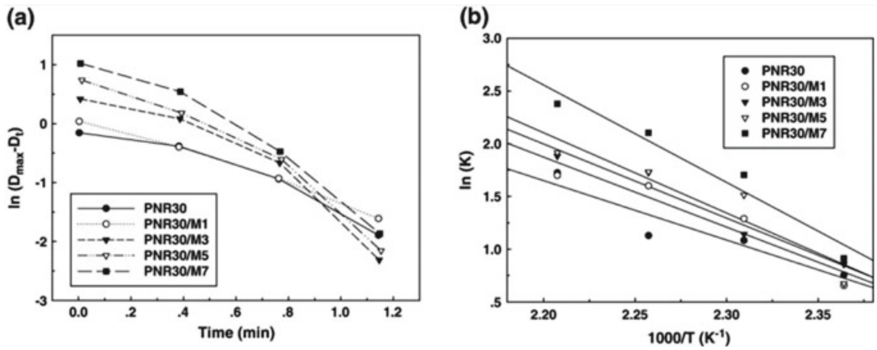


Fig. 9 **a** ln (Dmax–Dt) versus time and **b** Arrhenius plot of lnK versus 1000/Tversus [8]

The elasticity and equilibrium of CS-ɣPGA depend on many factors including charge density, cross-linking degree, microporosity of the polymer's network and the ionic strength of its surrounding medium. The PEC charged groups lead to weaker swelling capability and higher stiffness once the ionic strength is increased. Indeed, the swelling equilibrium of CS-ɣPGA hydrogel is maintained by balancing two driving forces: the inter-network osmotic pressure caused by the mobile counter ions surrounding the fixed charged groups and the network's elastic.

As shown in Fig. 10, the CS-100-mCS-100) hydrogels demonstrated higher swelling degree compared to PEC hydrogels (freeze dried mPEC and PEChydrogels). This may be attributed to the crosslinking effect that occurs between ɣPGA and the CS. Further, mPEC hydrogels demonstrated a lower swelling degree compared to PEC hydrogels processed by freeze-drying driven by the different porosity of the PEC constructs.

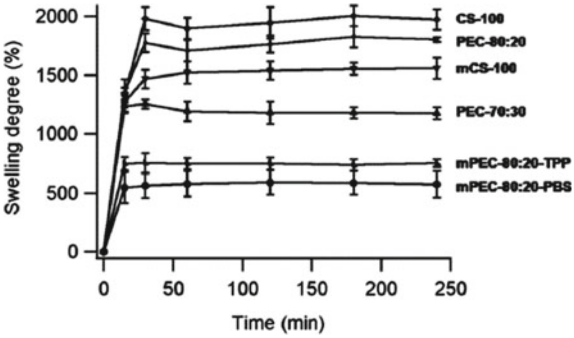


Fig. 10 Swelling kinetics of freeze-dried PEC (CS-ɣPGA) [10]

4 Mechanical Properties of Freeze-Dried PVC Nanocomposites

Using freeze-drying in PVC resins production was earlier reported [11] using cellulose fibers as filler and reinforcing material to support the PVC nanocomposites. During this process, avoiding cellulose fiber aggregation was a main challenge as fibers are susceptible to drop in their reinforcing properties upon mechanical stress application. In addition, the compatibility difference between the hydrophobic PVC and hydrophilic cellulose causing its easy wettability was another barrier. To overcome these challenges, many solutions can be utilized including dispersing cellulose fibers in the matrix and the PVC in an aqueous suspension. This prevents the cellulose matrix aggregation.

Other attempts to enhance the unique features of PVC are to insert different nanoparticles withing different matrices. When silica (SiO_2) was inserted, a drop in the ε_r and tanδ of PVC nanoparticles by 25% and 39%, respectively was observed, compared to pure PVC [12]. Further, mechanical properties such as elasticity and durability to stress as well as showing less degree of elongation were reported.

The SEM images of pure PVC, Fig. 11a, the absence of impurities or air bubbles which is vital for measurement of the dielectric properties of the film. However, (b) reflects the uniformed spherical aggregates with 3% vinyl-TiO_2 added to the polymer and shaped into PVC/TiO2 nanocomposites.

Nanomaterials are often added to polymer mixes to enhance their mechanical and thermal properties. For instance, Steel is enhanced by mixing with epoxy graphene nanocomposites to reduce its corrosive property. Glass fibers have been improved by using carbon nanotubes (CNT) (Abotet) leading to better mechanical tolerance. Graphene nanocomposites also improved the tensile strength (TS) of PVC composites (Fig. 12). Indeed, the highest TS was recorded for the graphene with 2% weight compared to all other composites. The proper adhesion and interaction between the graphene-glass fiber and the PVC becomes optimum under this concentration. In addition, nano-graphene becomes dispersed with low agglomeration [13].

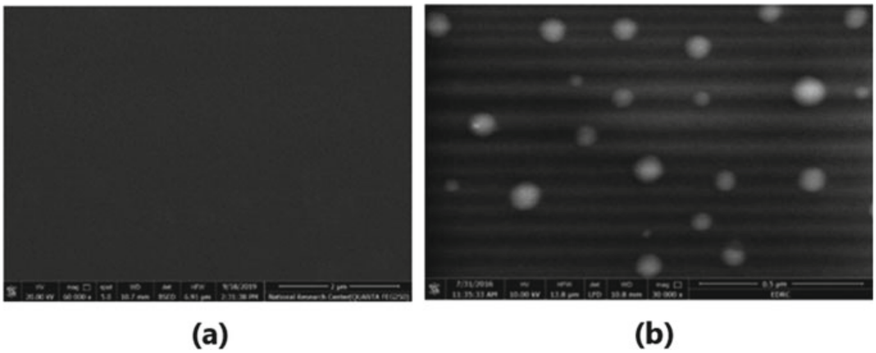


Fig. 11 SEM images of **a** Pure PVC, **b** PVC + 3% vinyl-TiO_2 nanocomposites [12]

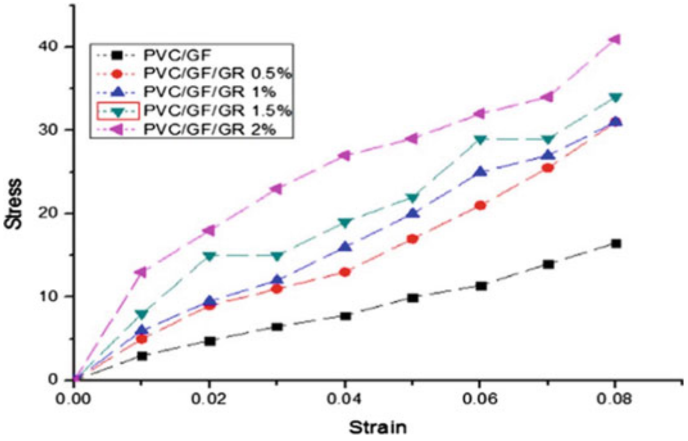
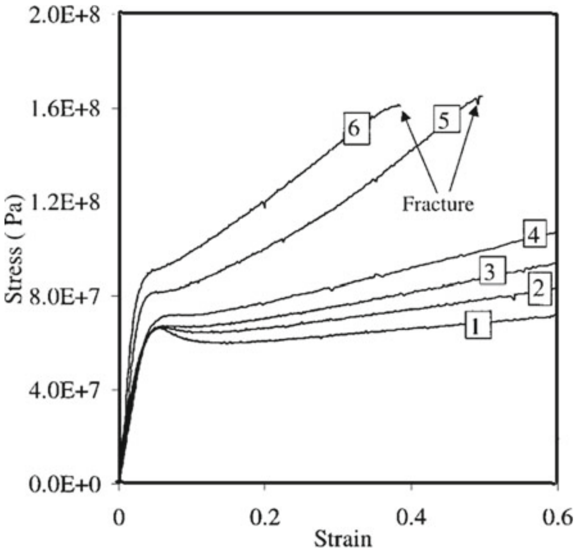


Fig. 12 Stress strain curve for the developed nanocomposites [13]

Freeze drying facilitates the regulation of aerogel particles and pore size distribution. It also aligns the orientation and shape of the aerogel. The mechanical features of freeze-dried PVC were thoroughly examined [14]. The PVC emulsion was mixed with cellulose whiskers and then freeze-dried. The resultant powder was mixed with di-ethylhexyl phthalate, tin stabilizer, a stearic acid lubricant, and mixed at 180 °C for 3 min. A final step of hot pressing was followed at 200 °C for 3 min. To test mechanical tolerance of the PVC-cellulose whiskers (12.4% vol) mix, a compression test was performed using an Instron 8561 machine (Fig. 13).

Fig. 13 The compression tests performed on PVC mixtures with varying added volumes of whiskers [14]



The yield strength and compression modulus increase proportionally with the content of cellulose whiskers in freeze-dried PVC while the compression peak drops. The higher degree of hardening noted upon the addition of whiskers as well as whitening compared to pure PVC what does not whiten at all. When the whisker content exceeded 6.6% by vol, the PVC started to fracture. However, the deformed PVC totally recovered after being kept for 24 h at room temperature, or 15 min at 70 °C even for strain levels that exceeded 100%.

To better understand the mechanical behavior of non-freeze-dried polymers, TiO_2-PVC nanocomposites were fabricated with chemically functionalized TiO_2 using different agents for coupling (amino and vinyl types). The coupling agents, different in their chain length and surface tension, improve the dispersion of the nanoparticles and thus enhance their mechanical and electrical properties (Fig. 14) [15].

Freeze-drying was compared to spray drying and spray freeze drying in terms of mechanical properties on cellulose nanocrystals (CNC) [9]. The microstructure strongly depends on drying method applied during manufacturing. When CNC powder was prepared, the suspension was refrigerated at −50 °C overnight. The frozen suspension was freeze-dried using liquid nitrogen (−52 °C and 0.05 mbar).

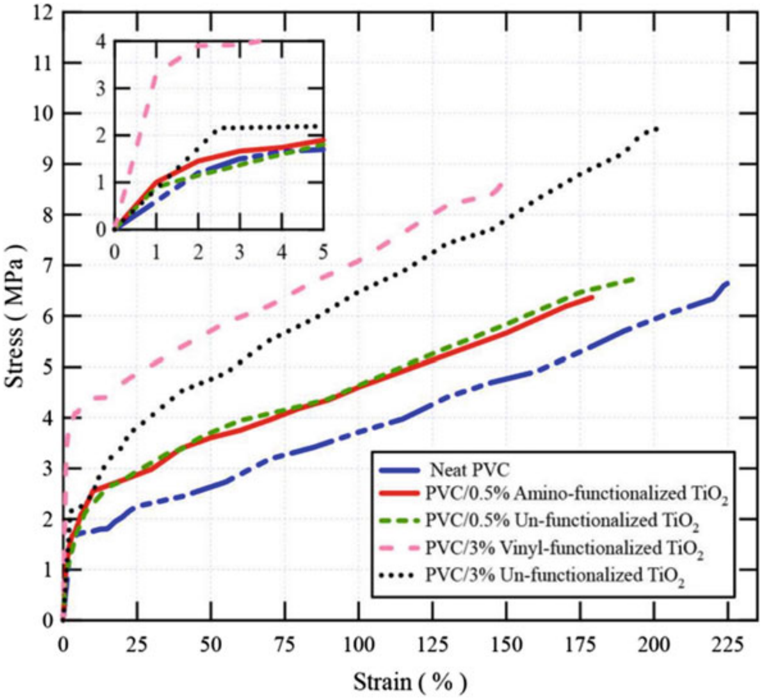


Fig. 14 The stress–strain behavior of pure PVC and PVC/unfunctionalized, vinyl-and amino functionalized TiO_2 nanocomposites [16]

The freeze-dried CNC were mixed with PP as a matrix polymer. To test the mechanical strength of the CNC-PP (CNC-PP) mixture, compression molds were utilized. The tensile performance was tested for the CNC-PP nanocomposites using MTS Universal Tensile Testing machine using a crosshead speed of 5 mm/min.

As shown in (Fig. 15), there was no significant difference between tensile modulus (TM) of neat PP and CNC-PP-5, whereas the CNC-PP-2-5 showed higher tensile strength TS (20%) compared to the former two. In addition, the modulus of CNC-PP-2-5 had 43% values compared to PP. In fact, spray-dried CNC agglomerates addition to PP did not enhance its modulus, thus encouraging its use in industry due to higher stiffness. The elongation capacity (E) of the CNC was lowered upon reinforcement with the polymer. The nanofiller addition reduced the viscosity of the polymer matrix, while it improved the elasticity. The CNC agglomerates intensified the brittleness due to stress concentration.

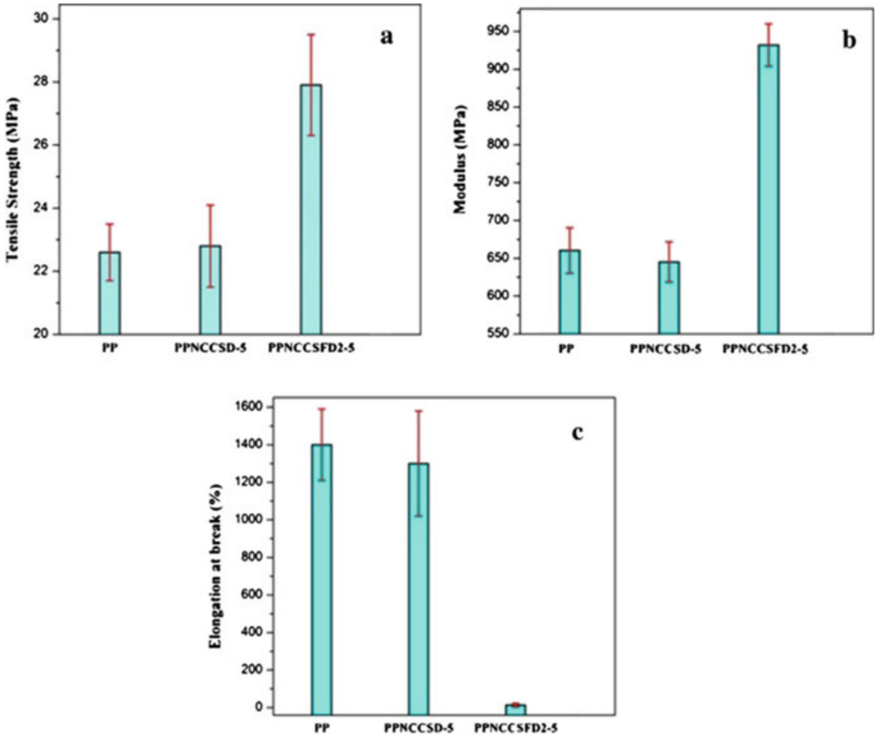


Fig. 15 The curves of TS, TM and E for PP, PPCNCSFD2-5, and PPCNCSD-5 [9]

5 New-Generation of Composites Using Flakes of Graphene

Graphene, as the most well-known member of the 2D materials family, exhibits mechanical, optical, and chemical capabilities that are not found in any other 3D materials. With the use of various graphene production processes, these properties can be shaped during the manufacturing process. Mechanical exfoliation, epitaxial growth, and chemical vapor deposition (CVD) are examples of these processes.[1] Graphene, despite its many advantages, has a number of drawbacks that prevent it from being widely used in industry. The most crucial is that it is currently physically impossible without a carrier in the form of other material [17].

Graphene without a substrate has yet to be realized, despite the development of numerous methods for its functionalization, including covalent and non-covalent methods. As a result, there is a need to research and develop a remedy to this limitation, which may lead to new applications for this intriguing material. The oxidized form of graphene flakes produced as a colloid in Hummer's process could be used as an intermediate product. Depending on the desired qualities of the finished product, numerous variations of this process are now used. The oxygen groups in the GO molecule make for appealing active sites for easy functionalization processes.[2] The employment of chemical compounds with at least two functional groups capable of interacting with, for example, hydroxyl group oxygen, may result in spatial cross-linking of GO powder.

Graphene-based polymer nanocomposites have been the topic of intense research among researchers all over the world since their discovery. Due to its ability to disperse in various polymer matrices and its extraordinary chemical and physical properties,[3] graphene has been used as a viable and inexpensive filler for polymer nanocomposite. If graphene is appropriately incorporated, it can significantly improve the physical properties of host polymers at extremely low loadings.[4] Because Graphene is a new material with extraordinary physicochemical properties that has been exploited in various fields of research.[5,6] Graphene derivatives are widely used in the manufacture of polymer nanocomposites as high-performance nanofillers. The goal is to improve interfacial adhesion between the polymer matrix and the reinforcing filler.

GO has recently gained a lot of attention as a viable precursor for graphene and graphene-based polymer nanocomposites. The emphasis is on the fabrication of polymer nanocomposites containing GO or its allotropes as a filler, with an emphasis on improving composite characteristics for various applications. Because of the presence of these functional groups, GO sheets are very hydrophilic, allowing them to disperse easily in water and form stable colloids. GO sheets can only be distributed

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[1] https://www.sciencedirect.com/science/article/abs/pii/S1385894716309615.

[2] https://www.sciencedirect.com/science/article/abs/pii/S1773224717305063.

[3] https://www.degruyter.com/document/doi/10.1515/ract-2016-2648/html.

[4] https://www.sciencedirect.com/science/article/abs/pii/S0003267015013707.

[5] https://www.sciencedirect.com/science/article/abs/pii/S1387700321006365.

[6] https://link.springer.com/article/10.1134/S1023193518120078.

in aqueous conditions, which is incompatible with organic polymers due to their hydrophilic nature. There are several key factors to consider in the fabrication of polymer nanocomposites to take advantage of the structure and physical properties of graphite derived carbon materials such as graphene, GO, chemically reduced rGO or thermally reduced GO (TRGO) or functionalized graphene sheets (FGS): degree of dispersion, orientation, and interfacial adhesion. Contact angle measurements were used to quantify the solid surface energy (SE) of composite films. The impact of graphene as a nanofiller in various polymeric systems such as PVC, polystyrene (PS), polycarbonate (PC), polyurethane (PU), polyethylenetrephthalate (PET), polyaniline (PANI), polyvinylidene fluoride (PVDF), Nafion, etc. has been studied with interest to develop high-performance graphene-based nanocomposites for a wide range of applications [18].

PVC was chosen as the host material because it is one of the most widely used commercial polymers, with a wide range of uses in the material sector, including flexible and rigid plastic moulds, pipes, electric cables, fibres, films, and laminates [19]. Because of its many desirable features, such as low cost, good processability, chemical stability, biocompatibility, and low flammability, it is one of the most essential and commonly used thermoplastics in the construction and automotive sectors. The combination of unique characteristics of GO and the polymer's superior processability could lead to enhanced polymer nanocomposites with novel physicochemical features. It is critical to have molecular level dispersion in the polymer matrix for efficient reinforcing in polymer composites. To achieve molecular level colloidal dispersion, we dispersed both GO and PVC in Tetrahydrofuran (THF).

Playing with the type of synthesis method and synthesis parameters, recently, researchers examined a range of new generations of PVC/graphene composites. For example, the colloidal blending method was used to produce PVC/GO composite. As a function of GO loading, morphological analyses revealed a network of denser stacking and randomly aggregated structures with rough surfaces. Contact angles decrease as GO loading increases for all of the liquids used. At 70 °C, a proper amount of PVC was first dissolved in THF. Before mixing the GO powder with the PVC solution, it was dispersed in THF and sonicated for 30 min at room temperature. The mixture was then sonicated for an additional hour. To obtain immaculate PVC/GO composite films, the homogenous dispersion was cast on a glass petri dish and maintained in an oven at 60 °C for slow evaporation of the solvent. The cast films were removed from the glass plate and studied further. The percent loading of GO in the PVC/GO composite ranged from 0.5 to 2.5 weight percent. Figure 16 depicts images of various cast PVC/GO composite film compositions. In Scheme 1, a schematic representation of the bonding interaction between PVC and GO is depicted, with chemical bonding between PVC and GO occurring as a result of the development of an ester linkage. Previous studies have shown that the oxygen-containing group of GO can halogen bond with PVC and serve as active sites for anchoring functional groups, making GO compatible with PVC [20].

The most popular chemical technique includes oxidizing graphite with strong acids and oxidants to form graphite oxide, which is subsequently reduced with a

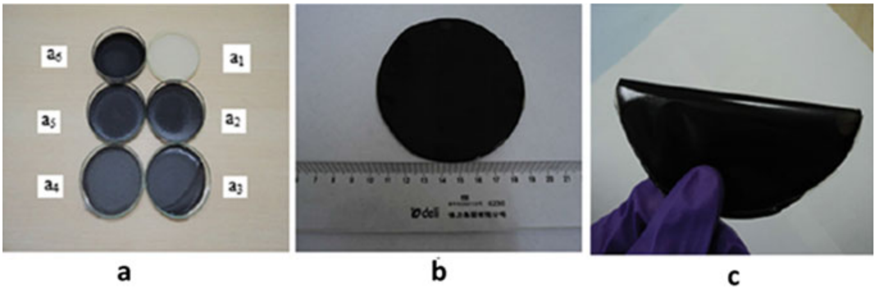
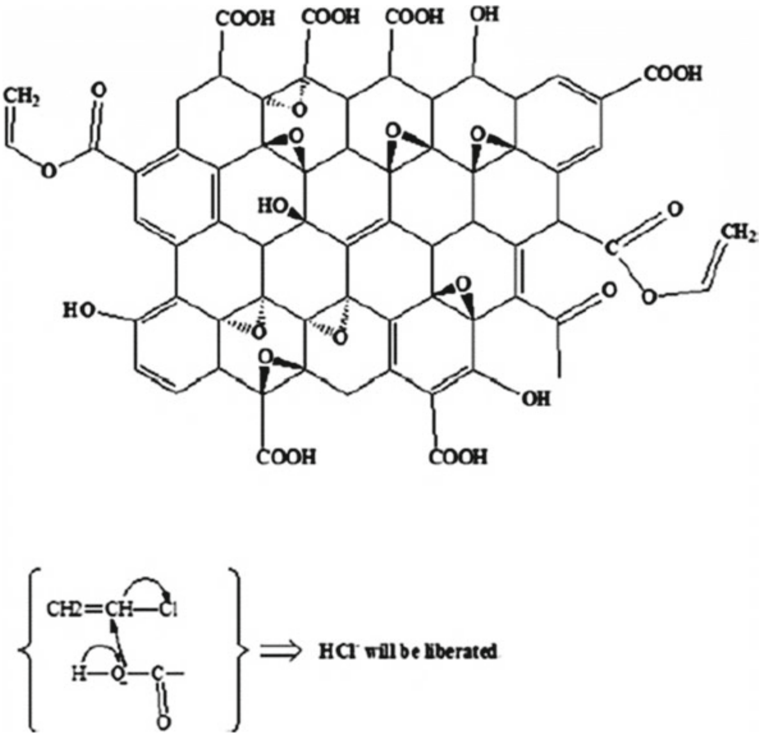


Fig. 16 PVC/GO composite films: **a** PVC/GO composite film cast on glass plates (a1) virgin PVC film, (a2) PVC/0.5%GO, (a3) PVC/1%GO, (a4) PVC/1.5%GO, (a5) PVC/2% GO, (a6) PVC/2.5%GO, **b** PVC/GO composite film indicating uniform dispersion of GO within PVC matrix, **c** composite films are bent, demonstrating its flexibility [20]



Scheme 1 The bonding formation between PVC and GO [20]

reducing agent, a thermal process, or an ultraviolet-assisted method to make chemically converted graphene (CCG). The best way to create highly electrically conductive CCG is hydrazine reduction. Due to electrostatic repulsion, CCG produced from hydrazine reduction is not well-dispersed in organic solvents but is well-dispersed in an aqueous primary state. Because CCG is only well diffused in aqueous conditions, which is incompatible with most organic polymers, creating polymer-CCG composites is a considerable challenge. Fortunately, novel latex-based techniques for the fabrication of polymer nanocomposites can be used to address this challenge. The excluded volume created by the polymer latex particles effectively pushes nanofiller particles into the interstitial space between them, drastically limiting the area available for the filler to form a conductive network. With a small amount of filler, this technique dramatically improves electrical conductivity. Therefore, the CCG was made by reducing GO with hydrazine at room temperature for 24 h. The produced CCG filter cake was redispersed into the SLS solution with the aid of 1 h of sonication after filtration and repeated washings with deionized water.

To improve CCG dispersibility in aqueous solutions through electrostatic stabilisation, the pH of the CCG dispersion was increased to 10 by adding an ammonia solution. CCG dispersions with varioussodiumlauryl sulfate (SLS)/CCG ratios were vacuum filtered, and free-standing SLS/CCG sheets were made to evaluate the effects of SLS on the electrical conductivity of CCG. To prepare PVC-CCG Composite, a predefined volume of CCG suspension (1.0 mg/ml, 1:2.5 wt/wt CCG/SLS ratio) was combined with 50 ml PVC latex (25 wt%) and sonicated for 30 min. The PVC-CCG colloidal nanocomposites were filtered with Advantec mixed cellulose esters filter paper (pore size 0.45 um), dried at 80 °C under vacuum for 12 h, and ground into a fine powder. The PVC-CCG nanocomposite powder was then compression moulded into 1 mm pellets between Teflon sheets using a Collin Press 200G at 60 bar and 175 °C [21]. The Morphology of PVC/CCG composite is shown in Fig. 17.

In another study, to prepare graphene nanoflakes, a few amount of graphite flakes were sonicated in glacial acetic acid for several hours with a 0.5 M CTAB solution, and the resulting solution was then heated at 100 °C for 48 h in a N_2 environment. To remove the excess acid and CTAB, the obtained black powder was rinsed with distilled water. Finally, the synthesized powder was dispersed in DMF. All composite thin films were coated using the liquid phase blending process.

On the other hand, to fabricate of Graphene/PVC composite thin films DMF was used to dissolve PVC. The graphene sheets were dispersed in DMF and sonicated for 2 h with appropriate weight fractions of PVC solutions. Subsequently, the mixes were dropped cast in glass cells and baked at 120 C to gently evaporate the solvent, yielding ultrathin graphene/PVC composite films. The films were peeled away from the cells and annealed at 100 °C for 3 h to eliminate any leftover solvent residues. As shown in Fig. 3, the thickness of the films was between 5 and 7 μm. As seen in Fig. 18, graphene nanoflakes are well dispersed in the PVC matrix. It also shows how graphene disperses randomly in a 3D polymer network. It's worth noting that graphene flakes tend to cluster inside the polymer matrix and are evenly distributed in PVC [22].

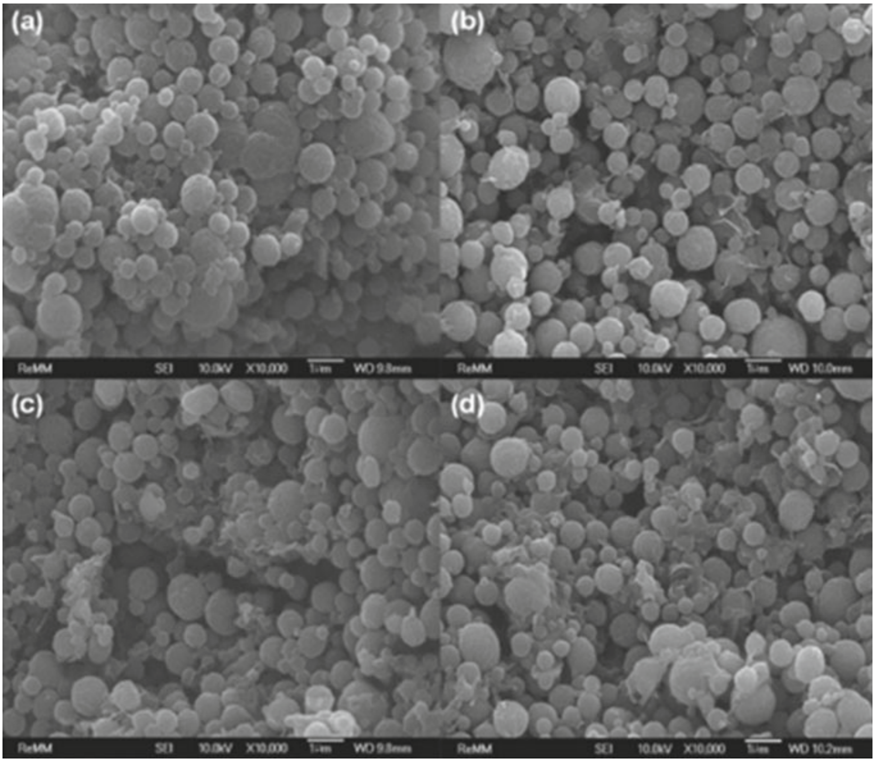
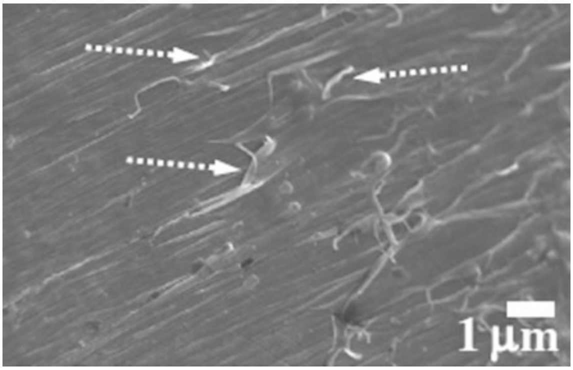


Fig. 17 SEM image of PVC/CCG composite powder. **a** 0.5 wt%, **b** 1wt%, **c** 2 wt%, and **d** 4 wt% [21]

Fig. 18 SEM image of PVC/GO composite thin film [22]



6 Long-Term Lithium Battery Using Lyophilization

Energy is inextricably linked to technological advancement, and developing energy storage technologies have fueled multiple industrial revolutions. Rechargeable lithium-ion batteries (LIBs) play an important role in the energy storage carrier's field in the use of electronic products in the current energy period. LIBs are flourishing at an incredible rate as secondary energy with the best overall performance, because of their unique properties including high lifetime, high capacity, no memory, and environmental friendliness. LIBs can be found in a variety of products in our daily lives, including portable electronic devices, electric vehicles, children's toys, medical equipment, and aerospace equipment, and are expected to be one of the primary power sources for future ships, automobiles, industrial machines, and other high-power devices like fixed large equipment [23, 24].

The separator, as one of the most important inner components in the structure of LIBs, is critical to the internal resistance, safety performance, power density, and circulating sections of the battery. Meanwhile, the separator has become a significant and popular research topic, as it has been the bottleneck preventing future LIB breakthroughs. Because of their outstanding mechanical qualities, high electrochemical stability, and cost-effectiveness, microporous membranes made of polyolefin, polyethylene (PE), and PP have always held the lead in the LIB separator market [25]. LIB separators should have strong heat resistance and electrolyte infiltration in addition to excellent mechanical qualities. However, due to their inherent material qualities and manufacturing process, commercial polyolefin separators will always have some defects:

(1) The poor porosity of polyolefin separators (three-dimensional (3D) through-pores) impacts not only lithium-ion transfer efficiency but also electrolyte infiltration.
(2) The separators have low thermal stability (melting temperatures of PE and PP are around 130 and 165 °C, respectively), limiting their operating temperature and posing a safety risk when using LIBs.
(3) The poor wettability of polyolefin separators (hydrophobic) and organic electrolytes has a significant impact on lithium-ion conductivity and consequently battery performance. To address these issues, researchers have focused on developing new coating metal oxides (such as MnO_2, TiO_2, and ZrO_2) and separator materials (such as fluorinated poly(aryl ether ketone) (FPAEK) and polyimide (PI)) for improved LIB performance, particularly in terms of safety and electrochemical properties. However, inorganic particles frequently detach from separators, and organic polymers (particularly inorganic-organic complexes) continue to be a source of significant heat shrinkage, affecting LIB performance. More importantly, it will complicate the composite separator preparation process and raise production costs, restricting their wide range of applications. As a result, creating a suitable separator for high-performance LIBs is in high demand [26].

PVC is the third most widely used polymer after polyethylene and PP. It is produced in 26 million tonnes per year around the world. Dialysis tubing, blood storage bags, and intravenous catheters are among the various medical field applications. The microelectronics sector has a strong demand for PVC matrix because it is a better insulating material with low conductivity and dielectric loss. Plasticizers alter the characteristics of PVC to make it more flexible and reduce the glass transition temperature. Some investigations on PVC modification (dechlorination) have been identified in the literature. The thermal deterioration of PVC has been documented to cause dechlorination at 260 °C. Thermal deterioration also produces polyenes and their cyclization, therefore the dechlorination process has limited use. The addition of specific additives such as plasticizers, stabilisers, and nanofillers improves the thermal stability of PVC. The strength, processability, and thermal stability of PVC mixes with other polymers have all increased. Because of their potential uses in technological domains, the polymer/graphite nanocomposite preparation has gotten a lot of interest. Due to its ease of synthesis and applicability in electrostatic charge dissipation and electromagnetic interference shielding, the PVC/graphite nanocomposite has become a new and alternate subject of study. Thermal stabilisers are required for handling at elevated temperatures since pure PVC is prone to autocatalytic dehydrochlorination (poor thermal stability). Several polymers use expandable graphite as a flame retardant (polyurethane foam and polyethylene). The electrical conductivity of expandable graphite and flake graphite is nearly same. PVC conveyor fastening with these qualities is ideal for deep-level mining applications. Because of the ease of electrode production and surface repair with low electrical resistance, PVC/graphite nanocomposites are employed as amperometric detectors [27, 28]. As a result, these electrodes have been designated for the detection of antioxidants. PVC that has been carbonised in the liquid phase has a low viscosity, allowing for an even carbonaceous layer coating. PVC/carbon is used to modify graphite to provide an active anode material for lithium ion batteries (Fig. 19).

The solution blending process was used to create PVC/GO polymer-based nanocomposites using GO as the nanofiller. PVC was also modified with the 4-ABA modifier. By introducing oxygen-containing groups, FTIR analysis validated the functionalization of graphite into GO. In comparison to non-modified PVC composites, XRD measurements revealed that modified PVC and GO have interaction. Furthermore, the modified composites had improved GO dispersion. The surface appearance of modified membranes further revealed that GO was well embedded in the PVC matrix. The modified PVC composites exhibit a bi-layered morphology that is uniform and homogeneous, with no aggregation. They also made modified PVC-based nanocomposite membranes more thermally stable. Using appropriate formulas, membrane parameters (porosity, solvent content, shrinkage ratio, and contact angle) were measured. With the addition of nanofiller, the shrinkage ratio and contact angle both reduced. The modified PVC and GO nanocomposite membranes showed promise as nanofiltration membranes for water purification, according to the findings [29].

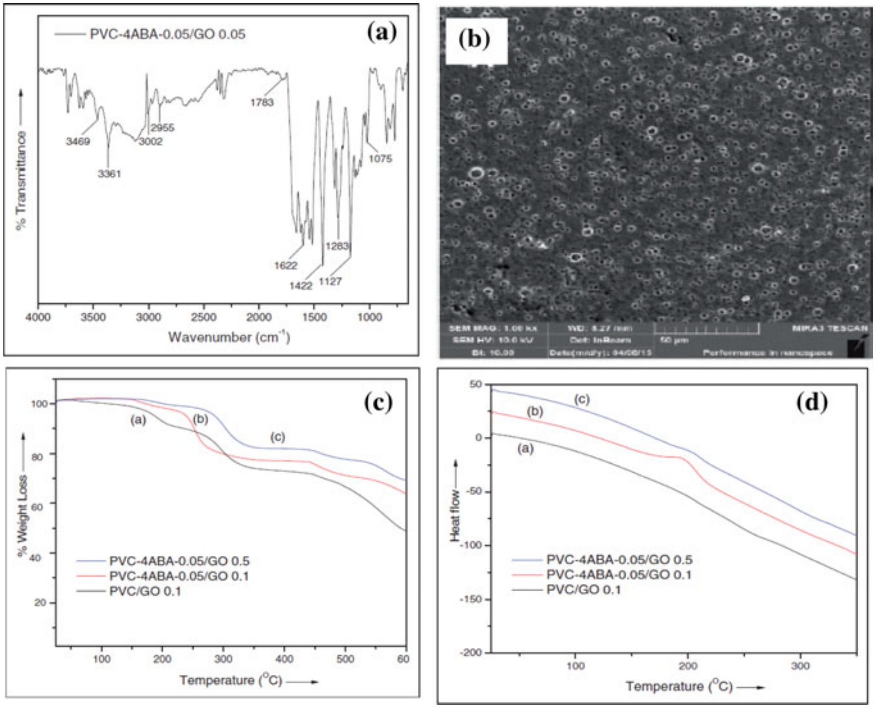


Fig. 19 **a** FTIR, **b** SEM, **c** TGA, and **d** DSC of PVA/GO nanocomposite

7 Conclusion

According to literature sources, graphene-based reinforcements are the best choice for PVC due to their remarkable qualities. The key advantages include simple manufacturing procedures, low cost, minimal time consumption, and ecologically friendly goods. Solution casting, in-situ, and melt-mixing processes are commonly employed for PVC nanocomposites. Researchers, on the other hand, prefer to use the freeze-drying technique. Because oxygenated active functional groups were available, morphological studies showed that GO reinforcement in PVC matrix had excellent results. Nanocomposites with higher nanofiller loading have better mechanical, electrical, and thermal properties. These polymer nanocomposites have high strength, toughness, modulus, transition temperature, and electrical conductivity. PVC/graphene nanocomposites had greater mechanical properties than other composites, but they agglomerated when utilized at higher weight percentages. Furthermore, the thermal and electrical properties of these nanocomposites were good, indicating that they have a wide variety of applications. Membranes for water purification, supercapacitors, electromagnetic shielding, lithium ion-batteries thermistors, antistatic textiles, biopolymer plates in the polymer electrolyte membranes fuel cell, and ion determination are among the applications of these nanocomposites currently attracting a lot of interest. The shortcomings of PVC/carbon filler nanocomposite may be overcome in the future to improve their efficiency for a variety of new applications.

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Interface Modification and Characterization of PVC Based Composites and Nanocomposites

Veerle Vandeginste and Dharmjeet Madhav

Abstract Weak interfaces in composites result in unsatisfactory stiffness and strength of the composites due to poor stress transfer from the matrix to the fibre. Better interfaces can be achieved by physical and chemical modification techniques. Recent studies show a high interest in incorporation of natural fibres in PVC composites as eco-friendly reinforcing component. Common fillers in PVC composites are calcium carbonate and wood flour. Carbon black, copper and nickel metal powders can be added for conductive applications, and ferrite powder for magnetic applications. Plasma treatment has been applied to wood flour and natural fibres to enhance the interface with PVC matrix. Besides this physical modification method, there are many chemical modification techniques, such as treatment of natural fibres with stearic acid or with sodium hydroxide. The use of coupling agents, such as maleic anhydride, silane, titanate, is also a common treatment method to enhance interfaces in composites. The interface can be characterized by several methods, including Fourier Transform Infrared spectrometry, scanning electron microscopy, X-ray computed tomography, pull-out micromechanical tests, dynamic mechanical analyses and rheological tests.

1 Introduction

Incorporation of a dispersed component into a polyvinyl chloride (PVC) matrix or continuous component can be associated with poor dispersion and poor interfacial adhesion, which results in inadequate properties of the final composites or nanocomposites [1]. For example, in composites with weak interfaces, efficient stress transfer from the matrix to the fibre is compromised, and stress becomes concentrated at the gap between the components which will eventually initiate failure. Moreover, a weak interface or poor dispersion of wood flour in PVC composites have shown to trigger creep behaviour of the composite [2]. Hence, if the bonding between the filler (fibres or particulates) and the polymer matrix is poor, then the intended enhanced

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stiffness and strength or other properties of the composite may not be reached satisfactorily. Therefore, some physical and chemical strategies can be adopted to modify the interface to optimize interfacial adhesion.

PVC is a common thermoplastic material used as matrix in composites with applications in the automotive, housing and construction fields based on the advantageous properties of high mechanical strength and corrosion resistance. A variety of fillers including calcium carbonate, silica, montmorillonite, carbon nanotubes, graphene have been incorporated in PVC composite to improve mechanical and thermal properties, such as elastic modulus, toughness, and heat resistance. Recent review works on PVC composites have focused on: the use of PVC composites as membranes in wastewater treatment, gas separation, pervaporation and electromembrane extraction applications [3]; incorporation of layered double hydroxides as thermal stabilizers in PVC composites [4]; sugarcane bagasse-filled PVC composites [5]; PVC composites with carbon nanofillers [6]; natural fibre reinforced PVC composites [7]; and compressive properties of closed-cell PVC foams [8]. Based on PVC composites studies of the last five years, the recent main interest is on PVC composite membranes for water treatment and electrochemical applications, PVC composites with photocatalytic, radiation shielding or better flame retardancy properties, or PVC composites with wood flour or natural fibres for more eco-friendly and better mechanical properties.

The global attention for natural fibre-based composites is because of the biodegradability, availability, low cost, low density, ease of implementation and good specific properties of natural fibres [9]. The incorporation of natural fibres in thermoplastic composites can increase the elastic modulus of the composite. However, it can decrease the impact strength of the composite [7]; and moisture absorption poses an additional challenge. The incompatibility between the hydrophilic natural fibres (with hydroxyl and other polar groups) and the hydrophobic thermoplastic matrix is the main factor leading to weak interfacial bonding between the fibre and the matrix [10]. Therefore, it is crucial to improve interfacial adhesion between the fillers and the PVC matrix.

The interface between the fillers and the polymer matrix is complex, and it is formed in two stages, first by the contact and wetting process, and second by the formation of the interface during polymer curing, physical and chemical changes. The compatibility between the matrix and fillers can be enhanced by physical and chemical modification, or addition of any compatibilizer or coupling agent [11], and graft polymerization of the polymer [1]. The most common physical treatments make use of plasma or irradiation. Chemical treatments of fillers involves acetylation [12, 13], alkali [14] and benzoylation treatments, and use of coupling agents such as silane [15], aminosilane and titanate. The different interface modification and characterization methods of PVC based composites and nanocomposites will be discussed in this chapter.

2 Fillers Used in PVC Composites

Calcium carbonate and wood flour are commonly used fillers in PVC composites. For conductive applications, carbon black and copper and nickel metal powders may be used, and for magnetic applications, ferrite powder is used. Other fillers involve dolomite, limestone, cellulose, silica, kaolin or montmorillonite clay, talc or calcium sulfate. Papers on PVC composites published in the last five years have a strong focus on the incorporation of natural fibres as eco-friendly reinforcing additives for PVC composites. These studies are on PVC composites with sorghum straw fibres [16–18], rice husk fibres [19, 20], cotton stalk fibres [21–23], palm fibres [24], Eucalyptus fibres [25–29], Citrus Maxima fibres [30], date palm fibres [31], areca sheath fibres [32], bamboo, rice straw, wheat straw and reed straw [33], bamboo fibres and coconut shell particles [34], bagasse fibres [35], corn stalk [36, 37] and coconut fibres [38].

Wood flour or other plant-derived fillers are also common in PVC composites, such as kenaf core powder [39], waste rice husk ash [40], corncob flour [41], wheat husk filler [42], bamboo particles [43], wood flour [44–47], wood flour and amorphous calcium carbonate [48], wood flour and precipitated calcium carbonate [49], olive pit flour and precipitated bio-calcium carbonate for wooden PVC composites [50], raspberry pomace filler [51], and flour of decayed wood [52]. A study on PVC composites with organically modified montmorillonite and pine wood flour suggested the latter can be considered a cheap, eco-friendly and renewable substitute for chalk as filler for PVC based cable insulators with improved mechanical and physical properties [53]. Modified eggshell biofiller has also been suggested as an alternative to conventional $CaCO_3$ from limestone or chalk [54]. Moreover, fly ash can also be used as reinforcement filler [55–59]. Calcium sulphate fibres [60], $CaSO_4$ whiskers [61, 62] and glass fibres [63] are also used in PVC composites for better mechanical properties.

Several fillers are added to improve the thermal stability of PVC composites such as organotin, calcium-zinc and titanium nanoparticles [64], talc, calcined kaolin [65], ground basalt rock microparticles [66], and basalt fibres [67]. Thermal stability and flame retardancy in PVC composites are enhanced by magnesium hydroxide particles, magnesium hydroxide whiskers[68], anhydrous $MgCO_3$ particles [69–72], and magnesium borate hydrate-mechanically activated lignin complexes [73]. Chitosan-modified zinc hydroxystannate and reduced graphene oxide can be used as hybrid flame retardant in flexible PVC composites [74], and chitosan-modified inorganic oxyacid as flame retardant in PVC composites [75].

Radiation protection of PVC composites or shielding against gamma and X-ray radiation is achieved by incorporation of micro-nano-structured PbO and CuO particles [76, 77], Bi_2O_3 particles [78, 79], tungsten microparticles [80], or $Pb(NO_3)_2$ particles [81]. Carbon nanotubes and carbonyl iron has been used for improved microwave absorbing properties of PVC composites [82, 83]. Hexagonal cesium tungsten bronze ($CsxWO_3$) nanoparticles are added in PVC composite films for near-infrared light shielding and high visible light transmission [84]. Solar reflectance and cooling performance of PVC composites is improved with TiO_2 particles [85, 86].

Thermal conductivity is improved in plasticized PVC composites by incorporation of fly ash and carbon black [87, 88], graphite and MgO [89], carbon microspheres [90], graphene [91, 92], multi-walled carbon nanotubes [93] and nanographite [94], reduced graphene oxide [95, 96], graphite and mica [97].

Electrical or electrochemical application studies involve the incorporation of multi-walled carbon nanotubes in PVC composite films with polyaniline for flexible and robust electrodes for high performance supercapacitors [98, 99], carbon nanotubes [100, 101], graphene [102], palladium nanoparticles in blended poly(vinylidene fluoride) and PVC composites [103], graphite with PVC composite as anode for electrochemical degradation of metoprolol [104], multi-walled carbon nanotubes for high water flux PVC composite membranes with effective electrically enhanced antifouling properties [105], functionalized reduced graphene oxide for highly electro-responsive PVC composite gel for advanced artificial muscles and tuneable soft actuator applications [106], carbon black for temperature sensor applications [107], salt-loaded PVC membranes for 3D printed electrodes [108], MoS_2 particles in composite PVC membranes for triboelectric nanogenerators [109], and graphite and chitosan for electrodes [110]. Thermal solar conversion is enhanced with multi-walled carbon nanotubes in PVC composites [111, 112].

Enhanced dielectric properties in PVC composites are obtained with $BaTiO_3$ fillers [113, 114]. Antistatic properties are achieved with multilayer graphene in PVC composite [115]. Nickel-zinc ferrite fillers are used for PVC composites with magnetic properties [116]. PVC composite membranes with magnetic Fe_3O_4/oxidized multiwalled carbon nanotubes composite nanoparticles have also been reported [117]. SiC aggregates are incorporated in PVC composites to increase the surface roughness of the composite and increase the coefficient of friction [118].

PVC composite materials are also used in water treatment applications with Al_2O_3, TiO_2, ZnO and SiO_2 nanoparticles in PVC ultrafiltration membranes [119], diatomaceous earth particles in composites for formaldehyde removal applications [120], Methylene Blue and TiO_2 particles in PVC composite film for photocatalytic technology [121], MnO_2 nanosheets in PVC composites for efficient removal of dye from water [122], and graphene oxide and p-phenylenediamine in PVC composites for heavy metal removal applications [123]. Zinc oxide nanoparticles are used for their antibacterial and antifungal properties [124, 125]. Cu nanoparticles contribute antimicrobial activity and better thermal stability of the PVC composites [126].

3 Interface Modification: Physical Modification Methods

The main types of physical modification methods involve electrical discharge methods such as corona treatment and plasma treatment. Also, ultrasonic irradiation is commonly employed to improve dispersion of fillers, in particular of nanoparticles which tend to otherwise agglomerate. Particles and fibres need to be well dispersed in the polymer matrix to achieve good material properties.

3.1 Plasma Treatment

Plasma treatment is a low cost technology and has a low environmental impact in comparison to the use of chemicals such as coupling agents [127]. Plasma treatment is employed to increase the surface energy through modifying the surface by activation, grafting and etching, which can result in better tensile strength and interfacial shear strength of polymer composites with plasma treated fibres [128–130]. For example, it can increase the surface energy of wood particles by oxidative activation, resulting in the formation of polar functional groups, such as hydroxyl, carboxyl and aldehyde groups [131, 132]. This can then also improve the bonding of these particles with silane coupling agents. The plasma method was used to treat wood particles before chemical modification with tetraethyl orthosilicate (TEOS) to improve the mechanical properties of wood flour PVC composites [46].

3.2 Ultrasonic Irradiation

Ultrasound is an efficient method in polymer chemistry, whereby polymerization reactions can be accelerated, or where higher yields can be obtained under milder conditions [133]. This is due to a unique interaction between matter and energy provided by cavitation-induced sonochemistry [134]. Moreover, ultrasound helps with nanoparticle dispersion and deagglomeration [135]. Mechanical properties of composites are generally improved by using fibres as reinforcement, but small particles can also provide more rigidity of the composite and other properties due to increased contact (surface area) between the filler and the matrix. In the fabrication process of PVC composite films, ultrasonic irradiation was used for dispersion of TiO_2 nanoparticles that were surface treated with vitamin B-1 to help prevent aggregation [136]. Similarly, TiO_2 nanoparticles were treated with bovine serum albumin protein and then incorporated in PVC nanocomposite using ultrasound in both processes [137]. Ultrasonic irradiation was also used in several steps of the preparation of PVC composites with ZnO nanoparticles modified with diacid containing alanine amino acid coupling agent, which led to uniform dispersion of the particles and improvement of the mechanical properties of the nanocomposites [138]. Similarly, ZnO nanoparticles modified with polyvinyl alcohol were dispersed using ultrasonication in the fabrication of PVC nanocomposite films with enhanced mechanical properties [139]. Ultrasonication was also employed in the preparation of melamine terephtaldehyde modified graphene oxide as anticorrosion additive in PVC nanocomposite, which showed a lower change loss percentage of tensile strength in acetone and sodium hypochlorite media [140]. Furthermore, fabrication of PVC nanocomposite with mixed graphene and carbon nanotubes was conducted with ultrasonic irradiation [141].

3.3 Surfactant Modification

A surfactant is a surface active agent, which means that it can reduce the free energy of surfaces and interfaces. Moreover, it self-assembles at interfaces, and forms monolayers at liquid-liquid interfaces and monolayers and aggregates at solid-liquid interfaces. Surfactants are amphiphilic molecules; they have at least one polar head group (hydrophilic) and one nonpolar tail group generally made up of a carbon chain (hydrophobic). In a study on PVC composites with rice straw fibres, graphene oxide nanosheets were modified with surfactant sodium dodecylbenzenesulfonate by adding 0.5 wt% to a solution followed by sonication, and added in the PVC composite to improve the mechanical properties [142].

4 Interface Modification: Chemical Modification Methods

Several types of chemical modification techniques have been applied on a variety of fillers in PVC composites. The focus here is on the main chemical treatment methods that have been applied in PVC composite studies published in the last five years.

4.1 Acid and Acetylation Treatment

Stearic acid is one of the most widely used materials for coating fillers, for example calcium carbonate, to enhance their properties and incorporation in polymer composites. Sorghum straw fibre was pretreated with a mixture of stearic and palmitic acids, which improved the water resistance of the fibre PVC composites [143]. Stearic acid was also used to modify fly ash, using 3 wt% stearic acid in comparison to the fly ash weight [88]. Titanium nanoparticles were modified with folic acid at 5 wt% during ultrasonic radiation at 25 °C (Fig. 1) for incorporation in PVC composites [144]. Acetylation involves the use of a catalyst, generally acetic acid, to remove hydrogen atoms from the hydrophilic hydroxyl groups of cellulose molecules by grafting acetyl groups on those sites [145]. Acetylation improves fibre hydrophobicity. Acetylated fibres have a better resistance against moisture absorption [146] and form strong covalent bonds leading to composites with higher tensile strength and Young's modulus [145]. Palm fibres were treated in an acetic acid solution at 25 °C for 45 min, and then put in an acetic anhydride solution with some drops of sulphuric acid at 50 °C for 2 h [24]. These acetylated fibres resulted in improved mechanical properties of the PVC composites due to a better bonding between the fibre surface and the PVC matrix, and the acetylated fibre PVC composites show the lowest rate of water absorption [24].

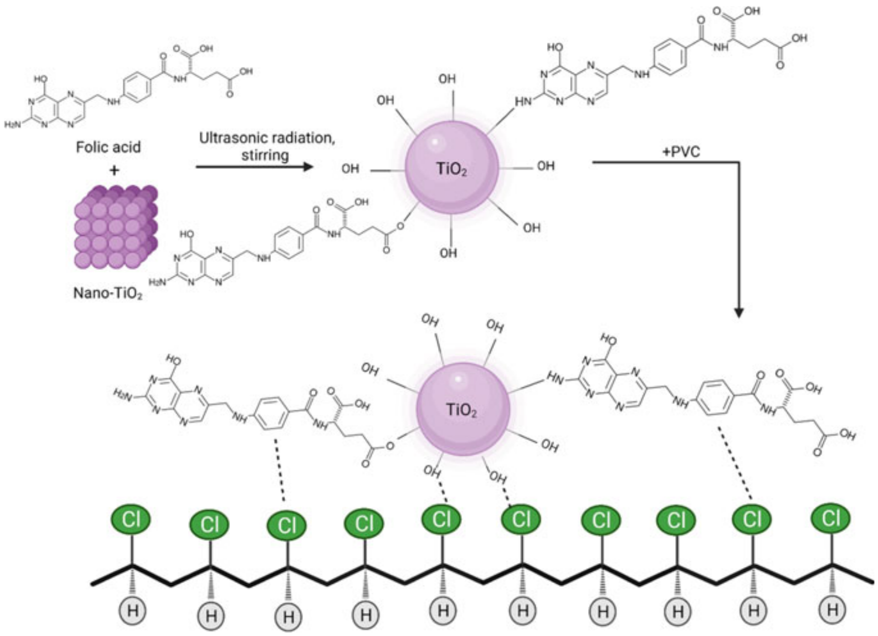

Fig. 1 Mechanism of the modification of TiO$_2$ nanoparticles with folic acid to incorporate in PVC composites

4.2 *Alkaline Treatment or Mercerization*

Natural fibres are generally treated with alkaline solutions (often NaOH) to improve the interfacial bonding between the fibre and the polymer matrix, as it can remove amorphous materials such as lignin, pectin and hemicellulose from the surface of cellulose fibre bundles [147]. Moreover, alkaline treatment aids in breaking down the fibres to smaller fibres, a process known as fibre fibrillation, which leads to a higher surface area [148], also favourable for the interfacial adhesion mechanism of mechanical interlocking. Cotton stalk fibres were soaked in a 4 wt% NaOH solution at 90 °C for 2 h under stirring [22]. Palm fibres were treated in a 5 wt% NaOH aqueous solution by immersion at 50 °C for 2 h, and this led to the partial removal of hemicellulose and lignin [24]. Pinewood flour was immersed in 2 wt% NaOH solution for 45 min as alkaline treatment to improve the particle-matrix interactions in PVC composites [53]. Similarly, rice husk filler was put in a 2% NaOH solution at room temperature for 24 h, to remove lignin and pectin and to enhance the compatibility between cellulose of the rice husk filler and the PVC matrix [149]. In another study, rice husk was treated with 5% (w/v) NaOH solution for 30 min at 30 °C, and then kept immersed in distilled water overnight and washed repeatedly before drying in an oven at 70 °C for 12 h [150]. A solution of 10% NaOH was used to treat bagasse fibres for 4 h at 60–70 °C, followed by rinsing with distilled water and drying in oven at 105 °C, and subsequent bagasse fibre surface functionalization through 2,2,6,6-tetramethyl piperidinyl-1-oxyl (TEMPO)-assisted oxidation of the lignocellulose fibres to form carboxylate groups on the fibre surface [35]. Corn stalk was stirred in an 8 wt% NaOH solution of 80% ethanol and with 1 wt% anthraquinone at 130 °C for 60 min to remove lignin [36]. In addition, in the latter work, a solution of pH 5.5 (by adding sulphuric acid) was used for immersing the corn stalk at 150 °C for 60 min, after the alkaline treatment to remove the hemicellulose component [36].

An alkaline solution can also be used as a pretreatment of inorganic fillers before grafting a coupling agent to improve the effects of grafting. Specifically, ground calcium carbonate powder was mixed with 1.0 mol L^{-1} and 0.1 mol L^{-1} Na_2CO_3 aqueous solution (with 10 wt% solids in the solution) at room temperature and stirred for 2 h to achieve more hydroxyl groups on the filler surface, which leads to more active sites for subsequent reaction with aminopropyltrimethoxysilane (APS) coupling agent [151] (Fig. 2). Similarly, calcium sulfate whiskers were stirred in a 0.03 mol L^{-1} Na_2CO_3 solution at 80 °C for 2 h, washed and dried at 105 °C for 12 h, before modification with silane coupling agent for incorporation in PVC composite [60]. Modification of silver nanoparticles was conducted by dispersion in an ethanol solution with ammonium hydroxide for alkaline treatment, and subsequently tetraethoxysilane was added for silane treatment of the nanoparticles [152]. Fly ash was treated with 6 mol L^{-1} NaOH solution to increase the hydroxyl groups on the surface of the fly ash particles, and subsequently a polyether titanate coupling agent was used for further modification of those particles to improve interfacial adhesion between particles and matrix in PVC composites [59].

4.3 Maleated Coupling Agent

Coupling agents have amphoteric structures, meaning one side of the substance has polar groups with can form strong chemical bonds with for example inorganic fillers, whereas the other side of the coupling agent has nonpolar groups which can form strong interactions with organic polymers. There are many types of coupling agents, and their impact on improved interaction between the polymer matrix and the fillers depends on the composition of those. Moreover, the effect of modification is dominated by the grafting ratio on the surface of fillers. Maleated propylene was employed in several studies on PP composites with wood flour or natural fibres [153–155]. In polylactic acid composites with natural fibre or wood flour, maleic anhydride served as coupling agent for functionalization of polylactic acid to improve compatibility with cellulose fibres [156]. Maleic anhydride was used as coupling agent in wood PVC composites [157], and maleic anhydride grafted on PVC (Fig. 3) was also used as compatilizing agent in olive husk flour PVC composites [42].

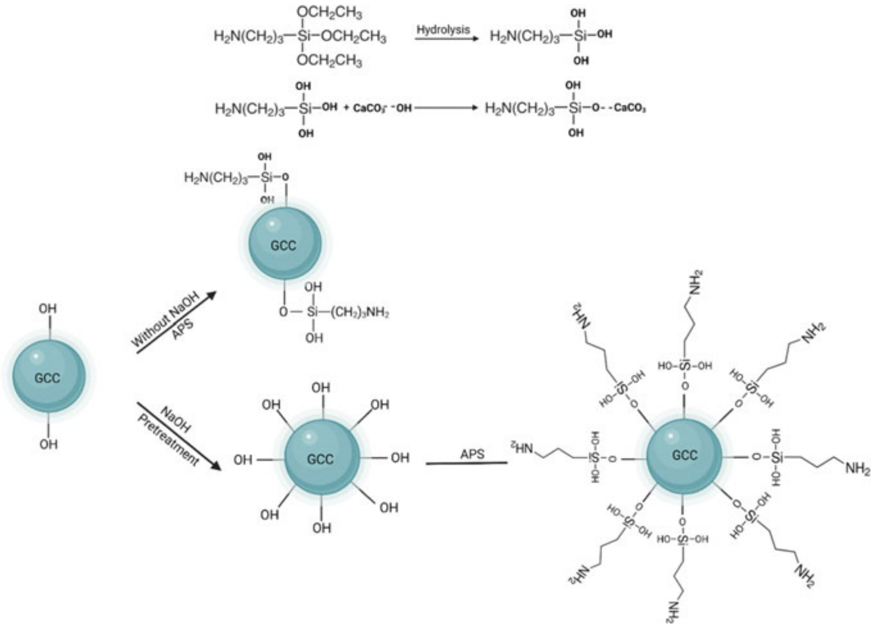

Fig. 2 Procedure of surface modification of ground calcium carbonate (GCC) particles for incorporation in PVC composite

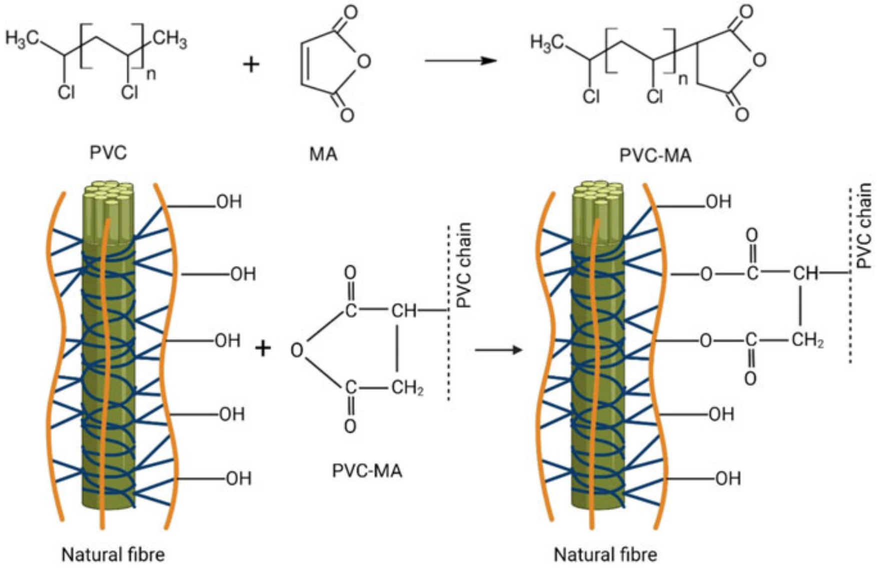

Fig. 3 Grafting of maleic anhydride on PVC to use as coupling agent in PVC composites with natural fibres

4.4 Silane Coupling Agent

The first discovered coupling agent is the silane coupling agent, and it is the most commonly used coupling agent. Silanes consist of a silicon atom which can have up to three reactive groups and one rest group that is generally attached via an alkyl chain. The reactive groups are generally hydroxyl, methoxy, ethoxy or chloride groups. Silane coupling agents can be diluted in either 0.1 wt% acetic acid aqueous solution or a solvent such as methanol, ethanol, propanol or benzene, or a mixture of water and ethanol. The generally recommended dosage of silane coupling agent is 0.8 to 1.5% of the material being processed. Silane is used as a coupling agent because it can interact both with organic polymer matrix and with, for example, inorganic oxide filler, and it aims to reduce stress at the matrix-filler interface and prevents the filler from being affected by moisture.

Zinc oxide nanoparticles were functionalized with polydimethylsiloxane by ultrasonic and constant temperature method for incorporation in plasticised [125] and rigid PVC composites [124]. Gamma-aminopropyltrimethyoxysilane (also called KH-550 or 3-aminopropyltriethoxysilane) was used as a compatibilizer for waste rice husk ash PVC composites [40]. Similarly, this coupling agent was used to chemically treat rice husk fibres (at 2 wt% of rice husk, and diluted with an 80/20 methanol/distilled water mixture with pH adjusted to 4 by using acetic acid) by soaking for 2 h and then drying, to achieve better mechanical properties of PVC composites [158]. The 3-aminopropyltriethoxysilane coupling agent (KH-550) was also used to treat sorghum straw fibre (at 3 wt% compared to fibre, dissolved in ethanol at a volume ratio of 1–5) by spraying and subsequent drying for incorporation in PVC composite [18]. Moreover, fly ash was chemically treated with this coupling agent in recycled PVC composite [56]. Ground calcium carbonate particles were modified with this coupling agent (at 1.5 wt% compared to ground calcium carbonate) in an aqueous solution at 60 °C and stirred for 2 h, to enhance the interfacial bonding with the PVC matrix [151]. Silane coupling agent KH-550 was used in PVC composites with chitosan-modified zinc hydroxystannate flame retardants whereby zinc ions are replaced by chitosan cations [74]. The interaction of this coupling agent with inorganic filler is depicted in Fig. 4.

The effect of KH-550 and methylene diphenyl diisocyanate (MDI) coupling agents were compared in wood veneer PVC (and other thermoplastic) composites and showed that the interfacial bonding was higher using these coupling agents in PVC composites compared to LDPE, HDPE or PP composites [159]. Moreover, the MDI coupling agent improved the interfacial bond strength between wood and thermoplastic and the mechanical properties more than the KH-550 silane coupling agent [159]. Calcium sulfate whiskers were modified with silane coupling agent by stirring in a solution with 90 wt% alcohol and 1 wt% 3-aminopropylsilane at 60 °C for 4 h [60, 61]. Diatomite was modified with gamma-methacryloxypropyltrimethoxysilane coupling agent to introduce hydrophobic chains and improve compatibility of this modified diatomite and PVC matrix [160]. Bismuth oxychloride (BiOCl) nanosheets were modified with methacryl-functional silane coupling agent (KH-570) at 2 wt%

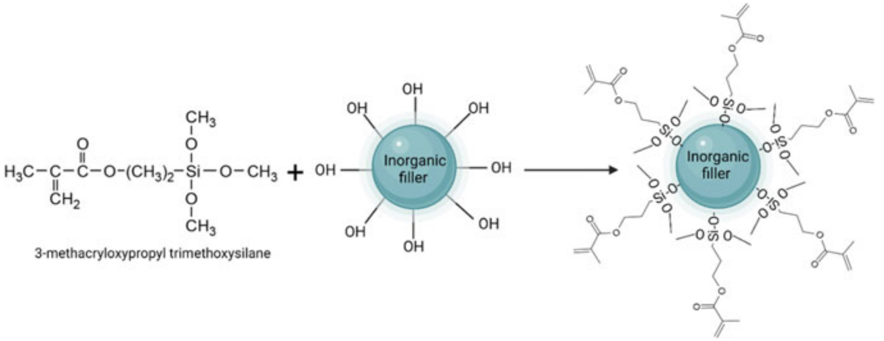

Fig. 4 Surface modification of inorganic filler with KH-550 coupling agent

compared to BiOCl in 95% ethanol solution by stirring and then drying under vacuum, and they were then used a green inorganic flame retardant in flexible PVC [161]. Hydrous manganese dioxide nanoparticles were functionalized with 3-mercaptopropyl trimethoxysilane coupling agent [162]. Furthermore, tetraethylorthosilicate (TEOS) is mainly used as crosslinking agent in silicone polymers, and it is also employed for surface modification, for example, to modify the surface of halloysite nanotubes in reed flour PVC composites [163].

4.5 *Titanate Coupling Agent*

Besides silane coupling agents, also aluminate, borate, rare earth and titanate coupling agents are used to improve bonding at the interface. There are more than 70 titanate coupling agents, and they are generally divided into four types, namely chelating, coordination, pyrophosphate and single alkoxy types. The choice of titanate coupling agent is related to the type of filler; they are suitable for calcium carbonate, titanium dioxide, barium sulfate, kaolin, talc, mica, but not really suitable for aluminium oxide and glass fibre. The general dosage of titanate coupling agent used is 0.1–2.0% of the material being processed. Using titanate coupling agent to modify inorganic fillers (Fig. 5) can help improve impact strength, mechanical properties of the composite, dispersion of the fillers and reduce the viscosity of the system. Commercial titanate coupling agents and a new polyether titanate coupling agent were used to modify calcium sulfate whiskers for incorporation in PVC composites for better thermal stability [61]. The latter titanate coupling agent was also used for surface modification of magnesium hydroxide particles and magnesium hydroxide whiskers for incorporation in PVC composites for better flame retardancy properties [68]. Moreover, carbon microspheres were modified with this polyether titanate coupling agent in PVC composite [90], and also basic magnesium carbonate was modified with this coupling agent [71]. Butyl titanate coupling agent was used to modify nanosized titanium dioxide to synthesize PVC composites [64], and isopropoxy trioleate acyl

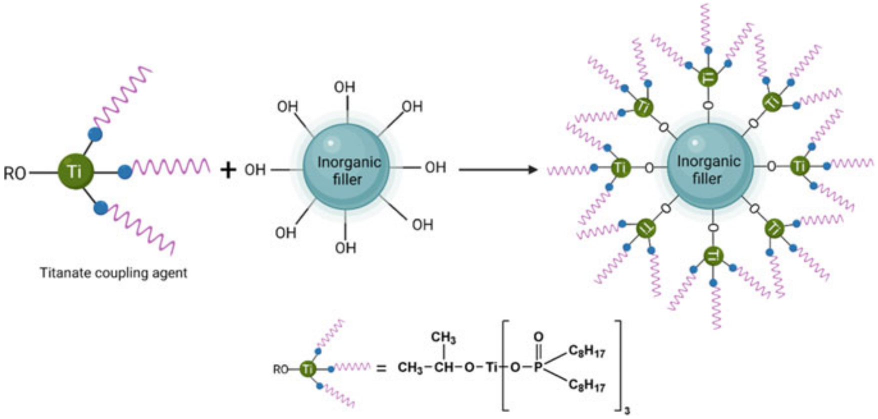

Fig. 5 Surface modification of inorganic filler with titanate coupling agent

titanate (KTTO) coupling agent was employed to chemically modify the surface of silica microparticles and improve the interfacial adhesion PVC composites [164].

4.6 Benzoyl Chloride Treatment

Benzoylation treatment of natural fibres involves the substitution of hydroxyl groups of cellulose for benzoyl groups (Fig. 6). This chemical treatment improves fibre-matrix adhesion, resulting in composites with higher tensile strength and toughness, better thermal stability and reduced water absorption [165]. Kenaf core powder was treated/grafted with benzoyl chloride in PVC composites [39]. Olive husk flour was also chemically modified through benzoylation, by first soaking olive husk flour in 18% NaOH solution for 30 min, then washing, before being stirred in a 10% NaOH solution with benzoyl chloride at room temperature for 15 min [11]. The benzoylation treatment led to higher Young's modulus and reduced moisture absorption rate of the PVC composite [11].

4.7 Chitosan-Based Treatment

Chitosan is an interesting biopolymer due to its biocompatibility, non-toxicity and good mechanical properties. Chitosan can be produced from chitin and it has many hydroxyl and amino functional groups. The amino groups of chitosan can be modified to form hydrophilic structures that can strengthen bonding with inorganic particles and polymers [166]. A cinnamaldehyde-chitosan derivative was synthesized as

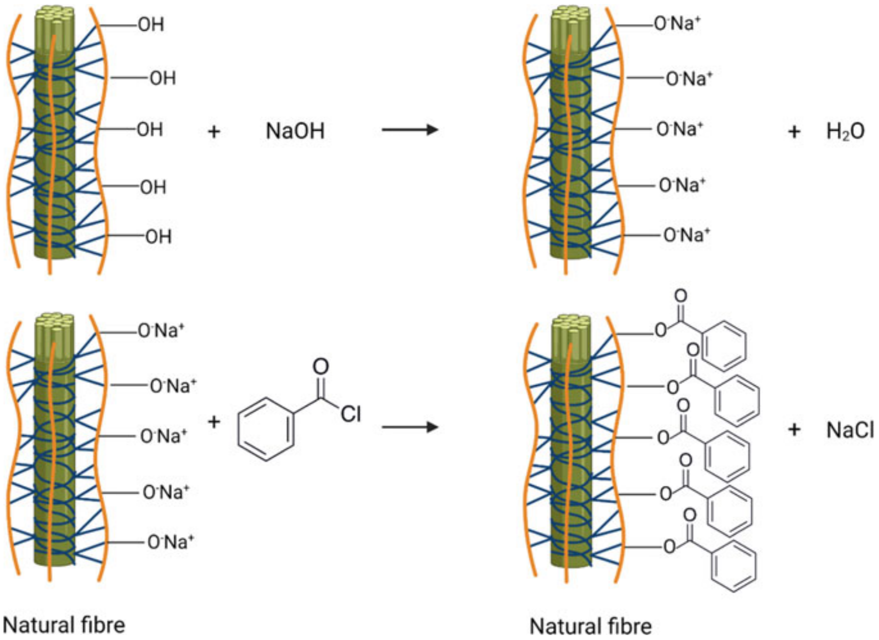

Fig. 6 Benzoylation of natural fibres by treatment with NaOH and benzoyl chloride solutions

a biopolymer coupling agent to modify carbon microspheres and improve compatibility between the latter and PVC composite [90]. Chitosan was coated on the surface of magnesium hydroxide sulfate hydrate whiskers, by stirring them in a mixture of 1% acetic acid aqueous solution with chitosan (of up to 0.5%) at room temperature for 2 h, for a better adhesion and compatibility with PVC matrix [167]. The mechanism of chitosan coating on inorganic filler is presented in Fig. 7.

4.8 Phthalate Treatment

Dioctyl phthalate is generally used as a plasticizer in the production of flexible PVC. It has also been employed to modify the surface of antimony trioxide nanoparticles (Fig. 8) using high energy ball milling to improve dispersion of the particles and compatibility with PVC matrix to obtain PVC composites with good mechanical and flame retardant properties [168].

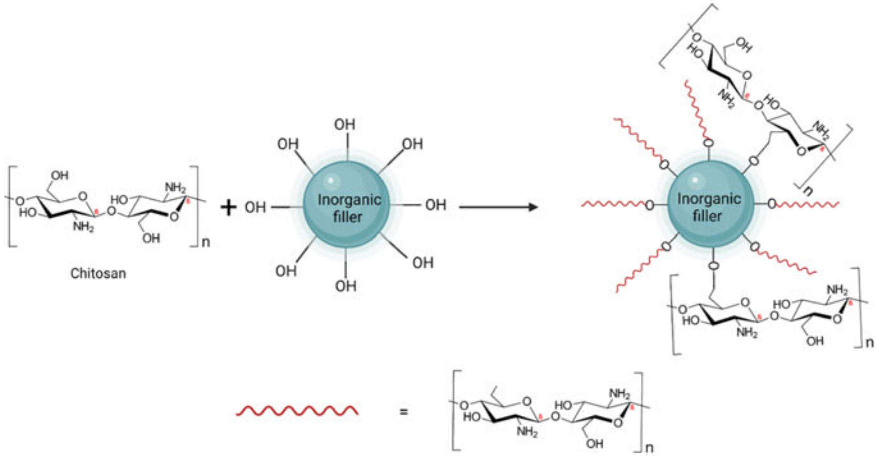

Fig. 7 Surface treatment of inorganic filler by coating with chitosan in slightly acidic aqueous solution

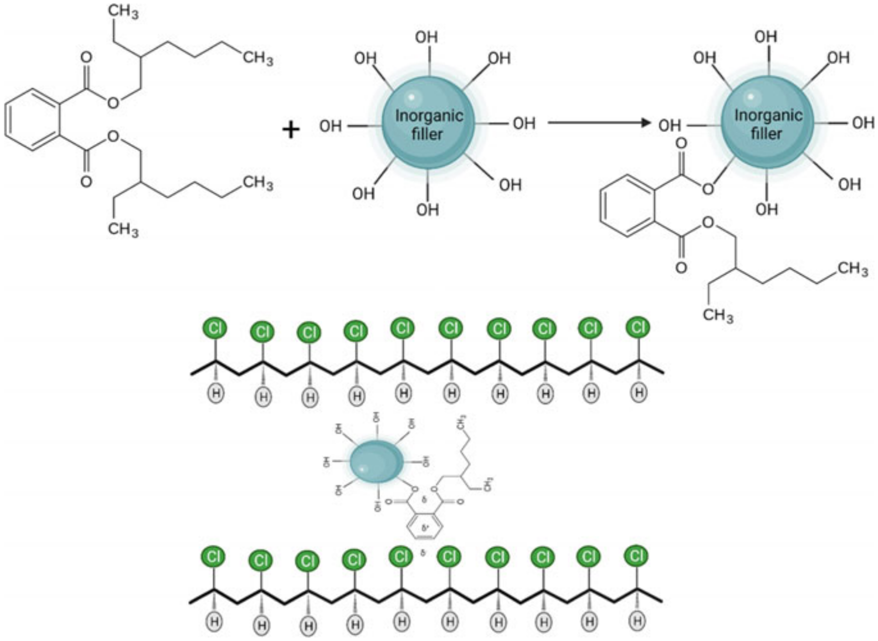

Fig. 8 Chemical modification of the surface of inorganic filler using phthalate compound

5 Interface Characterization Methods

The mechanical properties of composites that are commonly tested, such as tensile strength, tensile modulus, elongation at break, impact strength, give information on the reinforcing effect of the fillers in the composites. These properties are influenced by the adhesion strength between the filler and the matrix of the composite, and thus the measurements of these properties at the macro-level give indirectly an estimate of the performance at the interface. Still, here the focus lies more specifically on the interface characterization methods.

5.1 Fourier Transform InfraRed Spectrometry

Identification of functional groups in a material as well as the interactions of components in composites can be obtained by Fourier Transform InfraRed (FTIR) spectrometry. This method is applied to verify successful modification of fillers. For example, bonding enhancement of wood flour in PVC composite by adding natural chitosan was investigated with FTIR spectra [169]. A higher amount of chitosan added in the composite led to a higher transmittance of the C-Cl bond peaks and very slight decrease in wavenumber, meaning the C-Cl bonding was weaker and that both C and Cl had stronger interactions with other ambient atoms; similarly, the transmittance of amino and hydroxyl groups decreased, meaning higher bonding forces of chitosan [169]. The hydrolysis effect of alkali treatment on PET fibres was confirmed by the decrease in intensity of hydroxyl peaks in absorbance FTIR spectra [170]. The peak of olive pit flour for O-H stretching was shifted towards higher wave number upon addition of PVC, which was interpreted as the formation of H bonds among hydroxyl groups of cellulose or lignin in olive pit flour and hydrogen in PVC, confirming the interaction between olive pit four particles and PVC matrix [106]. Figure 9 shows FTIR spectra of the authors' research on PVC composite membranes with 8 wt% precipitated $CaCO_3$ microparticles of mussel shell $CaCO_3$ microparticles. The PVC composites were made with untreated microparticles and with stearic acid treated microparticles. The stearic acid treatment was conducted in two different ways: (i) in ethanol at room temperature, and (ii) in water at 45 °C. The stearic acid modification leads to a change in the transmittance of the peaks, and very slight shift in wavenumber.

5.2 Scanning Electron Microscopy and Energy Dispersive Analysis of X-rays

Scanning electron microscopy (SEM) can be used to study the morphology of the interface between fillers and the PVC matrix. Micro-scale damage characteristics

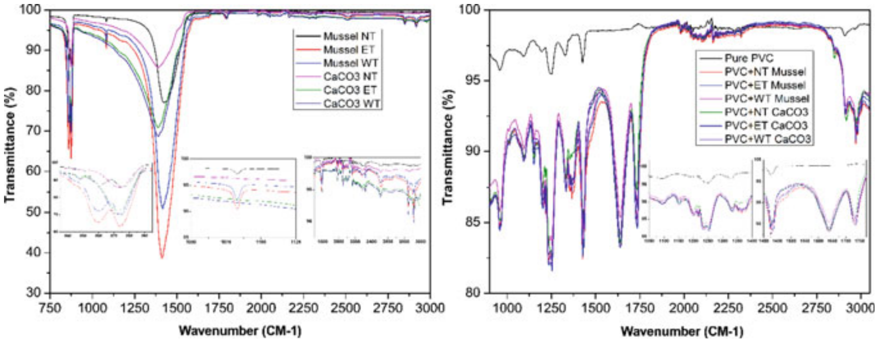

Fig. 9 FTIR spectra of mussel shell $CaCO_3$ microparticles and precipitated $CaCO_3$ microparticles that are untreated (NT), treated with stearic acid in ethanol (ET) or treated with stearic acid in water (WT); and FTIR spectra of pure PVC and of the PVC composites with the six types of (un)treated microparticles

from tensile tests can be investigated and identified using SEM imaging. For example, shear failure, matrix cracking, fibre breakage, fibre fracture and fibre pull-out were observed in PVC composites with untreated cotton fibres, based on SEM imaging [23]. Moreover, the dispersion of fillers in the polymer matrix can be evaluated. SEM images of PVC composites with $CaCO_3$ nanoparticles reveal that the nanoparticles treated with titanate coupling agent were better dispersed and showed better interfacial adhesion in comparison with nanoparticles that were treated with sodium stearate [171]. SEM pictures enable identification of smooth and clean surfaces due to pulling out of bagasse fibres from PVC matrix in fractured composites, whereas the surfaces are a bit rough in fractured PVC composites that contain bagasse fibres treated with benzoic acid [172]. Moreover, the untreated fibre PVC composite showed larger empty spaces due to the aggregation of fibres, in contrast to the observations in the benzoic acid treated fibre PVC composite [172]. SEM images show that addition of finer chitosan particles, with thus a larger specific surface, leads to a more effective bond at the interface of the wood fibre and PVC matrix [169]. In PVC composites with untreated calcium sulfate whiskers, SEM images demonstrated whisker pull-outs and gaps between whiskers and matrix, whereas whiskers treated with glutaraldehyde cross-linked polyvinyl alcohol were attached to the PVC matrix by a rough adhesive interface and the whiskers were well dispersed in the matrix [173]. In PVC composites with calcium sulfate whiskers that were treated with KH-550, titanate coupling agent or stearic acid, the interactions between the whiskers and the matrix seemed enhanced in comparison to untreated whiskers, but still some voids and gaps were observed in the composites [173]. The effect of alkali treatment of PET fibres, and subsequent coating with SiO_2/tributyl citrate hybrid sizing agent, was investigated with SEM, demonstrating the pits and grooves on the PET surface after alkali treatment and the deposition of nanoparticles scattered on the fibre surface upon treatment with the sizing agent, with both treatments increasing the specific surface area [170]. The surface of untreated glass fibres pulled out of PVC composites investigated with

SEM were very smooth, whereas the glass fibres treated with coupling agent had some PVC attached to them, with the effect being stronger with KH-550 coupling agent than KH-660 and KH-570 coupling agents, which was also confirmed by the mechanical property tests of tensile strength, flexural strength, impact strength and interlaminar shear strength [63]. Improved particle dispersion and enhanced interfacial adhesion was detected by SEM in olive pit flour PVC composites with loading of up to 10% precipitated bio-calcium carbonate particles, after which the properties deteriorated [106]. SEM imaging of PVC composite thin films with hybrid ceramic filler was also used to demonstrate effective hybridization between V_2C and Cu_2O phases with agglomeration of fine Cu_2O particles at the surface of V_2C phase due to the higher surface activity and the creation of a rough surface [174].

Also in the authors' research on PVC composites with 8 wt% nontreated $CaCO_3$ microparticles and stearic acid treated $CaCO_3$ microparticles, SEM images showed better dispersion of the stearic acid treated particles than the untreated ones in the PVC composite membrane. Energy dispersive X-ray (EDX) analysis was performed to map the distribution of the microparticles in the polymer composite, further confirming and visually presenting the better dispersion of microparticles in the composites with stearic acid treated particles (Fig. 10). With the increasing attention towards incorporation of renewable fillers or food waste, e.g. egg shell waste $CaCO_3$ fillers [175], the incorporation of mussel shell $CaCO_3$ microparticles (8 wt%) in PVC composite membrane was also tested, and an improvement in the distribution of the stearic acid treated particles was observed with less agglomeration in comparison to untreated mussel shell waste $CaCO_3$ microparticles in PVC composite membrane (Fig. 11).

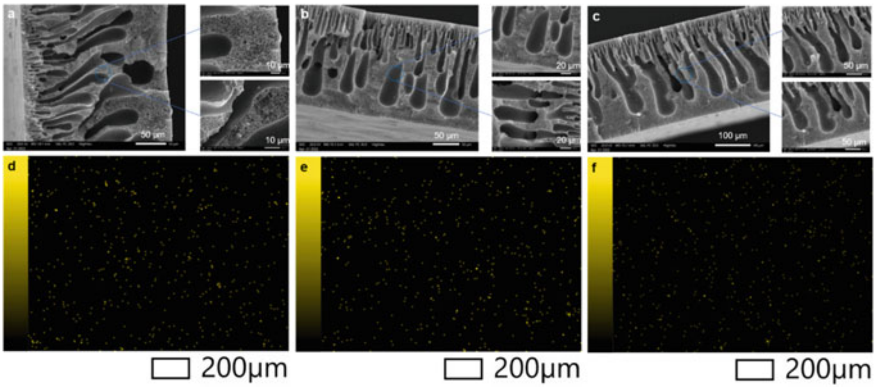

Fig. 10 SEM images of $CaCO_3$ PVC composite membranes with **a** untreated $CaCO_3$ microparticles, **b** $CaCO_3$ particles treated with stearic acid in ethanol at room temperature, **c** $CaCO_3$ particles treated with stearic acid in water at 45 °C, and EDX images of Ca distribution in $CaCO_3$ PVC composite membranes with **d** untreated $CaCO_3$ microparticles, **e** $CaCO_3$ particles treated with stearic acid in ethanol at room temperature, **f** $CaCO_3$ particles treated with stearic acid in water at 45 °C

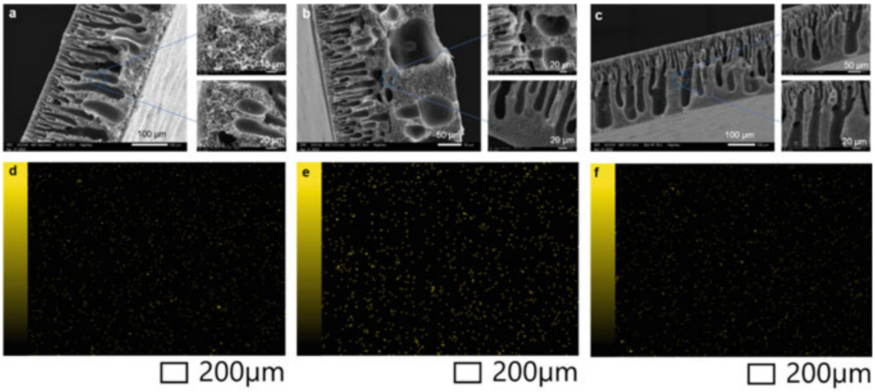

Fig. 11 SEM images of mussel shell waste $CaCO_3$ PVC composite membranes with **a** untreated mussel shell waste $CaCO_3$ microparticles, **b** mussel shell waste $CaCO_3$ particles treated with stearic acid in ethanol at room temperature, **c** mussel shell waste $CaCO_3$ particles treated with stearic acid in water at 45 °C, and EDX images of Ca distribution in mussel shell waste $CaCO_3$ PVC composite membranes with **d** untreated mussel shell waste $CaCO_3$ microparticles, **e** mussel shell waste $CaCO_3$ particles treated with stearic acid in ethanol at room temperature, **f** mussel shell waste $CaCO_3$ particles treated with stearic acid in water at 45 °C

5.3 X-ray Computed Tomography

The 3D structure of polymer composites can be imaged using X-ray computed tomography (XCT). It is a non-destructive technique that can generate a 3D image based on a stack of X-ray projections taken from several angles. The advancements in this technique over the last decade have enabled very high spatial resolution, in the form of nanotomography. Thus, this method allows the reconstruction of filler 3D distribution in the polymer matrix, filler percentage, orientation and dimensions of the fillers, and porosity. Moreover, at high resolution, the interface between fillers and polymer matrix can be investigated in 3D. Also, the effect of coupling agents or other interface modification techniques can be studied, for example, in terms of filler distribution. Imaging using XCT was used in the analysis and interpretation of shear fatigue of balsa wood and PVC foam sandwich core composites, whereby XCT analysis enabled quantification of the thickness of resin absorbed by foam core [176]. The XCT method was also applied to investigate deformation-induced dilation of PVC composites with mineral fillers, and different relative density distributions were identified for different geometries of the specimens that were subjected to tensile tests [177].

5.4 Pull-Out Micromechanical Test

A micromechanical analysis of the interfacial adhesion between a fibre and polymer matrix can be done using a pull-out test. This type of test has been commonly used on glass fibre reinforced composites, and is more recently also adopted for composites with natural fibres. The technique involves pulling a fibre out of a polymer block, small cylinder or micro-droplet, which is held by a microvise. A pulling force is then applied in the axial direction, which induces mainly tensile stress in the fibre and also shear stress at the interface of the fibre and the matrix, by increasing the displacement at constant rate while the force is monitored until the fibre breaks or is pulled out. Data generated with this test allow the calculation of the apparent interfacial shear strength. Although the pull-out micromechanical test is a common method to evaluate interfacial adhesion of fibres (and the effect of interface modification) in polymer matrices, the authors did not encounter studies focused on this technique in PVC composites.

5.5 Dynamic Mechanical (Thermal) Analysis

Dynamic mechanical analysis is used to study the viscoelastic response of polymers or polymer composites. This method is also applied to evaluate the interfacial interaction between particles and polymer matrix in composites. Generally, the motion of polymer chains is difficult near the interface, when there is a strong interfacial adhesion in the composite. Studies have reported that the storage modulus and loss modulus is much higher for PVC composites with calcium sulfate whiskers treated with titanium coupling agent than those with untreated whiskers, showing the efficient improvement of interfacial interaction, restricting deformation of the matrix [178]. A study on PVC composites with multi-layered graphene shows that the addition of graphene results in composites with a higher storage modulus than that of pure PVC, confirming the increase in tensile modulus or stiffness in static mode [179]. The composites have also a higher loss modulus and loss factor than pure PVC due to higher energy dissipation and higher damping of the composites under cyclic deformation conditions, which is interpreted by the larger interfacial area and interfacial friction-sliding between PVC chains and multi-layered graphene [179]. A lower value for the mechanical loss factor is measured in PVC composites with diatomite powder in comparison to pure PVC due to a restriction in the motion of molecular chains [160]. The mechanical loss factor in wood flour PVC composites showed a similar trend for pristine and recycled composites, and some recycled composites samples indicated a higher mechanical loss factor [45]. These higher values of the recycled composites suggest more viscous than elastic behaviour in comparison to the pristine composites. Moreover, the peak of the dynamic mechanical thermal analysis spectra showed a lower glass transition temperature of the recycled composites, which can be linked to the reduced fibre aspect ratio due to reprocessing, leading to easier polymer molecular motions, and thus reduced glass transition temperature [45].

5.6 Rheological Properties

The rheological behaviour of a polymer composite with fillers is affected by the affinity of the filler and the polymer. Adhesion of nanoparticles to polymer matrix leads usually to a higher viscosity of polymer composites, and the melt viscosity reaches a stable value at high shear stress range. A higher melt viscosity was also observed for PVC composites with $CaCO_3$ nanoparticles than for pure PVC [180]. Moreover, the melt viscosity of PVC composites with treated $CaCO_3$ nanoparticles was lower than that of PVC composites with untreated $CaCO_3$ nanoparticles, interpreted to be caused by the better dispersion of treated $CaCO_3$ nanoparticles in the PVC matrix and lower interaction between the nanoparticles [180].

6 Conclusion

Good adhesion between fillers and the polymer matrix is very important to reach the targeted performance and properties of the polymer composite. Conventionally, fillers are added to polymer composites to improve the mechanical properties, with a recent interest in the use of natural fibres as reinforcement. Moreover, other properties of PVC composites, such as radiation shielding and conductive properties have received more interest recently. In particular, PVC membranes for water treatment and electrochemical applications have attracted more attention in the last years. Physical and chemical modification methods can be applied to enhance interfacial adhesion in the composite material. This chapter has focused on plasma treatment, ultrasonic irradiation and surfactant modification as physical interface modification methods. In terms of chemical modification methods, acid, acetylation and alkaline treatment, the use of different coupling agents (maleated, silane, titanate), benzoyl chloride, chitosan-based, and phthalate treatment have been discussed. Furthermore, several interface characterization methods that have been used in research on PVC composites have been reviewed, with particular focus on the effect of interface physical and chemical modification methods, and Fourier transform infrared spectroscopy, scanning electron microscopy – energy dispersive X-ray analysis, X-ray computed tomography, dynamic mechanical analysis and rheological methods are reported.

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Natural Fiber Reinforced PVC Composites and Nanocomposites

A. Farrokhabadi and H. Arabqomi

1 Introduction

Polymers have many advantages over conventional materials, i.e., metals, and due to these advantages, many polymer materials have replaced conventional materials in various applications. Due to their easy process, high production rate, low cost, and multifunctionality, they have many applications [1]. However, some mechanical properties of polymer materials, such as strength and toughness compared to metals and other applied materials, may be insufficient for some specific uses, and these defects may limit their applications. Filler and fibers can modify the mechanical properties of polymers as reinforcement or just as filler. Properties of fiber-reinforced polymer composites are better than conventional materials, and their applications cover a vast area containing various fields from appliances to spacecraft [2]. Production of polymer fiber-reinforced composites initiated after the Second World War, which had limited their applications due to high production cost [3]. By the 1990s, their costs sharply decreased, and therefore, polymeric-based fiber-reinforced composites fund a more comprehensive range of applications which resulted in a massive amount of production, and thus, their wastes caused a severe environmental issue [3, 4]. The use of natural resources as constitutive materials in composites was a solution to reduce environmental issues. Green composites or biodegradable composites are a kind of composites using biopolymers and natural fibers and fillers in their structures and can dispose of them without deteriorating the environment. Using natural fibers with traditional petroleum-based nonbiodegradable polymer matrices including polypropylene, poly (vinyl chloride), polyethylene and epoxy result in a relatively biodegradable composite. Fully biodegradable composites are constructed

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of biopolymer as their matrix, reinforced with natural fibers. The reinforcement of the matrix phase (biopolymer or traditional polymer) with a combination of different natural fibers makes a hybrid green composite [5]. Other classifications of partially biodegradable or green composites can be based on the direction of fibers or functional behavior. Biopolymers are made up of living organisms containing monomeric units including saccharides, nucleic acids, and amino acids, in which the molecules are patterned with linearly or branched structures [6]. The prefix 'bio' refers to the living matter [7]. Biopolymers can be emanated from natural sources resembling plants, agricultural wastes, microbes, and animals [8]. Biopolymers include thermoset and thermoplastic polymers. However, if thermosets polymerize with synthetic monomers, they aren't fully green polymers [9]. Poly (lactic acid) (PLA), polyhydroxy butyrate (PHA), and thermoplastic starch are examples of biopolymers [10]. Natural fibers are fillers and reinforcements from renewable and non-man-made resources. Natural fibers can be categorized into three main classes: plant fibers, animal fibers, and mineral fibers. Plant fibers have two subgroups, namely wood and non-wood fibers. Wood fibers own a major contribution to natural fiber reinforcing biodegradable composites, but non-wood fibers also have a significant role. Wood fibers extract from softwood and hardwood. Non-wood fibers extract from seed, leaf, bast, fruit, and stalk [11]. Kenaf, jute, sisal, banana, cotton, coir, rice, bamboo are some common non-wood plant natural fibers [12–14]. Low cost, eco-friendly and low density of green composites are the characteristics that increase their importance, but due to some challenges in their process and nature of them, it is impossible to completely supersede all petroleum-based products with bio-based ones. The combination of both petroleum-based and natural materials can result in an optimum and useful product [15]. Inadequate mechanical properties, low permissible temperatures during process and operation, incompatibility between polymers and natural fibers are the significant challenges that can reduce the efficiency of the green composites [16]. While the natural fibers and most of polymers are hydrophobic, as a result, matrix and fibers become incompatible, and the interface of the matrix and fibers cannot quite transfer the loads. Physical and chemical treatments can reduce this incompatibility between fiber and matrix. Microwave processing, hydrothermal treatment, and steam explosion are physical treatment examples. Alkaline treatment, acid treatment, acetylation treatment, and benzoylation treatment are famous chemical treatments [17–22]. These treatment methods can have many positive influences on the quality and properties of natural fibers and their composites. Also, these problems limit natural fiber selection for reinforcement of polymers.

Poly (vinyl chloride), shortened as PVC, is an organ of vinyl polymers, and because of its low price, durability, and flexibility is widely used. Some other group members of vinyl polymers are polypropylene, polyethylene, polyvinyl acetate, polystyrene, polyvinylidene chloride and polymethyl methacrylate. PVC is a rigid thermoplastic polymer, and it becomes softer with the addition of the plasticizer; thus, it has many uses such as pipes, building materials, and many other applications. Low production cost, ease of fabrication, and long lifetime, which is because of the high resistance of PVC to various corrosive liquids, are the main reasons for the wide applications of PVC, which affects its usage significantly in comparison with other plastics [23]. PVC is one of the best petroleum-based thermoplastic polymers, which can be mixed with natural fiber to produce a partially biodegradable composite. This feature could decrease the disadvantages of using PVC and develop the benefits of the composites fabricated using this polymer [24]. PVC-based natural fiber composites (PNFCs) can be a competitor material to unfilled PVC. Fittings and electrical plugs, door lines and window, fencing, blinds, and decking are some applications of unfilled PVC that can be replaced with PNFCs. Substituting PVC with the PNFCs can lessen the growth rate of PVC productivity, reduce the environmental problems originating from the use of PVC and minimize the dependence on petroleum [25]. In recent researches, poly (vinyl chloride) is reinforced by bamboo, wood, coconut shell, rice husk, Areca Sheath, Sugarcane Bagasse, and date palm fibers [26–35]. This variety in natural fibers used with PVC shows that this polymer is a good candidate as a matrix in a green composite. PVC is a polymer, and as mentioned earlier, polymers are hydrophobic, and natural fibers are primarily hydrophilic. This difference between fibers and matrix in PVC-based biodegradable composites can decrease the mechanical, thermal, and other valuable properties of composites. Physical and chemical treatments of fibers can improve the quality of the composite.

This study introduces natural fibers used as reinforcement in biodegradable composites in detail. Then, general information and treatment methods of thermoset and thermoplastic green composites are presented, providing a good foundation for everyone interested in these topics. After, significant challenges, advantages, and disadvantages of the most applicable PVC-based partially biodegradable composites, which were interested in recent studies, are discussed.

2 Classification of Natural Fibers

Natural fibers are fillers and reinforcements from renewable and non-man-made resources. The use of natural fibers as a reinforcing phase in composites reduces concerns about environmental problems such as recycling of the materials and decomposition of them in the nature. Furthermore, natural fibers have a relatively low density compared to synthetic fibers; thus, natural fibers are a suitable alternative for low-weight applications where the weight of the material is a critical problem. However, natural fibers have poorer mechanical, structural, and water stability than synthetic fibers, so in most cases, using natural fibers in materials that have to carry high loads is inapplicable and risky. As a result, the primary use of materials reinforced by natural fibers is in secondary structures such as interior of automotive (side panels, seat frames, and central consuls) [36]. Properties of natural fibers are dependent on growth conditions. Natural fibers can be categorized into three main groups: plant fibers, animal fibers, and mineral fibers. Plant fibers have two subgroups, namely wood and non-wood fibers [37]. Wood fibers own a major contribution to natural fiber reinforcing biodegradable composites, but non-wood fibers also have a significant role [37]. Wood fibers extract from softwood and hardwood. Non-wood fibers extract from seed, leaf, bast, fruit, and stalk (Fig. 1).

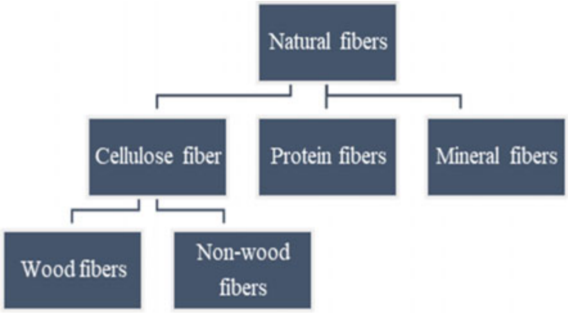


Fig. 1 Classification of natural fibers

3 Plant Fibers

All plant fibers are constructed of cellulose, including bast fiber, leaf fiber, seed, fruit, wood, cereal straw, and other grass fibers [38]. Jute, kenaf, date palm, coir, sisal, flax, hemp, bamboo, Sugarcane bagasse, and ramie are some of the most plant fibers which have many uses in the fabrication of green composites. The diameter of plant fibers is about 1–100 μm and has a noticeable variation. Fiber length depends on the plant species [11].

Plant fibers, or lignocellulosic fibers due to their chemical composition, are made up of three primary chemical matter, namely cellulose or α-cellulose, hemicelluloses, and lignin. They also have a few amounts of pectin, waxes, and water-soluble substances in their constructions. The quantity of these components varies from plant to plant and could also vary in different parts of the same plant. Age and species of plants are the reason for this variety [39]. For example, cellulose and hemicellulose make up about 45% and 25–30% of total wood dry weight, respectively [40]. The chemical composition and cell structure of plant fibers are illustrated in Fig. 2. The anatomy of plant fibers is quite complex and is a natural composite. In fiber plants, soft lignin and hemicellulose encompass rigid cellulose microfibrils like matrix in composites. Also, microfibrils are helically twirled along the fiber axis to form ultimate hollow cells [41].

The structural integrity of the fibers is due to the existence of the Cellulose. Cellulose consists of β-D-glucose units. These units produce a linear polymer chain by connection using β-1, 4-glycosidic linkages at C1 and C4 points [39]. $(C_6H_{12}O_5)_n$ as cellulose is a polysaccharide that can be changed to the simple form of glucose $(C_6H_{12}O_6)$. Cellobiose which is also recognized as anhydro cellobiose, is the shortest unit, repeated in structure, and is made of distillation of two glucose units, as shown in Fig. 3a. All lignocellulosic fibers are hydrophilic. This essential property is due to the existence of six hydroxyl groups in Each repeated unit, and these groups shape intermolecular and intramolecular hydrogen bonds with the macromolecule and other cellulose macromolecules or polar molecules [42].

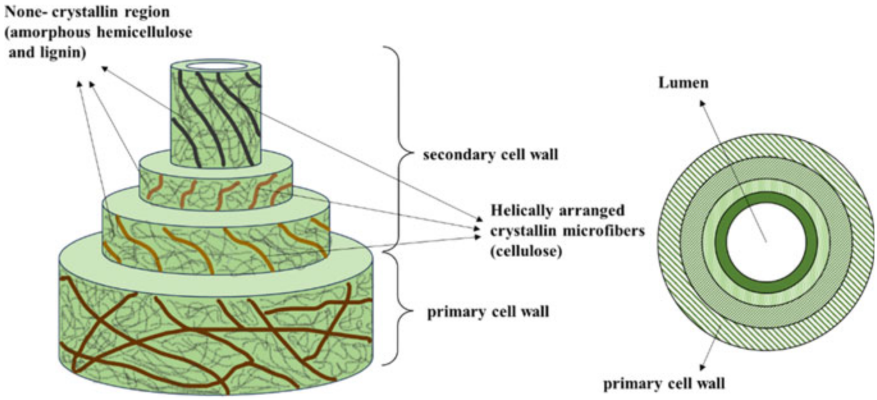
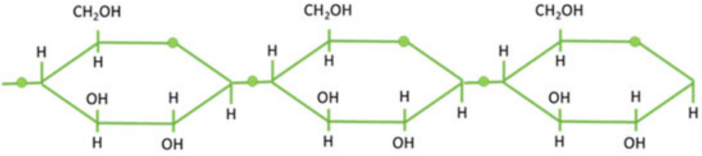


Fig. 2 Composition of plant fibers

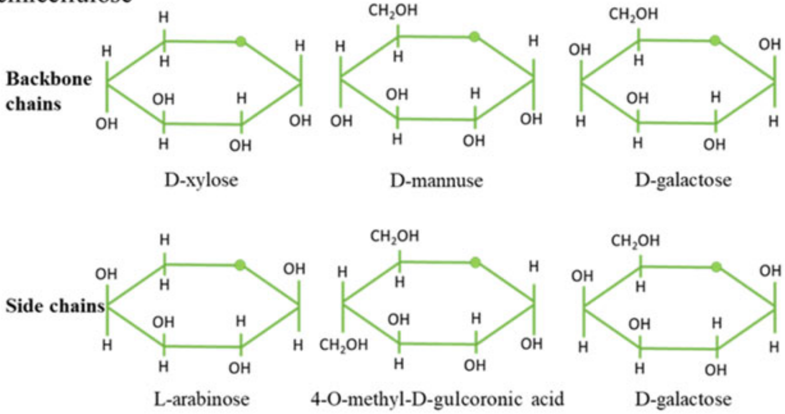
Hemicellulose keeps pectin and cellulose side by side, forming a network, and after cellulose, it is the second most plentiful organic material on earth. The structure of Hemicellulose is presented in Fig. 3b, and it is more complex than cellulose. Covalent and non-covalent bonds link Hemicelluloses to cellulose and lignin, and how they are in contact determines the flexibility and rigidity of the cell wall. Hemicelluloses are a group of homopolymers and heteropolymers. Mannopyranose, glucopyranose, anhydro-β-(1–4)-D-xylopyranose, and galactopyranose main chains with several substituents constitute Hemicelluloses [43]. The principal hemicellulose constituents are mannan-based in softwood and xylan-based in hardwood [38].

Lignin is the most generous polymer in nature which is a natural polymeric product originating from an enzyme-initiated dehydrogenative polymerization of three primary precursors, including trans-coniferyl, trans-sinapyl, and trans-p-coumaryl, shown in Fig. 3c [44]. Lignin fills the spaces between pectin, hemicellulose, and cellulose in the cell wall. It exists in the cellular cell wall conferring structural support, impermeability, and resistance against the oxidative stress and microbial attack. Hemicellulose and cellulose are macromolecules of diverse sugars, while lignin is an aromatic polymer synthesized from phenylpropanoid precursors. Pectin and wax are two constituents of plant fibers that exist at a low percentage in plant fibers. Pectin connects the plant cells and specifies the shine and touch of the fibers. It consists of heterogeneously branched polysaccharides. The high accumulation of pectin appears in the primary cell wall and middle lamella of fiber. The simplest form of pectin is homogalacturonan (HG), an unbranched polymer of α-(1–4) connected D-galacturonic acid, as shown in Fig. 4d. Waxes are also a critical constituent element of the fiber cell wall. This element specifies smooth touch, low friction, and thus the case of moving the fiber [44]. Waxes comprise various alcohols soluble in water and acids, including phenolic, greasy, and stearic acid [38]. The chemical composition of common lignocellulosic fibers is presented in Table 1.

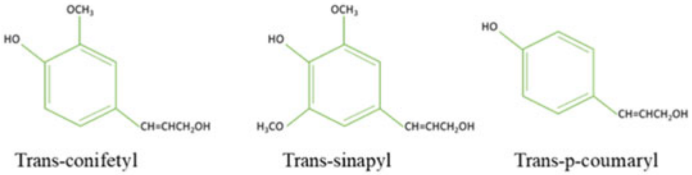
(a) Cellulose



(b) Hemicellulose



(c) Phenols in lignin



(d) Pectin

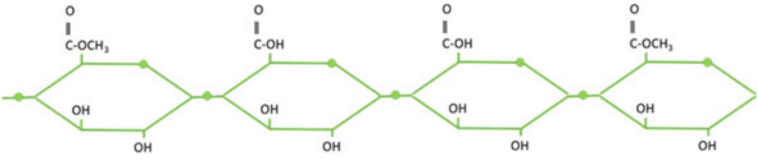


Fig. 3 Chemical organization of the primary constituents in the fiber cell wall

4 Animal Fibers

Animal fiber composites possess higher strength, flexibility, and corrosion resistance. Animal fibers contain proteins. Sheep wool, bird feathers, human hair, and (spider/moth) silk are examples of applied animal reinforcements. They are also called protein fibers [46]. Numerous reactive functional groups are present in protein

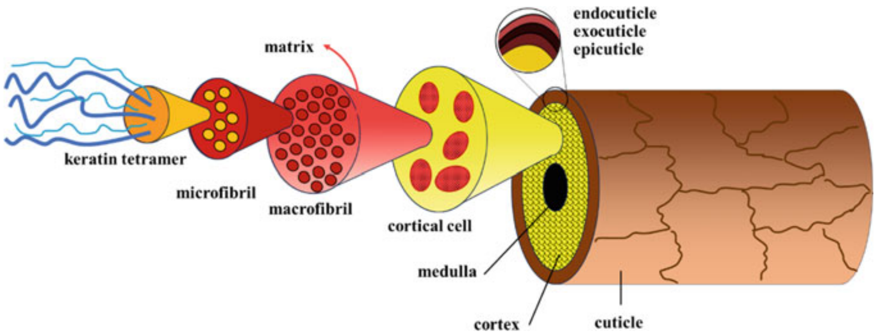


Fig. 4 Human hair structure

Table 1 Chemical composition of some plant fibers [38, 45]

Fiber	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Pectin (wt%)	Wax (wt%)
Flax	71–78	18.6–20.6	2.2	2.3	1.7
Kenaf	45–57	21.5	8–13	3–5	0.5
Hemp	70.2–74.4	17.9–22.4	3.7–5.7	0.9	0.8
Ramie	68.6–76.2	13.1–16.7	0.6–0.7	1.9	0.3
Jute	67–71.5	13.6–20.4	12–13	0.2	0.5
Rice husk	35–45	20	19–25	–	14–17
Sisal	67–78	10–14	8–11	10	2
Pineapple	80–83	15–20	8–12	2–4	4–7
Abaca	56–63	21.7	12–13	1	0.2
Cotton	85–90	5.7	0.7–1.6	0–1	0.6
Coir	36–43	0.15–0.25	41–45	3–4	–
Bagasse	55.2	25.3	16.8	–	–
Bamboo	26–43	21–31	30	–	–
Soft wood	43–45	25–35	16–24	–	–
Hard wood	40–44	25–29	25–31	–	–

fibers, with amino acids interconnected by peptide bonds. Protein contents are oriented parallel to the fiber axis. Numerous reactive functional groups are present in protein fibers, with amino acids interconnected by peptide bonds. Protein contents are oriented parallel to the fiber axis.

Smoothness, durability, and non-sticky surface are some properties of wool fibers. These properties give the excellent ability to elongate and elastic recovery of fibers [47]. Wool fibers have the protein content as keratin with five main elements: carbon 50%, hydrogen 6–7%, nitrogen 15–21%, oxygen 21–24%, sulfur 2–5%, and other elements. Keratin is a tough protein in hair fiber and has high flexural strength and acceptable thermal stability. It exists in sheep wool fibers and exhibits advancement in the mechanical properties of the composite. Wool fibers layers include two types of cells. Cells include the internal cells of the cortex and external cuticle cells that constitute a sheath around the fiber [48].

Human hair is an essential biomaterial fiber created with protein and significantly alpha-keratin, which rises from follicles in the skin or dermis [49]. The cross section of human hair shaft comprises the medulla, cortex, and cuticle, Fig. 4. The cuticle layers are flat, thin cells like roof shingles overlaying one another. The cortex possesses the keratin bundles in cell structures that stay roughly rod-like. The medulla is a rambling and open area at the fiber's center. The constitutive elements of hair are about 50.65% carbon, 20.85% oxygen, 17.14% nitrogen, 6.36% hydrogen, and 5.0% sulfur [50]. Amino acids in hair retain arginine, valine, leucine, glycine, serine, threonine, cytosine, and glutamine [51]. Goat hair fiber, also named diamond fiber, is more costly than human hair and has exceptional insulating characteristics, flame resistance, fine elasticity, crease-resistant, moisture-wicking properties.

Chicken feather fiber is an aviculture waste. Crafting, textile, and biocomposite products are practical applications of the feather in industries. Crafting, textile, and biocomposite products are practical applications of the feather in industries. It has an incredible agreement in common with reptilian keratin from claws. The amino acid row of a chicken feather is very analogous to the other feathers. The feather contains approximately 91% keratin, 7.9% water, and 1.3% fat. The row is composed primarily of cystine, glycine, serine, and proline and contains nearly no histidine, methionine, or lysine [52]. The fibers are like a narrow thread. It is joined to the quills. The quill is a tough, central axis off which smooth, interlocking fibers branch. The existence of a quill among fibers results in a more granular, light, and massive material. Smaller feathers have a more significant proportion of fiber, which has a higher aspect ratio than the quill. The dimensions of a standard quill including the length and diameter are in the range of centimeters and millimeters respectively, and fiber is in the range of 550 μm (Fig. 5).

Silk is a strong and expensive protein fiber. Moth and spiders are two familiar sources of it. However, Bombyx mori moth silk produces Most of the saleable silk fiber. Cocoons are natural polymeric composite shells comprised of fibroin and sericin binder and crafted by a single continuous silk strand [25]. The length of the continuous silk strand of the cocoon is in the range of 1000–1500 m and bound by sericin. Silk fibroin is a natural protein and possesses a semicrystalline structure. This structural characteristic makes fiber stiff and strong. The sericin binder holds the structure of the fiber as an adhesive binder. As an application in medical industries and tissue engineering, recently, silk fiber has been employed as reinforcement in biopolymers. A spider produces another type of silk fiber and can have six different silk fibers. Major and minor ampullate silk, aciniform silk, flagelliform silk (capture core threads), piriform silk and tubuliform silk (outer egg sac) are six different silk fibers that a spider can produce, as shown in Fig. 6 [53]. Wool, hair, and feather fibers are different from silk fibers in many perspectives. The first group of fibers contains keratin protein which growth from an external skin layer like a goat, sheep or chicken. The silk fiber is a protein fiber from the silk glands of an insect.

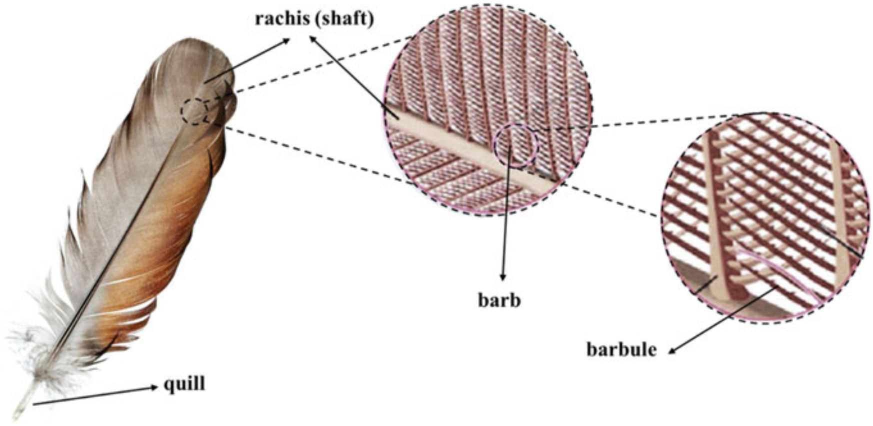


Fig. 5 Structure of a regular chicken feather

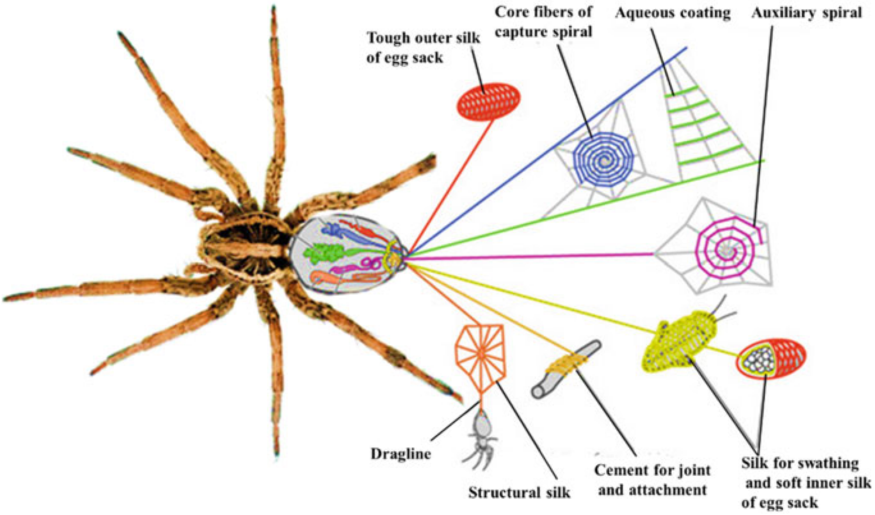


Fig. 6 The spider silk types, and their applications

5 Mineral Fibers

Asbestos is the only natural mineral fiber used as reinforcement. Asbestos is a broad name used for a cluster of silicate minerals that naturally appear in fibrous form. Chrysotile, Actinolite, Amosite, Anthophyllite, Crocidolite, and Tremolite are six principal asbestos minerals. These six types divide into two leading mineral groups: amphibole and serpentine asbestos. The serpentine group has a layered silicate structure, and the amphibole group has a chain structure [54]. The significant distinction between amphibole and serpentine asbestos is fiber appearance. Serpentine fibers are flexible, twirly, and long while amphibole fibers are inflexible, linear, needle-like, and short. Asbestos materials are either brittle or non-brittle, depending on how easily the material can be broken down by hand. Brittle asbestos can granulate or break by hand, but non-brittle asbestos cannot granulate or break by hand and may be ground by sanding, cutting, or sawing. Asbestos use peaked towards the late 1900s. Earlier, asbestos was applied primarily for fireproofing and heat resistance in various products. The mineral was utilized in roofing, flooring, cement, insulation, and fire-proof products [55]. From the 1930s to the 1970s, the extraction and application of asbestos were widespread, but animal studies reveal that inhalation of asbestos can result in lung cancer, pulmonary fibrosis and mesothelioma [56]. Asbestos fibers are harmful when inhaled or ingested and accumulate in organ linings and tissues. In 1979, these health concerns forced manufacturers to use securer asbestos alternatives based on asbestos regulations. The use of asbestos has been limited or forbidden in the U.S. and several other countries, but in developing countries, the use of asbestos continues to increase. Brittle products generally cause more of a health hazard than non-brittle asbestos.

Chrysotile also is referred to as white asbestos, and it is one of the most typically found types of asbestos. No type of asbestos is safe for humans, but chrysotile is not the most fatal for raw exposure. Actinolite was popular for embedding in gardening materials, diverse shapes of fireproofing, and insulation products. Actinolite fibers are microscopic and can readily pierce the lungs, much like most other shapes of asbestos, making it very harmful to respire in. Due to Amosite's appearance being similar to a rich, dark wood in terms of color, it is called brown asbestos. Amosite doesn't absorb water very well. Anthophyllite contains extremely firmly packed mineral-based fibers, much like some other shapes of asbestos, and respiring in or handling the material can be too toxic, especially to those with pre-existing lung diseases. Crocidolite is the most fatal and detrimental kind of asbestos. Crocidolite has a fairly blue tint and is soft. Any shape of direct exposure to this material is seriously toxic. Tremolite is one of the most aged and old-time shapes of asbestos that was used. It has been used since at least the late 1780s. Like other shapes, it can beget everything from lung cancers to forms of mesothelioma.

6 Physical and Mechanical Properties of Natural Fibers

The physical properties of the natural fibers influence their mechanical characteristics. Natural fibers, mainly plant fibers, that have the most application as reinforcement in poly (vinyl chloride) in industries compared to other types, have lower mechanical properties and strength than synthetic fibers such as glass and carbon fibers. They also have a lower density than synthetic fibers. The specific properties, stiffness and strength of natural fibers are analogous to the values of man-made fibers because of their low density. Cellulose content and microfibrillar angle specify plant fibers' mechanical properties. Growth of diameter in natural fibers reduces

Young's modulus. Increasing cellulose content and decreasing low microfibril angle make plant fibers more suitable as reinforcement in polymeric-based biodegradable composites. The physical and mechanical properties of some common natural fibers are listed in Table 2 and compared to man-made fibers.

The matrix and reinforcement interaction at the interface is recognized as interfacial bonding. Four kinds of interfacial bonding exist, namely mechanical interlocking, interdiffusion bonding, chemical bonding, and electrostatic bonding, as illustrated in Fig. 7 [60]. The interdiffusion bonding is referred to as the Physical adhesion interface. Wettability is a powerful governing mechanism of Interdiffusion bonding. In interdiffusion bonding, optimum surface energy and polarity on both matrix and fibers form enduring adhesion through covalent, electrostatic forces, and Van der Waals. Plant fibers have non-polar waxes on their surface, with somewhat lower surface tension. Polar components such as lignin and fats have more surface tension than non-polar waxes [61]. The entry of molten polymer into micron-diameter holes on the coarse fiber surface causes mechanical interlocking. Electrostatic adhesion results from the attraction of positive (cations) and negative (anions) charges for creating the interface. Covalent and ionic bonding between atoms forms the interface of the matrix and fibers in a chemical bonding.

Table 2 Physical and mechanical properties some natural fibers [57–59]

Fibers	Length (mm)	Diameter (μm)	Density (g/cm^3)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation (%)
Flax	4–140	5–76	1.27–1.55	27	345–1500	3–4
Kenaf	1.5–11	12–50	0.15–0.55	23–27	215–930	3.4
Hemp	8–55	5–40	1.48	32	550–900	1.6
Ramie	–	–	1.5–1.56	22	220–938	1.2–3.8
Jute	1–5	5–30	1.46	20–25	393–800	1.8
Sisal	0.5–8	4–47	1.33	17–22	400–700	4.3
Pineapple	–	–	1.25–1.60	50–71	170–627	0.8–14.5
Abaca	2–12	6–46	1.5	41	12–980	1.6
Cotton	–	–	1.54	6–10	287–597	3–10
Coir	150–300	10–30	0.67–1.15	4–13	175–220	1.17–2
Bagasse	–	–	1.45	15–19		3–7
Bamboo	–	–	0.8–1.32	35.45	140–230	16
Wood	1–6	10–50	1.5		1000	
Wool	–	–	–	2.3–3.4	120–174	25–35
Spider silk	–	–	–	11–13	875–972	17–18
Eglass	–	–	2.5	70	2000–3500	2.5–3
Aramid	–	–	1.4	63–67	3000–3150	3.3–3.7
Carbon	–	–	1.4	230–240	4000	1.4–1.8

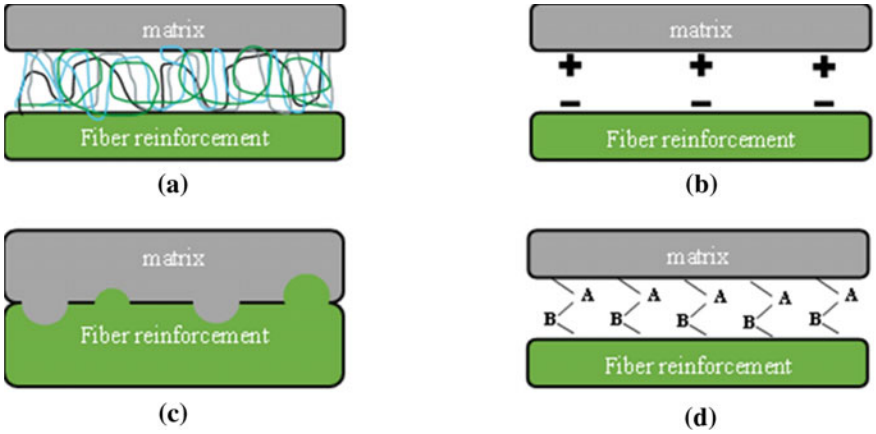


Fig. 7 **a** Molecular inter diffusion, **b** electrostatic bonding, **c** mechanical interlocking, and **d** chemical bonding

Interface bonding can primarily influence the properties of fiber-reinforced composites. A lousy interface may have a notable decline in mechanical and thermal properties. It mainly relies on the compatibility of the matrix with the reinforcements and the surface conditions of the reinforcements. Micro-mechanical techniques, Spectroscopic techniques, microscopic techniques, and thermodynamic methods are four methods that can characterize the interface [61]. Numerous treatments have been applied to the composites to enhance physical, mechanical, and thermal characterizations and establish good compatibility between matrix and reinforcement. Physical treatment methods include discharge and radiation treatments such as UV radiation, corona, plasma radiation, and gamma which have considerable utilization in the treatment of plant fiber composite. Physical treatments alter surface properties and the structure of the plant fibers. A typical gamma radiation treatment is identified to deposit energy on the plant fiber in the composite, producing radicals on the cellulose chain by hydroxyl and hydrogen abstraction, ruptures of some carbon–carbon bonds, and chain scission. Irradiation of matrix polymers in the existence of oxygen causes the production of peroxide radicals simultaneously. These active zones in both matrix and fiber made by the gamma radiation cause better adhesion between the fiber and polymer matrix [62]. Plasma treatment utilizes the elements like high-energy photons, electrons, ions, radicals, and exciting species to improve the surface properties of the plant fiber and polymeric materials. The improvement of plant fiber by the treatment in cold oxygen plasma achieved in a corona discharge under optimal operating states makes the fiber semi-active for the cellulosic compounds that increase bonding at the interface of fibers and matrix [63]. Corona treatment utilizes a low-temperature corona discharge plasma to modify the surface energy. The sharp tip of an electrode generates the corona plasma when a high voltage is applied to it. The corona treatment of plant fiber forms high-energy electromagnetic fields near the charged points, with resulting ionization in their nearness [63].

Chemical treatment methods include alkaline treatment, silane treatment, acetylation treatment, benzoylation treatment, etc. Alkaline treatment, or mercerization, is a popular chemical treatment method for natural fibers in thermoplastics and thermosets and is usually carried out in NaOH aqueous solution. Alkaline treatment interrupts hydrogen bonding in the network structure, withdraws a certain amount of lignin, wax, and oils from the outer surface of the fiber cell wall, depolymerizes cellulose, and reveals the short length crystallites. Alkaline treatment breaks the hydroxyl groups (OH), and they react with water (H–OH), quitting the ionized reactive molecules to construct alkoxide with NaOH. This chemical reaction reduces the hydrophilic OH groups on the surface of the fibers and increases the surface roughness of the fiber, as shown in Eq. (1) [58].

$$\text{Fiber} - \text{OH} + \text{NaOH} \rightarrow \text{Fiber} - \text{O} - \text{Na} + \text{H}_2\text{O} + \text{impurity} \tag{1}$$

Silane is an inorganic chemical compound with the chemical formula SiH4. It is a multifunctional molecule operated as a coupling agent to adjust fiber surfaces. Silane coupling agents may decline the number of interfacial cellulose hydroxyl groups. A routine silane coupling agent handles two reactive groups. One end of the silane agent with alkoxysilane groups can react with the hydroxyl-rich surface, i.e., wood or other plant fibers. In contrast, the other end interacts with the polymer matrix. The silane could react with water to create silanol, additional reacting with the hydroxyl groups bound to the cellulose, lignin, and hemicellulose molecules in the fiber via an ether connection with water removal. Furthermore, the polymer matrix could react with the hydrophobic adhesives in silane molecules. Thus, the hydrocarbon chains provided by the silane application control the fiber's bulging by creating a twisted/crosslinked network because of covalent bonding between the matrix and the fiber. Besides, the hydrocarbon chains were thought to influence the wettability of the fibers and enhance the chemical attraction of the polymer matrix; thus, treatment enhanced the interfacial bonding between fiber and matrix [63]. This reaction is shown in Eq. (2).

$$\text{Fiber} - \text{OH} + \text{R} - \text{Si(OH)}_3 \rightarrow \text{Fiber} - \text{O} - \text{Si(OH)}_2 - \text{R} \tag{2}$$

Acetylation treatment (Eq. 3) also is known as the esterification method for plasticizing natural fibers. Acetylation represents a reaction presenting an acetyl functional group (CH_3CO) into an organic blend that reacts with the fiber's hydrophilic hydroxyl groups (OH) and takes out the existing moisture. Thus, the hydrophilic essence of the fiber is decreased. In acetylation treatment, an acid catalyst such as sulfuric acid and acetic acid is typically utilized to accelerate the reaction and maximize the degree of acetylation [63].

$$\begin{aligned}\text{Fiber} - \text{OH} + \text{CH}_3 - \text{C}(=\text{O}) - \text{O} - \text{C}(=\text{O}) - \text{CH}_3 \rightarrow \text{Fiber} - \text{O} - \text{COCH}_3 \\ + \text{CH}_3\text{COOH}\end{aligned} \tag{3}$$

Benzoylation treatment is another treatment with the aim of reducing the hydrophilicity characteristic of plant fiber. This method employs benzoyl chloride to reduce the fiber's hydrophilic essence and improve interfacial bonding. Initially, the plant fiber should be pretreated with NaOH aqueous solution before reacting between the benzoyl groups and fiber. It activates and reveals the hydroxyl groups on the fiber surface. Thus, the fiber can be treated with benzoyl chloride, which the benzoyl group further replaces. This causes fibers to find a more hydrophobic property and enhances fiber-matrix bonding; thus, composite strength and thermal stability considerably increase [64].

$$\mathrm{Fiber} - \mathrm{O} - \mathrm{Na} + \mathrm{C_6H_5} - \mathrm{COCl} \rightarrow \mathrm{Fiber} - \mathrm{O} - \mathrm{CO} - \mathrm{C_6H_5} + \mathrm{NaCl} \tag{4}$$

7 Thermosets and Thermoplastics Based Natural Fiber Composites

A composite is a material constructed from two or more phases that produce a new material with characteristics distinct from the constitutive materials. Fiber-reinforced plastic composites, or in abbreviation FRPCs, are a contemporary category of composite materials. When high modulus fibers add to a polymer matrix, plastics' low mechanical and thermal properties enhance, and fiber's properties overcome to weak properties of the plastic matrix. Glass fibers and ceramics are old filers and fibers utilized as reinforcement for composites. However, lately, organic fillers, like lignocellulosic-based and protein-based fibers, have arisen in the market. They offer benefits over classic inorganic fillers, such as cheapness, having lightweight, collected from renewable resources, accessible and biodegradable. These new composites have many applications, from various automotive components to building structural pieces. Natural fibers can mix with thermoset (such as unsaturated polyester, phenol–formaldehyde, novolak-type phenolic formaldehyde, and epoxy resins) and thermoplastic (such as Polyethylene, Polypropylene, and Polyvinyl chloride) polymers to form composite materials. The thermosetting matrix comprises two or more components. A multifunctional monomer is one of the thermoset matrices constitutive that crosslinks the material. In thermoset matrix composites, fibers are saturated with blended thermosetting resins. Then, it is maintained at room or high temperature to harden. Vacuum infusion, modified lay-up/press molding, pultrusion, hand lay-up, and resin transfer molding (RTM) are accepted manufacturing methods for Composites with thermosetting matrices. Thermosetting resins have high impact resistance but cannot be reshaped after curing or polymerization. The combination of untreated natural fibers and thermoset matrix causes inefficient interfacial bonding due to the existence of a hydroxyl group. Cured thermoset matrix can turn into particles as recycling prosses reused as fillers in new laminates or other products. As mentioned earlier, natural fibers can be utilized as reinforcements in thermoplastics. Thermoplastic matrixes don't need to cure, and they have less hazardous chemical constitutive components. Besides, the recycling of these polymers is easy and convenient. These advantages of thermoplastics over thermosets cause thermoplastics to find significant attention as polymer matrices. Also, thermoplastic composites can reshape after fabrication. Injection molding, vacuum forming, extrusion, rotational molding, and compression molding are some fabrication methods for thermoplastic resins. Extrusion, compression molding and injection molding are more common fabrication methods in comparison to other for thermoplastic base composites.

Compression molding is proper for industries such as automotive, which need mass production volume. Cooled compression molding and hot compression molding are two types of this process. Polypropylene (PP), polyether ether ketone (PEEK), Poly (Vinyl Chloride) (PVC), and polyamide are some thermoplastic matrixes that can be used. Wirawan et al. used compression molding to fabric sugar cane bagasse and poly (vinyl chloride) (PVC) composite specimens. They placed materials into the mold under pressure at a temperature of about 170 °C for 12.5 min, and then the sample was cooled under pressure to room temperature.

Injection molding is used frequently to manufacture plastic components. Composites that are fabricated using this method should contain only short fiber in the form of powder and particles. In this method, a twin-screw extruder prepares the injection molding compound granules. Then a heating process in a barrel melts the granules, and the molten composites transfer to a mold to form the desired shape. After cooling, the part is ejected from the mold. Kiani et al. used the injection molding method to fabricate PVC-based natural fiber composites. They used pulp fiber and wood flour as reinforcement and studied the water resistance and thermal stability of components. Fibers were milled to the size of 345 μm.

The extrusion process is similar to Injection molding, but the molten composite extrudes continuously through a nozzle and makes a component with a constant cross-section profile. The extrusion method has the capability of using long fibers, and this is an excellent advantage over the injection molding method because using long fibers create incredible strength. Zolfaghari et al. used the extrusion process to prepare wood plastic composites reinforced with continuous glass fibers and high-density polyethylene (HDPE) as the matrix.

8 Natural Fiber Composites Applications

In addition to stiffness and lightweight properties, natural fibers can be used as a good insulator in thermal or acoustic applications. Due to these advantages, they can be applied in many applications such as doorframes, partitioning, false ceilings, and surface paneling which are parts of the construction industry. In 1941, Henry Ford used natural fibers (flax and hemp fibers) in the automotive industry [65]. Interior automotive parts, i.e., cushioned seats, door panels, and cabin lining, are some applications of biodegradable composites in the Automotive industry. In

2016–2017, the biggest contribution of the natural fiber composite market belonged to the automotive and construction industries. Sporting equipment, packaging, Aircraft components, electrical parts, and biomedical industries are more applications of these composites. Due to low durability in wet areas, some applications like piping, boats, and kayaks are not safe for these composites. Low mechanical properties and low durability in wet areas are two major limiting factors in applying biodegradable composites. Because of the governmental regulations about using eco-friendly products, the natural fiber composite market's worth is expected to attain $46.3 billion by 2025. Tecnaro GmbH (Germany), FlexForm Technologies (USA), Fiberon LLC (USA), Trex Company Inc. (USA), Meshlin Composites ZRT (Hungary), Jelu-Werk J. Ehrler GmbH & Co. KG (Germany), UPM (Finland), Green Bay Decking (USA), Toray Industries Inc. (Japan), Universal Forest Products Inc. (USA), and Owens Corning (USA) are some of the existing foremost companies in the global natural fiber composite market [65].

9 Natural Fiber Poly (Vinyl Chloride) Composites

Over the last few decades, many articles have been reported in biocomposite materials. It indicates the growing appeal of using natural fiber as a substituted reinforcement for glass, carbon, and other synthetic fibers in composites. Environmental issues are one of the principal causes of this interest. It has minor ecological damage at the production and processing stages and less waste than any synthetic fiber. Low cost, lightweight, and good thermal or acoustic insulator are other reasons. Both thermoplastic and thermoset polymers can reinforce with natural fibers. In the case of thermoplastic polymers, the temperature is one of the main parameters which limit the production of biodegradable composites. Natural fibers cannot fabricate at too high temperatures, and thus there are restricted thermoplastic polymers that can use with natural fibers without degradation of fiber properties. Poly (Vinyl Chloride) (PVC) is a thermoplastic resin that can be used with different natural fibers to produce partially biodegradable composites. It can have flexible and rigid forms. The rigid form of PVC is a high-strength thermoplastic polymer and is highly resistant to corrosive liquids. The wide application of PVC is due to a combination of these attributes with the low price of PVC. Like other thermoplastics, PVC is a pollutant polymer with environmental and safety issues. It generates some harmful chemicals in the environment, such as hydrogen chloride and dioxins, when it is processed or decomposed. However, due to the economic advantages of this thermoplastic, the growth of PVC is unstoppable. Blending PVC with natural fibers could reduce the environmental issues and health effects caused by the usage of PVC and may increase the growth rate of PVC production. Besides, it simultaneously develops the advantages of the composites. Nowadays, Unfilled PVC has many applications, such as electrical plugs and fittings, window and door lines and blinds, fencing, and decking applications. Most of these PVC products can be made from natural fiber

PVC composites. As in other biodegradable polymer-based composites, compatibility is a significant challenge in natural fiber PVC composites, reducing the quality of the final products. common treatment methods can apply to PVC-based partially biodegradable composites to enhance their properties. Natural fibers used with poly (vinyl chloride) in recent studies are listed in Table 3. The variety of natural fibers used with PVC show that this thermoplastic is a good candidate to mixing with natural fibers to make biodegradable composites. About 22% of reports which is investigated, show that wood fibers are main natural fiber reinforcement for mixing with PVC (Fig. 8). Date palm, rice Straw, rice husk, bamboo, Sugarcane Bagasse also used in many studies but their contribution is lower than wood fibers. In addition to plant fibers, mixing PVC with Animal fibers and reinforcements have got many attentions in biodegradable composites filed. Chicken feathers, egg shell, cow horns, leather fiber are animal fibers or fillers used with PVC matrix. However, studies on mixing PVC with animal fibers compared to Plant fibers have lower variation. Approximately, 88% of investigations is about plant reinforcement and only 12% of them is dedicated to Animal reinforcement, as shown in Fig. 9.

Wood Polymer Composites (WPC) have been increasingly utilized in the modern construction segment for four decades. The market for PVC-based WPCs is the most favorable one among various plant fiber-reinforced polymer composite markets, with a growth rate of 200% from 2002 to 2010. Over 80% of natural fiber-reinforced composites are created from wood fibers. Window profiles, door profiles, decking, railing, and siding are equipment made from PVC-based WPCs and have the prospect of being cut, sawed, nailed, screwed, and processed. The advantages of wood are low density, excellent mechanical properties, good biodegradation, non-toxic, recyclable, and aesthetically pleasing. UV radiation, biological attack, degradation from high temperatures, and the air moisture content are disadvantages of wood. Due to thermal degradation, wood is only suitable for some types of plastic, such as PVC, PE, and PP. Also, it is challenging to reach strong adhesion between hydrophilic cellulose and hydrophobic polymer like most plant fibers. Wood fiber and wood flour are common wood reinforcement shapes for mixing with PVC. Wood density is the significant distinction between hardwood and softwood. Hardwood trees usually have sluggish growth and are regarded as angiosperm, deciduous trees. Their leaves are shed yearly, which causes denser wood than softwood. Softwood trees are gymnosperms (they are evergreen trees), and thus they do not shed their leaves.

Sombatsompop et al. [90] investigate the influences of cross-section configuration and testing conditions (span length,loading directions, and rate of loading) on the flexural properties of wood/PVC composite beams. They produced samples by an industrial-scale twin-screw extruder. Wood sawdust particles used had an average size of 100–300 μm. They used chemical treatment and treated wood fibers with 1.0 wt% of N-2(aminoethyl)-3-aminopropyltrimethoxysilane. To make wood fibers dry, they kept at 80 for 24 h, and the weight of the fibers became constant. PVC and dried wood fibers are mixed utilizing a fast mixer for 2 min, then the mixture melt in a twin-screw extruder. The diameter of the screws was 90 mm, and the length of it was 3,240 mm. Five different cross-sections of WPVC samples were used to test. A cooling system and a size control device were used to solidify samples and give

Table 3 Some natural fiber PVC composites

Reinforcements	Treatment methods	Shape	Fabrication methods	References
Plant reinforcement				
Cotton	Alkali treatment, CE treatment	Very fine sizes	Extrusion, compression molding	[66–69]
Date palm\Leaf\Kernel	Alkaline treatment, silane treatment	Very fine sizes	Compression molding, extrusion	[27, 35, 70–72]
Sorghum straw	Alkaline treatment	Very fine sizes	Extrusion	[73, 74]
Banana	Alkaline treatment	Very fine sizes	Compression molding	[75, 76]
Kenaf	Alkaline treatment	Very fine sizes	Compression molding	[77–79]
Wood	Silane treatment, maleic anhydride treatment	Very fine sizes	Compression molding, extrusion	[26, 80–94]
Jute	–	Plane woven, 152.4 mm	Compression molding	[95–97]
Oil palm empty fruit bunch	–	Very fine sizes	Compression molding	[98]
Rice straw	Silane treatment, alkaline treatment	Very fine sizes	Compression molding	[99–101]
Rice husk	Benzoylation and alkaline treatment	Very fine sizes	Compression molding	[102–105]
Coconut shell	Alkaline treatment	Very fine sizes, up to 3–4 mm	Extrusion, compression molding	[28, 30, 106]
Bamboo	Alkaline treatment	Very fine sizes, up to 1 mm	Compression molding	[29, 107–110]
eucalyptus	Alkaline treatment	Very fine sizes	Extrusion	[111]
Alfa fiber	–	Very fine sizes	Compression molding, Injection molding	[112–114]
Sugarcane Bagasse	Alkaline treatment, H_2O_2 and ultrasonic treatment	Very fine sizes, up to 10 mm	Compression molding	[115–117]

(continued)

Table 3 (continued)

Reinforcements	Treatment methods	Shape	Fabrication methods	References
Sisal fiber	Benzoyle peroxide treatment	Very fine sizes	Compression molding	[118]
Citrus maxima fibers	–	Particle	Solvent casting method	[119]
Raspberry pomace	–	Particle	Compression molding	[120]
Olive husk	–	Very fine sizes	Compression molding	[121]
Animal reinforcement				
Chicken feathers	–	Very fine sizes, up to 4 mm	Extrusion, compression molding	[122–125]
Egg shell	–	Very fine sizes	Compression molding, extrusion	[126–128]
Cow horns	–	Very fine sizes	Extrusion	[106]
Leather fiber	–	Up to 2 mm	Extrusion	[129]

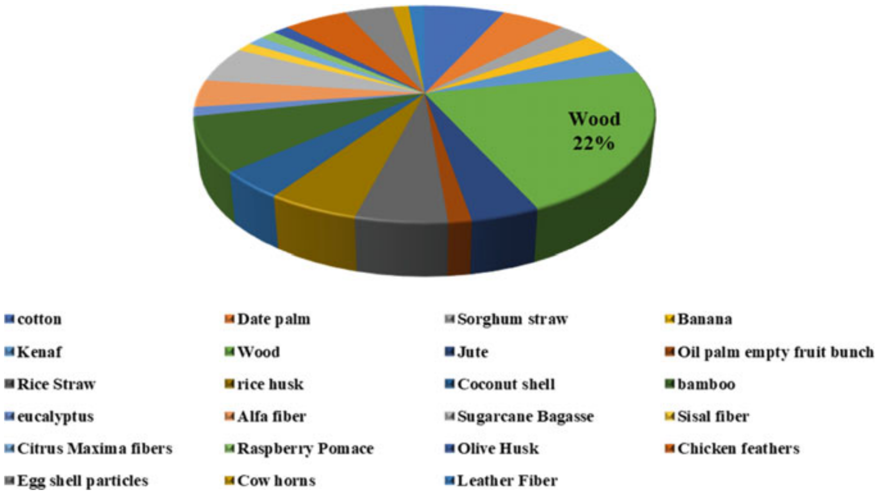


Fig. 8 Natural fibers contribution to mixing with PVC matrix

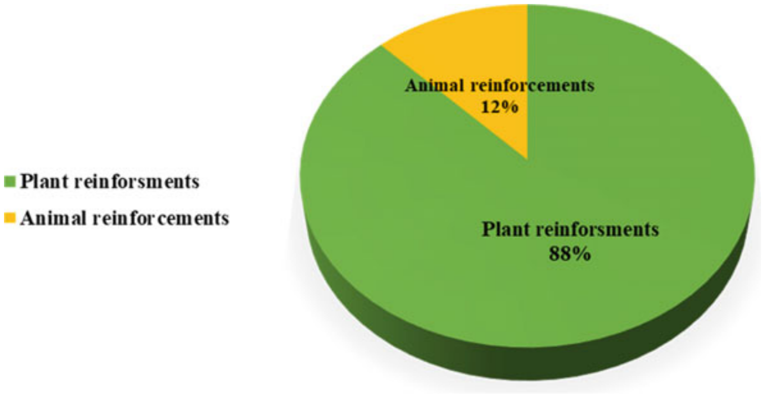


Fig. 9 Plant fiber PVC composites versus animal fiber PVC composites

them better mechanical characterizations. They showed that due to changes in the inherent properties of the WPVC during processing, the form of the cross-section significantly influenced the flexural properties. The number of hollow cores, the thickness of flanges and webs, and the density of the WPVC composite were the main parameters that affect the flexural properties of samples in different cross-sections.

Kiani and Ashori [93] studied the results of two variable factors, namely the filler shape and filler loading level, on the physical characteristics of composites based on polyvinyl chloride (PVC), pulp fiber (PF), and wood flour (WF). Fibers had a size of up to 354 and then were dried to less than 3% moisture content. Hybrid composites were constructed with wood fiber plus pulp fiber to a PVC mass ratio of 40/60 (w/w). Natural fibers (wood and pulp) were mixed with PVC by a co-rotating twin-screw extruder at a melt temperature of 185 and speed of 60 rpm. The extruded strand was passed through a water bath, granulated, and dried at 105 for 24 h to remove any moisture. Later, the consequent granules were injection molded at 190 to create standard ASTM specimens. They found that the water absorption in the lignocellulosic material base composites is extremely higher than the unfilled PVC, and the water absorption rose sharply with raising cellulosic filler loadings in the composites.

Hosseini [89] evaluated the influences of Dioctyl phthalate (DOP) and various densities on the physical and mechanical characteristics of PVC-based wood flour composite panels utilizing a traditional flat-press method under laboratory states. They measured Hardness, tensile strength, water absorption, and thickness swelling. Wood flour has dimensions of 25-mesh. Wood flour was dried at a temperature of 103 for 24h. The moisture of fibers reached 2% in oven-dried prosses. They mixed wood flour and the PVC powder, and then the mixture was shaped into a mat on an aluminum plate using a forming box. Each mat was then hot-pressed by a manually controlled electrical-heated press. The maximum press pressure, pressing temperature, and total press cycle were 50 kg/cm^2, 180, and 25 min, respectively. The board was removed from the press for cooling at the end of the press cycle. Hardness and tensile strength increase by decreasing DOP content and increasing density. Also, reducing DOP content and increasing density decrease water absorption.

Shankar et al. [81] studied the mechanical properties of WPCs. Their samples were created by mixing teak wood flour (wastes got from wood cutting mills), polyvinyl chloride (PVC), and Calcium Carbonate as significant ingredients. Teak wood powder of size 50 μm was used as wood-based filler, and PVC of size 212 μm and calcium carbonate were used as matrix and mineral fillers, respectively. Fabrication of WPC is done using the extrusion process. In the hot mixing chamber, raw materials were melted and mixed thoroughly at 350 rpm for 4 min at 110 °C to form a homogenous paste-like mixture. The mixture from the hot mixing unit was transferred to the cold mixing chamber maintained at ambient temperature and again mixed thoroughly at 350 rpm for 3 min to convert the mixture to the amorphous form suitable extrusion process. The raw material required for WPC preparation was further fed to the hopper of the extrusion equipment. The various temperature levels maintained across the barrel were, feeding zone at 150 °C, melting zone at 155 °C, mixing zone at 158 °C, and molding temperature at 172 °C. These temperature zones helped to produce the product with less porosity and a good surface finish. Extruded part of WPC was hot with a temperature of 170 °C approximately, making cooling essential. The indirect cooling method was preferred by maintaining the cold water outside the dies to achieve dimensional stability primarily. They determined ultimate tensile strength, compressive strength, flexural modulus of rupture, and maximum impact strength of WPC as per ASTM standard testing method D 4761-19.

Arthur et al. [26] investigated some mechanical properties of PVC-Wood fiber composite. The sample was molded and formed at a temperature of 150 using a hydraulic hot press and pressure of 3bar for 5 min. The mechanical properties of the composite were analyzed based on changing the wood fiber contents from 0 to 50%.

The worldwide production of date palm fiber yearly is 42% more than coir and 20–10% more than hemp and sisal, which are popular fibers for biodegradable composites. Surface modification of palm date fibers is essential to refine and cleanse the surface of the fibers from many pollutants and improve the bonding of fiber and matrix. Date palm fiber is one of the more available natural fiber resources and includes appropriate chemical constituents. It has better mechanical strength than other natural fibers. It contains polysaccharides cellulose in 38–40%, lignin in a negligible share, and rarely fat, wax, pectin, inorganic substance, etc. These fibers can be mixed in both thermoset and thermoplastic matrixes.

Awad et al. [35] investigated the effect of date palm fiber dimensions on the mechanical and physical properties of composites. Properties that they covered in their work include the tensile strength, flexural strength, impact strength, moisture absorption, water absorption, and thickness swelling of four different fiber loading contents and six diverse fiber diameters. Properties were analyzed in 10, 20, 30, and 40 wt% content of fibers, and dimensions of fiber varied in ranges of less than 125 μm to unsieved fibers, which was bigger than 1000 mum. Fibers were washed with distilled water to clear pollutants from the surface of the fibers, and then they dried at 60 °C for 24 h. Also, the PVC powder was dried at 60 °C for 24 h to confirm that the polymer had minimal moisture content. They used melt-mix blending and compression molding processing technologies to prepare samples. The flexural strength, tensile strength, and impact strength were reduced as the loading content raised. The maximum reduction of properties was at 40 wt% loading, changing depending on the dimension of the fibers.

Maou et al. [70] investigated the mechanical, morphological, and thermal properties of composites based on PVC/Date Palm Leaf Fiber (DPLF). DPLF was washed, grounded, and sieved. The sieved wood was dried at 50 to 3–4% moisture content in a laboratory oven. Processing temperature varied from 135 to 170, and compression molding press at 150 for 2 min at a mechanical pressure of 300 bar.

10 Natural Fiber Poly (Vinyl Chloride) Nanocomposites

One of the exciting topics in composite materials is the usage of different nanoscale fillers with different composites, which lead to improvements in mechanical and physical properties. Nanofillers have at least a dimensional property in the nanoscale and can be in the shape of a rod (1D), plate (2D), and sphere (3D). Based on the shape of the nanofillers, polymeric nanocomposites can be categorized into three main types. The first type has nanofillers with two dimensions in the nanoscale, and one dimension is significantly larger than the others, like carbon nanofibers. The second type of nanocomposites is mixed with nanofillers with one dimension in the nanoscale, such as MXene, layered silicate, and graphene. The third type contains nanofillers, such as spherical silica, with three-dimensional aspects in a nanometer scale. Proper dispersion of nanofillers in a polymer can create an ultra-large interfacial area per unit volume between polymer and nanofillers. The large interface between polymer and nanofillers and the molecular distance between nano elements can create superior properties in nanocomposites. Mixing nanoparticles with natural fibers and polymer matrix enhances the properties of the biodegradable composites, including thermal and mechanical properties, dielectric behavior, tribological properties, and corrosion resistance. Thus, the problems that limit the application of biodegradable composites will be reduced.

Dutta and Maji [130] studied rice husk PVC composite with montmorillonite clay (MMT). They used polyethylene-grafted maleic anhydride (PE-g-MA) as a compatibilizer to improve adhesion between rice husk and PVC. Rice husk fibers were treated using soap solution, a mixture of alcohol and benzene, and NaOH solution in an ordered process. Fibers were ground and passed through a 50-mesh sieve. They mixed 40 parts per hundred rice husk fibers with 60 parts per hundred PVC, 5 parts per hundred PE-g-MA, and 2–10 parts per hundred montmorillonite clay. Samples were prepared by compression molding at 190 and 6 min under 5–6 tons. Results show an improvement in flexural and hardness properties with the addition of MMT to the polymer matrix. They also studied thermal and other physicochemical properties.

Allahbakhsh [100] studied the effects of sodium dodecylbenzene sulfonate (SDBS)-modified graphene oxide nanosheets on the viscosity of PVC reinforced rice straw in mixing prosses. The addition of these nanosheets to the mixture caused low morphological defects in the composite and thus improved the morphological and structural characteristics. They reported that the existence of 1 phr (SDBS)-modified graphene oxide nanosheets in PVC/RW composite with 15 phr RW fibers enhances the ultimate tensile strength of the product by more than 41% compared to the same PVC/RW composite without any nanosheets. Also, they showed that PVC/RW/(SDBS)-modified graphene oxide nanosheets nanocomposite can be an acceptable isolating material for related applications. The electrical conductivity of this nanocomposite is between 10–9 and 10–5 s/m.

11 Summary

This study briefly studied biodegradable composites and especially PVC-based partially biodegradable composites. Recent research shows that poly (vinyl chloride) is a suitable matrix for most natural fibers, including plant and animal fibers. Mineral fibers (asbestos), due to their health issues, haven't significant usage in biodegradable composites. Wood fibers have the most contribution to the reinforcement of PVC, and their composites have many applications in construction industries. Extrusion and compression molding are two popular fabrication methods in PVC-based biodegradable composites. Silane treatment and alkaline treatment are two treatment methods used in many studies. However, other treatment methods, like Benzoylation, also was used. PVC is one of the highest-strength thermoplastics and is highly resistant to corrosive liquids, but like many other thermoplastics, it can pollute the environment. Mixing natural fibers with PVC cause a low need for this plastic and thus low production and pollution. Besides, the advantage of PVC will be improved by the advantage of composites. Mixing nanoparticles with natural fibers and polymer matrix enhances the properties of biodegradable composites.

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Chitin and Chitosan Based PVC Composites and Nanocomposites

Marcelo Bruno de Oliveira Silva and Derval dos Santos Rosa

Abstract Poly(vinyl chloride) is a thermoplastic material quite versatile and with wide application in society. Still, the application possibilities can be expanded through composite material with PVC as a matrix associated with biopolymers. These developments allow for improving chemical, thermal and mechanical properties and contributing to more environmentally friendly technologies. Among the biopolymers, chitin and chitosan stand out given their natural occurrence, abundance, biodegradability, biocompatibility, adsorption capacity, antimicrobial action, and easy modification. This chapter will be addressed some of the PVC-based composites containing chitosan and possible applications of these materials.

Keywords Chitin · Chitosan · Polysaccharide · Biopolymer · Biomedicine · PVC resin

1 Introduction

Nowadays, one of the most versatile and widely used polymers is the poly(vinyl chloride) or poly(-1-chloroethylene), according to the IUPAC systematic name orientations, but also commonly shortened as PVC [1]. Due to the need to incorporate additives in the formulation of PVC thermoplastic resin, the properties can be widely altered, allowing from very flexible to rigid products [2]. PVC can be applied to pipes or profiles, coating, laminates, packaging, films, and many other applications. Also, PVC has the properties of insulation material, good mechanical and chemical resistance, low toxicity, lightweight, high toughness, and low cost of production. Consequently, PVC has become an essential material in our daily lives and one of the main resins produced worldwide, with a presence in the construction, electronics, food, clothing, and biomedicine sectors [3].

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Despite the vast advantages, PVC presents in its structure a chlorine atom located in each alternative carbon in the polymer chain, resulting in a much rigid plastic. Therefore, pure PVC shows elevated fragility to be submitted to processing directly [4]. In addition, PVC has lower thermal resistance than other traditional polymers on the market, such as polyethylene, polypropylene, and polystyrene, due to the unstable segments, such as C–Cl bonds. The low thermal stability can disturb some applications undergoing high temperatures, such as biomedicine, which habitually requires sterilizing the products for safety against contamination [2, 5, 6].

In this context, many plasticizers or additives are used for better processing and performance of PVC resins by improving thermal stability, mechanical toughness, and stiffness [5, 7]. However, some properties may be undermined, such as fire resistance, for example. The PVC naturally has an excellent fire resistance because of the high chlorine content in its structure. During the burning of PVC, there is the release of hydrochloric gas, which inhibits the flame's propagation by decelerating free radical chain reactions. Nevertheless, some traditional plasticizers, such as dioctyl phthalate, impair the high fire resistance of pure PVC [4].

In this scenario, the study of new additives becomes essential to preserve or promote new properties of PVC-based composites according to the application of interest. In addition, additives are vital for developing more sustainable PVC products. Moreover, it is part of the responsibilities of the PVC industry to reevaluate the technology employed concerning environmental aspects to gradually eliminate constituents potentially polluting, especially if there is the possibility of accumulation or toxic effects on nature [3]. Among the promising materials to be used with PVC, the polysaccharides chitin and chitosan can be highlighted because of their natural abundance, biodegradability, biocompatibility, and low cost. In addition, the antibacterial capacity stands out, enabling more effective use of PVC-based composites, mainly in applications focused on food and biomedicine [2, 8–10].

2 Chitin and Chitosan

The discovery of chitin occurred in 1811 by Henri Braconnot from fungi, so initially called 'fungina'. The term 'chitin' was attributed by Odier in 1823, after isolating the polysaccharide from insects and observing its protective function in the exoskeleton, such that chitin refers to the Greek term 'quíton' (χιτών), which means tunic [11].

Chitin is the second most abundant biopolymer on the planet. It is formed by the repetition of the N-acetyl-D-glucosamine units with glycosidic bonds β(1–4), shown in Fig. 1. In addition, the deacetylated unit D-glucosamine may occur to a lesser extent. This biopolymer act as a component for mechanical and chemical resistance in exoskeleton of crustaceans, such as shrimp and crabs. Also, it participates in the exoskeleton of insects and mollusks, and in the cell wall of some fungi and algae [12–14].

The primary source of chitin is the exoskeleton of crustaceans. It can be obtained by means of chemical methods, by reusing the waste generated in the production

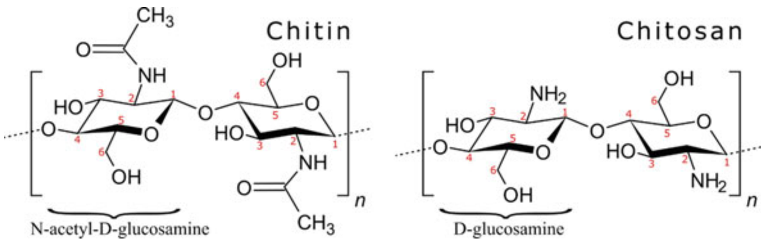

Fig. 1 Chitin (left) and chitosan (right) chemical structure. *Source* Elaborated by authors

of shrimp, lobster, or crabs farming. This residue can become polluting agents due to clandestine disposal in landfills, sea, or rivers adjacent to fishing and farming facilities, causing environmental disturbance and contamination of natural resources. In the case of shrimp farming, for example, the cleaning process eliminates the cephalothorax, exoskeleton, and segments of the abdomen and tail, representing about 47% of the total shrimp mass [15–18].

The chemical composition of the shrimp exoskeleton may vary according to the environment, species, and seasonality, and consists of 20–40% chitin, 30–40% protein, and 30–50% calcium carbonate. Also, there may be pigments [19]. Accordingly, the process of obtaining chitin can be carried out easily through demineralization and deproteinization through chemical compounds common to the industry, such as hydrochloric acid (HCl) and sodium hydroxide (NaOH). Therefore, besides being a natural polymer that is easy to obtain, chitin can contribute to the revaluation of waste, contributing to the development of more sustainable technologies [20–23].

Chitin has three allomorphic structures identified with α, β, and γ. The α-chitin is characterized by the antiparallel organization of polymer chains and it is the most common allomorphic of chitin. It is generally found in the exoskeleton of crustaceans. The β-chitin presents the parallel chains in the same direction, and the γ-chitin has parallel chains in the same direction interspersed with an opposite chain, as shown in Fig. 2. The β-chitin can be obtained from mollusks and γ-chitin from fungi organisms [12, 21]. The conformations adopted by the polymeric chains of chitin result from the strong intramolecular and intermolecular interactions promoted by hydrogen bonds between the amide and hydroxyl groups present in the structure. For α-chitin, there is additional intermolecular interaction with hydrogen bonds with the hydroxymethyl group [24, 25].

The strong interactions between the chains make chitin a material with a high tendency to aggregation, such that it is insoluble in common inorganic and organic solvents. A few solvents are capable of solubilizing chitin, such as hexafluoroisopropyl alcohol, lithium thiocyanate, phosphoric acid, or N-methyl-2-pyrrolidone. However, several of these chemical compounds are toxic to the environment, corrosive, or mutagenic. Thus, the industrial scaling of chitin-based products is limited by the difficulty in processing [21, 25, 26]. It is stressed that the degree of deacetylation (DD) and chemical modifications, such as phosphorylation, quaternization, and carboxymethylation, can alter the solubility of chitin. Naturally, chitin has a DD, i.e.,

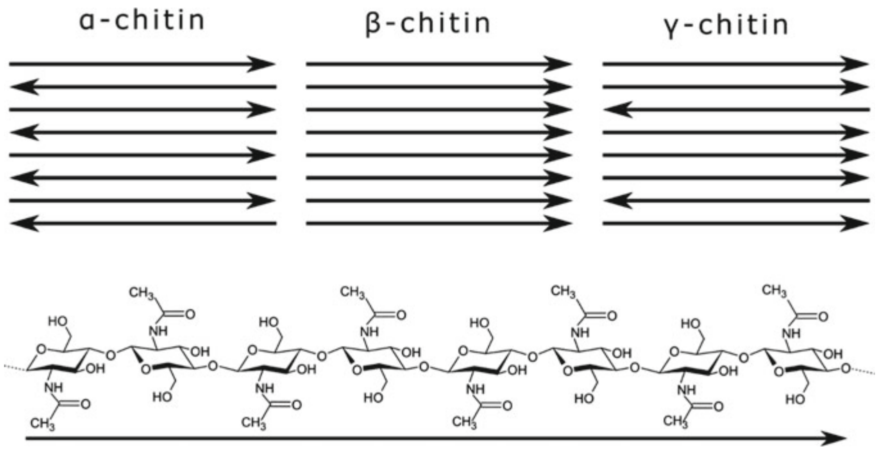

Fig. 2 Chitin allomorfic structures (α, β and γ-chitin conformation). *Source* Roy et al. [25]—adapted

the presence of D-glucosamine units, close to 10%, such that this is the only positively charged natural biopolymer due to the amino lateral group (–NH_2), enabling a wide range of applications [13, 20, 25].

If greater deacetylation is promoted, such that DD is higher than 60%, chitin has a change in properties and is now called chitosan (Fig. 1). In an acidic solution ($pH < 6$), protonation of the amino group occurs, characterizing the properties of a positively charged polyelectrolyte, enabling the formation of ionic complexes with negatively charged compounds. In addition, due to the higher degree of –NH_2 groups present in the structure, chitosan can be readily solubilized in acidic solutions. The amino group also allows electrostatic interactions and can react with functional aldehyde groups and ketones for the formation of Schiff bases in order to encourage solubility [25, 27–29].

The deacetylation process can be performed by alkaline treatment of chitin. Generally, highly concentrated solutions of sodium hydroxide (NaOH) or potassium (KOH) (40–50% m/v) are used at high temperatures (close to 120 °C), and agitation can be used. Alkaline hydrolysis for the removal of the acetyl groups contributed to the solubility of chitin due to the breakage of the intermolecular interactions and exposure of the –NH_2 group. However, it is emphasized that chitin presents regions of the amorphous and crystalline domain. Since amorphous domains allow greater permeation of water molecules, they are more hydrated compared to the more organized domains, allowing the interaction of the acetyl groups with the basic solution. Thus, amorphous regions can be deacetylated more efficiently, and crystalline regions can be deacetylated only at the boundaries of the domain. It can lead to partial deacetylation of chitin, which remains insoluble in acidic solutions, especially for α-chitin [12]. Thus, the reaction time, temperature, and concentration of the reagents are impacting variables in the DD of chitosan, in order to favor greater permeation of the alkaline groups through destruction of the crystalline domains [14, 18, 21, 26, 30–34].

In addition to deacetylation, the presence of amino groups allows the functionalization of chitin and chitosan through changes in phthaloylation, acylation, quaternization, phosphorylation, and sulfonation. The hydroxyl groups present in the structure also allow the easy functionalization of chitin, such as carboxymethylation through reaction with monochloroacetic acid [13, 14, 21, 23].

It is significant to say that others essential factors to the properties of chitosan are the molecular weight (Mn) of the polymer and the conditions of the solution, such as ionic strength and temperature. The solubility of chitosan increases the lower the Mn of the polymer since, in the case of smaller polymer chains, the formation of hydrogen bonds in intermolecular interactions is not favored. In addition, it reduces the effect of hydrophobic interactions and van der Waals forces. This phenomenon eventually increases the solubility range by allowing the dissolution of chitosan at a pH lower than 8.0 rather than 6.0. On the other hand, higher Mn values imply more significant interaction between the chains, such that the increase in the degree of crystallization and viscosity of chitin is favored. In solution, the interaction of the chains is also influenced by ionic forces resulting from the presence of salts. Chitosan, for example, acts as a polycation in acidic solutions by protonation of the amino group, so that repulsive electrostatic interactions are developed between the chains. However, with the increase of ionic forces, by adding anions such as CH_3COO–, the repulsion between chitosan charges is repressed by the interaction with anions, such that there is a reduction in the solubility of chitosan. The increase in temperature, though, tends to break the hydrogen bonds between the chains, increasing the solubility of the biopolymer [12, 24–26].

Chitosan has been associated with several materials and applied in various sectors as a promising raw material for more environmentally friendly technologies, given its biodegradability, biocompatibility, regular source, and low toxicity. The applications of chitosan are vast, including tissue engineering, drug delivery, antimicrobial and antifungal agent, membranes, crop protection, adsorption of contaminants, packaging, capacitors, etc. Thus, chitosan is a versatile material with excellent growth potential in technologies and products [10, 28, 29, 35].

3 Chitosan and PVC Composites

Due to their versatility and attractive properties, chitin and chitosan can be used to optimize various properties in PVC-based composites. Among these, higher thermal stability is of great interest. Chitosan can be used in association with inorganic particles and assist in their interaction with the matrix in composite materials. Composite PVC materials with chitosan and zinc oxide nanoparticles (ZnO), for example, were prepared by solvent casting. To do this so, PVC was dissolved in N,N-dimethylformamide (DMF), and added polyamide (1% m/m) and a solution of chitosan dissolved in acetic acid modified with trimellitic anhydride and nano ZnO dispersed by ultrasonication (1% m/m). The greater collaboration between the materials, given the interaction of the functional groups, allowed the increase of thermal stability from 245 to 265 °C for a 10% mass loss of pure PVC and composite material, respectively. In addition, there was mechanical property improvement, such as tensile strength, young's modulus, and elongation at break [5].

Inorganic particles can also be applied to improve flame retardance in PVC composites. Among them, zinc hydroxystannate ($ZnSn(OH)_6$) has a synergic effect avoiding the spreading of combustion by flame poisoning and temperature reduction. However, there is low compatibility between PVC and $ZnSn(OH)_6$, which may lead to regions with particle agglomeration, non-uniformity, and composite fragility. Chitosan modified with $ZnSn(OH)_6$ can be prepared to promote greater compatibility with PVC. Cations sites in solubilized chitosan interact with anions, partially replacing the Zn. Using modified chitosan-$ZnSn(OH)_6$ with PVC can improve the limit oxygen index from 26.6 to 30.6%, to pure PVC and composite material, respectively, maintaining a good dispersibility and low change in mechanical properties [7, 8, 36].

Among the applications of PVC-based products, the use for biomedical is emphasized as one of the most fascinating and promising applications. For application in polymeric medical devices are crucial chemical and mechanical resistance. PVC also has good biocompatibility, and the presence of chloride assists in combating microorganisms, justifying its application in catheters, blood bags, lung bypass, dialysis tubing, and other medical devices. Still, microorganisms may be gripped to the surface of these products with the formation of a biofilm, bringing risks of contamination to patients. Therefore, chitosan and PVC-based composites have been widely considered for developing products mainly for biomedical applications [2].

Composite material developed with chitosan, PVC, and glycerol by casting shows good potential for blood bag application, for example. With the increase of chitosan content, higher hemocompatibility is observed. Moreover, the $–NH_2$ groups in the biopolymer allow electrophilic attack with the destabilization of the membrane of microorganisms [37]. The reaction of the amine group with aldehydes also enables the formation of Schiff bases, with antimicrobial action for Gram-positive and Gram-negative bacterias. The association of chitosan, PVC, and other antibacterial components, such as silver (Ag) particles, permits composites' formation with a self-sterilizing effect with significant interest in the biomedicine field [6, 38, 39].

For better interaction between PVC and chitosan, as well as synergic antimicrobial action, chitosan can be grafted on the surface of PVC. For this purpose, PVC can be modified through amination, in which a primary amine group replaces a chlorine atom by the reaction with ethylenediamine (EDA). The binding of PVC modified by amination (amino-PVC) and chitosan can be performed employing crosslinking agents, such as glutaraldehyde, or by reaction with acetic acid disubstituted by halogens, such as bromoacetyl bromide or chloroacetyl chloride, as represented in Fig. 3 [6, 9, 38].

Another important characteristic for biomedical applications, in addition to the control of microorganisms, is to achieve adequate mechanical and chemical properties. For cardiovascular application, for example, it becomes crucial to simulate myocardial or arteries stiffness and hydrophilicity for better interaction with the cells around the polymeric device [40]. The increase of chitosan in the composition of

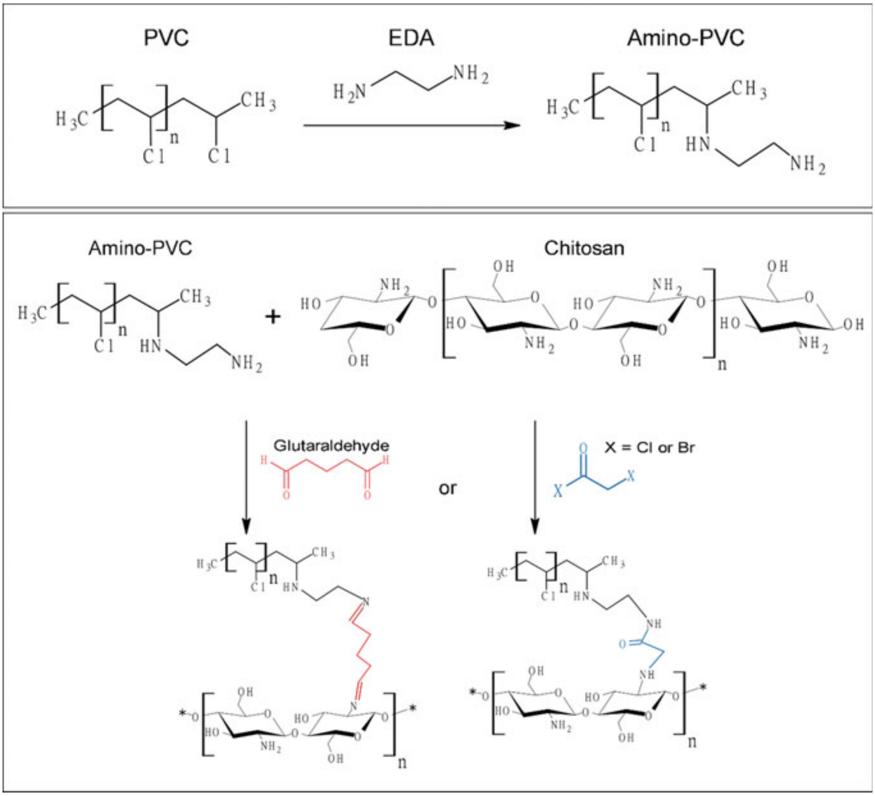

Fig. 3 Synteshis of Chitosan and amino-PVC. *Source* Elaborated by authors

composites with PVC matrix tends to increase the stiffness and the resistance to impact. However, it is also emphasized that the high share of chitosan promotes a lower elongation capacity at the break [7, 37].

Besides the applications in biomedicine, composites of PVC and chitosan have been used to treat pollutants from water. In this case, it is interesting for the composite to affinity with water so that it can permeate the polymer structure. It allows a higher composite contact with the pollutant [41]. Chitosan becomes an exciting material due to its functional groups, which have good interaction with water and potentially polluting compounds, such as metal ions, dyes, and pesticides [22, 42, 43]. For example, membranes of PVC with chitosan and activated carbon nanoparticles were produced by solution casting technique. The membranes showed higher hydrophilicity and good adsorption capacity of íons copper (Cu^{+2}), nickel (Ni^{2+}), and lead (Pb^{2+}), reaching 98, 84, and 62% of íons removal efficiency from water, respectively [43].

Chitosan can also be applied with PVC to recover organic solvents such as acetone. For separation by pervaporation, it is necessary to promote high selectivity. It can be achieved by selecting materials with close solubility parameters. PVC and polymethyl methacrylate (PMMA) have similar acetone solubility parameters and a low affinity with water, but PMMA has a fragile characteristic. To overcome this scenario, chitosan grafted PMMA nanoparticles can be prepared and used as filler in PVC-based composites membranes. The use of chitosan is essential due to the polycationic property of chitosan in acidic solutions, promoting macroradicals sites for polymerization and grafting of PMMA. However, the percentage of chitosan has to be carefully evaluated. With high chitosan share, the selectivity required for separation by pervaporation of the acetone, or other solvents with close solubility parameters, can be lost by improving the affinity with water and allowing the water flux through the membrane [44].

Chitosan can also be used for the degradation of dyes. These components are used by various industries, such as textiles, paper, and cosmetics. However, the presence of these dyes in the environment can bring problems to human health and the aquatic environment, such as eutrophication and carcinogenic potential. For the degradation of these dyes can be used the treatment by electrochemical oxidation. Chitosan can be applied as a constituent base material of the electrode, with PVC as a binder, essential for maintaining mechanical stability and the adherence of chitosan. In the literature, chitosan and PVC electrodes were applied associated with graphite or carbon for degradation via electrochemical oxidation of dyes, such as Reactive Red 4 (RR4) and methylene blue (MB), with 95 and 100% efficiency, respectively [45, 46].

Technologies with the association of chitosan and PVC can also promote more sustainability through the revaluation of lignocellulosic residues, such as decayed wood and sawdust. Combining lignocellulosic residues with thermoplastic resins is a challenge because lignin and cellulose have difficulty in compatibilization with the polymeric matrix, given the discrepancy in polarity and affinity with water of these materials properties. Chitin and chitosan may act as intermediates between lignocellulosic components and PVC. Composites of decayed wood and chitosan with PVC matrix can be produced as panels, with advantages in lightness, corrosion resistance, and cost reduction, and applied as coating and decoration products [47, 48].

4 Future Trends and Perspectives

Composite materials based on PVC and Chitosan have a vast field of application and can contribute to various sectors of society. Among the main benefits of using chitosan, the best performance of products in technologies associated with biomedicine and the treatment of pollutants can be highlighted due to the functional groups amino and hydroxyl in the structure. These functional groups also allow extensive and easy modification of chitosan, bringing versatility to the biopolymer [6, 9, 31, 38, 44, 45].

Analysis of processing conditions, though, is still needed. Many PVC and chitosan composites involve the mixture of these materials in solution, through the application of appropriate solvents, to generate good dispersion of chitosan in the PVC matrix.

However, several PVC products are produced through thermomechanical treatment since PVC resins are thermoplastic; in other words, they merge with heating, enabling the molding of the product, and remain in the format defined after cooling. Chitosan and chitin are not polymers capable of melting. With the temperature rise can occur the thermal degradation of these biopolymers. Therefore, for the conformation of composites by thermomechanical process, the incorporation of chitosan should occur as particles. In this case, it is crucial to control the particle size and homogenization methods to avoid fragility points due to the accumulation of chitosan particles [6–9, 38].

Composite materials with chitin also should be better investigated. Despite the problematic solubility of chitin, it shares biodegradability, low toxicity, the possibility of modification, and biocompatibility with chitosan. In addition, chitin particles have high chemical resistance, interesting mechanical properties, and greater thermal stability than chitosan. Thus, PVC resins can also bring advantages in properties and applications [12, 20, 25, 33].

There are also trends for PVC and chitosan or chitin composites studies concerning plasticizers and additives already consolidated in the plastic resin processing industry. Sustainability does not only involve the development of new applications and viable products with biodegradable and natural polymers. These actions are essential for the appreciation of these resources. However, it is also necessary to review the technologies used in the market and identify possible opportunities that can be optimized by using renewable resources to minimize environmental impacts without harming social and economic aspects. Therefore, it is necessary to mature the life cycle assessment (LCA) analysis, covering the impacts generated by all resources involved in the production, i.e., raw materials, equipment, energy costs, processing, disposal, etc. Only by the LCA is it possible to adequately compare the impacts of one technology against others, aiming to choose the most appropriate one. It is noteworthy that a vital aspect of PVC and chitosan composite materials is the practical evaluation of their biodegradability and toxicity based on proper standards [1, 3, 47, 49, 50].

The mindful development of chitin and chitosan composites with PVC matrix, aligned with the sustainable principles, contributes to the best use of the planet's resources and to the achievement of the Sustainable Development Goals, such as promoting decent work, economic growth, health to society, responsible consumption, and innovation [51, 52].

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Carbon Fiber and Carbon Black Reinforced PVC Composites and Nanocomposites

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Abstract PVC is the most widely employed resin because of its cost-effectiveness, mechanical durability, resistance to flame and chemicals, and excellent insulating properties. However, the development of sensitive applications is limited by PVC's imperfect heat and UV stability. In order to improve the material's ultimate qualities, researchers have recently developed innovative and sustainable PVC-based composites and nanocomposites. In this chapter, authors shed light on carbon-based nanofillers especially carbon fibers (CFs) and carbon black (CB) to improve the PVC characteristics. Besides altering physico-mechanical behavior and stability against thermal and UV exposure, PVC finds its way for new applications like electronic devices, electroactive materials, strain sensors for wearable flexible electronics, etc. This chapter introduces a cutting-edge research platform for next-generation of PVC materials for sustainable environment.

1 Introduction

Nanocomposites have gained much attention as a result of the advancement of nanomaterials and their wide applications [1]. Many researchers have focused on the usage of polymer-based nanocomposites because of their broad range of applications, simplicity, and low-cost production methods [2]. Polymer science is primarily concerned with the creation and production of novel resins for various fields of applications. Industrially produced resins involve polyvinyl chloride (PVC), polypropylene, and polyethylene [3]. Polymeric nanostructured composites offer high elasticity, tensile modulus, mechanical, and thermal properties [4]. The effect of adding nanofillers to various polymers can enhance the nanocomposite's physico-mechanical features.

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PVC is the most widely employed resin because of its cost-effectiveness, mechanical durability, and resistance to chemicals and flames [5]. It is a versatile thermoplastic resin with low production costs and excellent insulating properties. However, development of conjugated polyene sequences and allylic chloride internal structures is caused by PVC's limited heat stability. Generally, PVC is available in two unique thermoplastic forms: rigid PVC and flexible PVC resins. The rigid type of PVC accounts for about two-thirds of all PVC used. PVC is made by using bulk, suspension, or emulsion polymerization processes to create free radical polymerization of vinyl chloride monomers. Metal vapour deposition, surface grafting, and arc-discharge procedures have all been utilized to modify polymers [6]. PVC polymers have many applications including wires, cables, coated fabrics, flooring, coatings, frames of windows and doors, bottles, pipes, medical tubing, hoses, and automotive materials (Fig. 1).

Chemical stabilizers in the PVC matrix help protect the matrix from potential degradation. Nanofiller loading improves both thermal and mechanical stability [7]. In order to improve the material's ultimate qualities, researchers have recently concentrated on innovative ways of fabricating PVC-based composites [8]. To meet

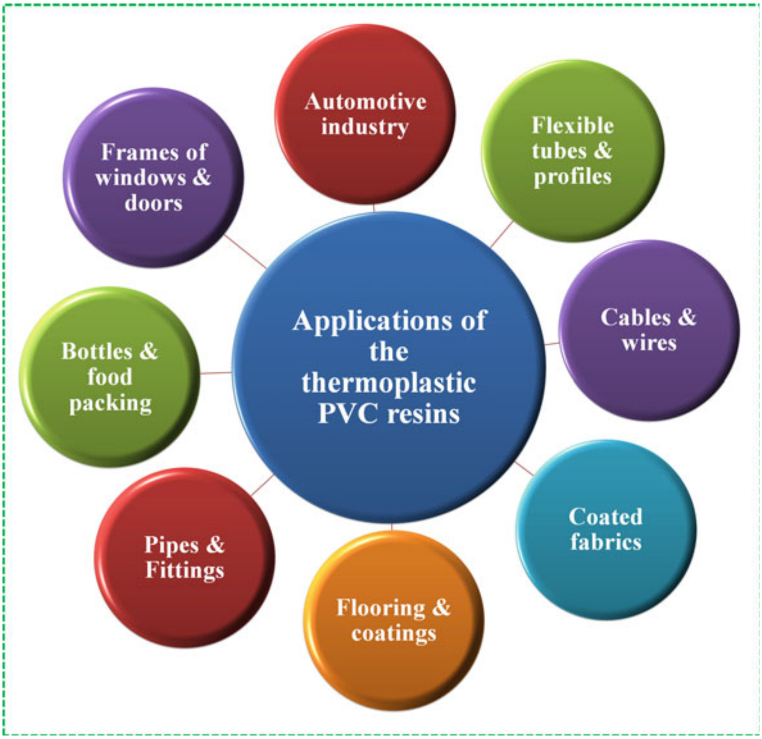


Fig. 1 Applications of the thermoplastic PVC resins for industrial fields

the demand for improvement, there is a pressing need to develop new nanocomposites with enhanced properties [9, 10]. To improve the characteristics of the polymer matrix, carbon-based compounds especially carbon fibers (CFs), and carbon black (CB) nanofillers have been employed. Conductive polymer composites are made by dispersing conductive nanofillers (including CFs and CB) into the PVC resin which is non-conductive [11].

CFs and CB nanomaterials, according to the literature, are appropriate fillers for the construction of PVC nanocomposite compared to other carbon-based fillers because of their homogenous distribution in PVC resin. Agglomerations can occur for PVC composites filled with un-exfoliated graphene-materials. PVC filled with CFs or CB exhibited higher thermal, electrical, and mechanical features than PVC/ graphene nanocomposites.

In this chapter, PVC resins enriched with CFs and carbon black nanocomposite are the main topics. Section 1 introduces an introduction of PVC polymer, while Sect. 2 covers its history and sustainability. Section 3 covers the polymerization, structure, and additives of PVC resins that are relevant to composites and applications. PVC may be blended with a wide range of additives, making it a highly adaptable polymer that can be used in a variety of applications. Section 4 contains a detailed investigation of PVC-based CFs and carbon black nanofillers. Section 5 introduces PVC reinforced with CFs and carbon black nanocomposites. This section will consider the advantages and limitations of the developed nanocomposites. Detailed effects of nanofillers on the physico-mechanical properties have been considered in Sect. 6. A panorama of the detailed information mentioned in the whole chapter is illustrated in the conclusions Sect. 7. Challenges and future perspectives on PVC-based carbon black and CFs nanocomposites are discussed in the last part of this chapter (Sect. 8). A comprehensive reference list is provided.

2 PVC History and Sustainability

2.1 PVC History

Four Dutch scientists created an original compound called dichlorethane in 1795 [12]. Several works studied the nature of this compound and its amount of ethane and chlorine. Regnault was the first to introduce vinyl chloride in 1835. Regnault's fascination with these compounds was entirely academic, and he conducted subsequent studies with bromine and iodine analogues [13]. In 1838, PVC was introduced as a polymer. PVC is a white powder made by polymerizing a large number of vinyl halide units in the presence of sunlight. Later research revealed that the Regnault polymer was actually made up of poly (vinylidene chloride) [12]. Bauman, who performed polymerizations of several vinyl compounds in enclosed tubes, did not create PVC until 1872. In 1912, Klatte reported a new manufacturing technique to prepare PVC [12] by processing PVC over a substrate for lacquers and fibers. When heat and light were applied to PVC, it became brittle and deteriorated. Process technology advanced throughout World War I, and less intractable PVC copolymers were produced. In Germany, emulsion polymerization was used to produce PVC on a commercial basis. While in 1933, Semon reported that by heating PVC with tritolylphosphate to 150 °C, rubber-like masses could be formed that remained homogeneous at RT [14]. The product was flexible plasticized PVC resin. A suspension polymerization of vinyl chloride was developed in 1934. PVC was first produced in 1936 by Union Carbide and F. Goodrich. The capacity of PVC production in 1945 was 35,000 tons. In 1947, Zn, Cd, Ca, and Ba were synergistically combined in the PVC resin. Unplasticized PVC, a rigid polymer that only became popular in the United Kingdom in the 1960s, was also developed on the continent of Europe, particularly in Germany. In 1962, vinyl chloride was subjected to bulk polymerization via a two-step reactor. PVC was being produced in a large number of nations by the early 1970s, and it was competing with polyethylene for the title of world's most consumed plastics material. To polymerize vinyl chloride, scientists developed a one-stage reactor in 1975. In 1979, the United States alone produced about 6 billion tons. PVC is now the most widely produced product on the planet, and its demand is growing by the day [15]. Its polymers are among the most commercially significant polymers, alongside polyethylene and styrene resins. The history of the development of PVC polymers is shown in Table 1.

PVC is a desirable material because of its mechanical, corrosion-resistance, and anti-chemical characteristics. Suspension is a common consignment production method that uses a monomer of vinyl chloride [16]. PVC is made up of chlorine (58%) and hydrocarbon (42%). Numerous approaches have recently been explored to achieve a well-distribution of nanofillers in the polymeric matrix, including melt blending, solution-casting, and in-situ polymerization. Xie et al. [17] developed a nanocomposite of PVC-polymethylmethacrylate copolymer enriched with Sb_2O_3 nanofillers via in-situ polymerization. Nano-Sb_2O_3 particles totally diffused in PVC, according to the results. Turhan et al. [18] used the solution-blending approach to create PVC nanocomposites from natural and modified kaolinite.

2.2 PVC Sustainability

PVC has become an important eco-friendly elastic resin standpoint since the 1970s, due to several concerns expressed about its use. In the 1990s, pressure groups such as Greenpeace were at their most active, focusing on chlorine chemistry in particular. In 1996, a working group of PVC retailers was established to be responsible for protesting against merchants in the UK selling PVC items [19]. On the balance of probabilities, such group has authorized the National Centre for Business and Ecology (at Manchester University) for assessing the PVC impact on the environment and human health. This center concluded that there was no compelling scientific reason for shops to stop selling PVC products as long as their industry, application, and recycling met the highest standards. As a result, the retailer's group was renamed the PVC Coordination Group in 1998. This group also concentrated on solving the

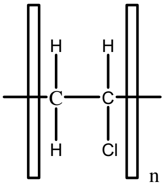
Table 1 The historical development of PVC materials [12]

Timeline	Description
1835	Vinyl chloride was discovered by Liebig and Regnault
1872	Baumann observed the light-induced polymerization of VC
1912	Vinyl chloride was prepared by Zacharias and Klatte via adding HCI to acetylene
1913	Using organic peroxides, vinyl chloride was polymerized by Klatte to produce PVC for fibers and film applications
1915	During World War I, process technology was improved and less intractable PVC co-polymers were developed
1926	PVC patents were allowed to lapse by Griesheim-Elektron and surfaced the way for other companies' innovations
1928	Copolymerization of vinyl chloride and vinyl acetate was performed by Union Carbide and Du Pont
1930	Emulsion copolymerization was carried out by K-value (Fikentscher) for Vinyl chloride, acrylic ester, and vinyl ethers in the presence of alkali salt as a stabilizer
1932	PVC was successfully chlorinated by IG-Bitterfeld
1933	Phosphates and phthalates were used as plasticizers by Semon
1935	Suspension polymerisation of VC (Wacker) (capacity, 1945: 35,000 tons). PVC pilot plant in Bitterfeld (600 tons/year)
1936	Manufacturing of PVC by Union Carbide and F. Goodrich
1945	The capacity of PVC production was 35,000 tons
1947	Zn, Cd, Ca, and Ba were mixed synergistically in PVC resin
1962	Bulk polymerization of VC (two-stage reactor)
1975	A one-stage reactor was introduced by St. Gobain and Pechiney, Rhone-Poulenc
1979	PVC production in USA was more than 6 billion tons
Recently	PVC is the world's chief product and ranks with polyethylene and styrene resins

PVC challenges. The Department for Environment, Food and Rural Affairs (DEFRA) conducted many life cycle assessments in the UK and EU in 2001 and 2004, respectively. The results showed that PVC is eco-friendlier accepted material than other plastics. Anti-PVC activities were carried out by other EU member states, mainly Denmark and Sweden, in addition to pressure from the UK. As a result, four European PVC groups collaborated on Vinyl 2010, a voluntary pledge to improve PVC's environmental footprint. In 2000, Vinyl 2010 agreed on a ten-year strategy for enhancing the manufacturing procedures and yields for reducing the emissions and increasing end-of-life product collection and recycling. In 2010, the vinyl 2010 could recycle 842 tons of unregulated wastes and establish a novel recycling method in Europe [20]. In 2015, Cadmium stabilizers were phased out in the EU-27, and lead stabilizers were substituted in 75.9% of cases, putting the EU-27 on track to complete the transition. After the Vinyl 2010 study was released, the EU industry established Vinyl Plus (A new sustainable program) to achieve more sustainability improvement [19]. This program included many challenges of sustainability: (1) Safe transportation of organic chlorine materials, (2) Recycling issues, (3) Use of raw materials, energy, and additives in a sustainable method, and (4) sustainability awareness. These challenges can provide advanced and sustainable PVC materials.

3 PVC Structure and Additives

Plastics are used in a wide variety of critical applications, ranging from packaging to power cable insulation. Plastics have become ubiquitous in the environment over the last seven decades as a result of their ever-increasing global production, and they have emerged as a key geological indicator of the Anthropocene [21]. PVC is a white solid soluble in tetrahydrofuran and its structure as the following.



Due to its high cost-efficiency, PVC is one of the most widely produced synthetic plastics. UV irradiation is a known degradant of PVC photolysis. This is accomplished by initiating a photocatalytic reaction which results in PVC dehydrochlorination and chain scission. As with other types of plastic, research on PVC photodegradation was conducted. Historically, this effort has been motivated by a desire to improve the stability of PVC products. Thermal decomposition of PVC has also been a problem. Due to the interest in the application of PVC products in the environment, research has taken a new direction with an abnormally high temperature, as well as PVC waste recycling. PVC is a carbon–carbon based polymer backbone. As a result, it is not hydrolyzed. However, PVC can be biodegraded by certain microbial strains [22]. PVC polymer is widely employed in a variety of industries, including aerospace engineering, biomedical engineering, and more. Extruders are prominent equipment in food, plastics, metals, and extrusion of these industries are especially frequent in the manufacturing of products that implement the use of polymers as a primary ingredient.

3.1 PVC Polymerization and Structure

PVC and polyvinylpyrrolidone polymers and tetrahydrofuran and N-methyl-2-pyrrolidone solvents were used to successfully manufacture novel composite membranes by phase inversion technology. Scanning electron microscope and Fourier transforms infrared spectroscopy were used to examine structure of produced membranes [23].

3.2 PVC Fusion and Processing

When it comes to the qualities of PVC plastisols and the migration of plasticizer from flexible plastic, we found that a cyclodextrin known as Bz-b-CD had an effect on both. PVC resin was mechanically mixed with two types of plasticizers, DINP and Neocizer, together with Bz-b-CD as a migration inhibitor, to produce plastisols. As expected, the presence of Bz-b-CD in flexible PVC would make it easier to build stable complexes with DINP or Neocizer. The process ability requirements for PVC plastisol processing emphasize the viscoelastic behavior, such gelation and fusion, of the plastisol [24].

3.3 PVC Degradation

PVC biodegradation by marine bacteria is a long-term solution that yields several byproducts, but their toxicity must be assessed. Bioactive PVC breakdown products generated by three marine bacterial isolates in the culture supernatant were investigated for their toxicity on Vigna radiata germination and the development of Ulva lactuca [25].

3.4 PVC Formulations and Additives

In situ polymerization of vinyl chloride in the presence of $CaCO_3$ nanoparticles was used to construct poly(vinyl chloride)/calcium carbonate nanocomposites. Dynamic mechanical analysis and thermal gravimetric analysis were used to evaluate their thermal, rheological, and mechanical properties, as well as tensile and impact fracture tests for their thermal and rheological stabilities and mechanical properties [26]. PVC additives are huge kilograms up to 2 billion kg equal 4.4 billion pounds Heat stabilizers with 32% of global PVC additives demand. Table 2 shows PVC additives by type. The market size of PVC additives is more than 24,000 million in 2021.

3.4.1 Lubricants

It is becoming more common for European PVC producers to employ calcium/zinc-based (Ca/Zn) stabilizers instead of lead stabilizers as an extrusion lubricant [27].

Table 2 The percentages of PVC additives by type

PVC additives	Percentage (%)	Advantages
Heat stabilizers	32	Improve of heat properties of PVC by neutralize vinyl chloride
Impact modifiers/ processing aids	31	Improved melt homogeneity, increased strength, as well as a better ability of the melt to be extensible and elastic
Lubricants	15	Friction is reduced, thus preventing a rise in temperature and decomposition of the PVC polymer, which would otherwise occur
Flame retardants	12	Utilizing these substances in polymers has the potential to significantly alter the mixture's thermal, mechanical, and electrical properties
Chemical blowing agents	5	An inert gas, low-boiling liquid, or solid body can be used to blowing agent (BA) into plastic input, which can then be extruded into gas under specific extrusion conditions, to create a desired structure
Antioxidants	1	The colour and overall quality of the polymer left over from production should be improved upon
Organic peroxides	1	To optimize the polymerization rate

3.4.2 Plasticizers

An external plasticizer for food packaging films made of polyethylene terephthalate is acetylated monoglyceride (AMG), a carboxylic ester and an ester with unique interactions with PVC. AMG is an approved food additive. As the alkyl chain length is mainly derived from vegetable oils, monoglyceride moieties may vary, but AMG enhances the flexibility and elasticity of PVC polymers [28].

3.4.3 Heat Stabilizers

Crompton Vinyl Additives GmbH of Lampertheim in Germany has developed a range of organic-based heat stabilizers as alternatives for use in the fabrication of rigid PVC pipes and fittings in light of new environmental regulations that will limit the future use of traditional lead-based heat stabilizers [29].

3.4.4 Flame Retardants

The first description of a plasticizer with phosphaphenanthrene groups is based on soybean oil (PSPE). This flame retardant PVC additive has been developed and is currently being used in the production process. FT-IR, ^{1}H NMR, and ^{31}P NMR spectroscopy were used to determine the molecular structure of PSPE. Based on mass loss, limiting oxygen index values, morphologies of residues, smoke production rate, smoke extinction area, mass loss rate, and heat release rate, thermal degradation processes and modes of flame retardant action have been proposed for PVC blends plasticized with different amounts of DOP and PSPE [30].

3.4.5 Biocides and Fungicides

Only plastisol formulations, which are not susceptible to the heat and shear histories of calendared and extruded formulations, have been able to use zinc-containing biocides. Patented technology has been created that addresses many of the stability difficulties that arise when zinc-containing biocides are added to PVC [31].

3.4.6 Fillers

Artificial neural network (ANN) models are built to forecast the load–displacement curves for better understanding the behavior of cotton fiber/PVC composites. Tests were conducted in the laboratory using a variety of fiber percentages and a specific load. On the TensorFlow backend, using the Keras library in Python, ANN models were trained and tested by implementing the back-propagation approach [32].

4 PVC-Based Nanofillers

Polymer/nanofiller composites have recently gained popularity in various industries because of their cost-savings, facile processing and modeling, reduced weight, and anticorrosion performance [33]. Typically, nanofillers can be mixed with polymers to improve their chemical and/or physical properties. Nanoparticles, nanolayers, nanowires, nanorods, and nanotubes are the three types of nanomaterials classified by their type, size, and morphology. The addition of CFs and CB fillers to the PVC resin could enhance the elasticity, impact strength, and mechanical durability.

4.1 CFs

In 1860, CFs were prepared for the first time by Sir Swan [34] through light bulbs early incandescent. In 1879, Thomas Edison used cellulose (cotton and bamboo) to create CFs for the first electric light bulbs [35]. The 1950s saw a resurgence of interest in CFs, beginning in the United States, where Union Carbide established the Parma R&D Center near Cleveland. CF market demand was anticipated to reach $1.7 billion in 2012, with an annual increase of 10–12% expected from 2012 to 2018. The carbon fiber industry is expected to increase at an annual rate of more than 8%, from

$7 billion in 2020 to $8.9 billion in 2031 [36]. The overall name plate capacity in 2022 is around 160 ktons/year and the main producers are listed in Table 3 [36].

CFs and glass fibers are conventional inorganic fillers used for enhancing the resin's mechanical durability. The CFs have different building blocks, including yarns, uni-directional, and weaves which are employed to fabricate nanocomposites. CFs' properties are close to that of steel, while the weight is close to plastic material. Moreover the CFs' strength-to-weight ratio and stiffness are much higher than either steel or plastic. Nanofibers have greater reinforcing powers than microfibers as the fibers' filling capacity increases as their diameter decreases [37]. Furthermore, due to the smaller size of the filler, nanofillers produce a better surface finish than microfillers [38]. As a result, nanofiber/polymer composites are becoming more popular as a replacement for traditional microfiber/polymer composites and attracted much attention [39]. CF-reinforced polymers (CFRPs) are a type of advanced composite in which CFs are a dispersed phase and a continuous phase of the polymer matrix. This structure gives them exceptional features such as lightweight, high strength, high stiffness, thermal stability, and anticorrosion features (Fig. 2) [40]. The CFs have high strength-to-weight ratio.

In terms of the amount of CFRP used globally, the compound annual growth rate is expected to be around 12.5% until 2018 [41]. Because of its low density, lightweight, increased corrosion resistance, and greater stiffness, it is considered to be able to replace traditional metals [42]. Shrinkage and warping are also reduced when CF reinforcement is added. Each CF is composed of thousands of carbon filaments and is a long thin thread [43]. Carbon microscopic crystals link together in a configuration that runs parallel to the fiber's long axis. Chemical and mechanical methods are used to create CFs including: Spinning, stabilizing, carbonization, surface treatment, and sizing.

Table 3 The capacity and producers of CFs

Country	Manufacturer	2022 (kilotons)
Japan	Toray (incl. Zoltek)	55
	Teijin company	14
USA	Hexcel	16
	Mitsubishi chemical carbon fiber and composites	16
	Solvay (Cytec)	4.4
Germany	SGL carbon	13
Taiwan	Formosa plastics	9
USA/Turkey	Dow/Aksa	3
South Korea	Hyosung	2
China	Various companies	21.8
Rest of world	Various	5
Total Approx.		160

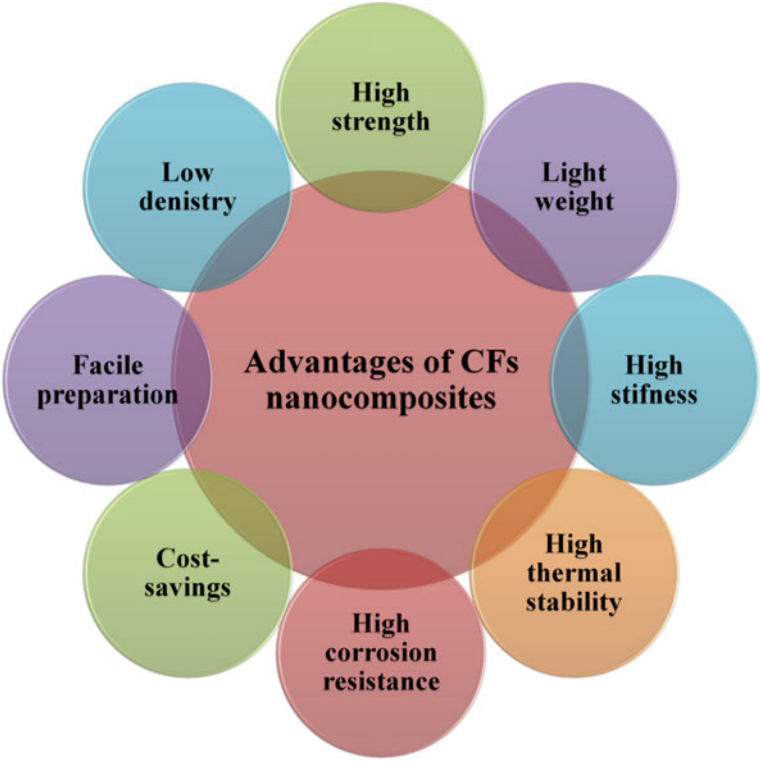


Fig. 2 Advantages of CF-based nanocomposite for industrial applications

Because CFRP's modulus of elasticity is three times that of steel [44]. CFRP was first used in the aerospace industry [45]. This was mostly due to the fact that it possessed certain characteristics (strong and lightweight). The demand for CFs has increased dramatically over the last decade, with a compound annual growth rate of 13%, and reached 140,000 tons in 2020 [46]. There is a growing interest in a cost-effective recycling PVC technology that produces recycled valuable materials [47]. CFs can provide cost-saving and ecofriendly properties for thermoplastic polymer matrixes.

4.2 Carbon Black

CB is made up of meticulously designed elemental carbon. It typically contains >97% pure carbon that distinct it from impure soot by-product produced during incomplete combustion of carbonaceous materials or biomass (contains < 60% carbon, polyaromatic hydrocarbons and oil residues) [48]. The particles of CB are quasi-spherical with amorphous core and almost concentrically oriented graphene like shell [49]. These primary particles grow to form aggregates that define the structure of CB [50]. As the size of primary particle increases (>100 nm) the tendency of aggregation decreases and low structure CB is formed whereas high structure CB is formed by coalescence of fine primary particles agglomerated in a branched shape. Such aggregates form loosely bounded agglomerates through van der Waals forces.

CB is industrially prepared as a commodity chemical by thermal decomposition of different hydrocarbon feedstock—either gas or liquid- under controlled conditions. Different processes are used for manufacturing CB namely furnace, channel, gas, lamp, acetylene and thermal blacks. Pyrolysis of waste tires into CB is recommended for environmental issues [51]. Additionally, demineralization process using HNO_3 suggests a promising method for reclaiming CB with acidic surface groups that facilitate distribution in rubber matrix for better reinforcement [52]. Particle size of CB is an important property upon which CBs are classified into series (namely, 100, 200, 300, …900). 100- series blacks with highest specific surface area are suitable for reinforcing whereas 900- series with smallest surface area have little reinforcement ability. In addition, a common nomenclature is widely used to designate CBs according to application field and production technique besides ASTM classification [53]. ASTM categorizes rubber grade CBs using four characters. The first character dictates curing rate of rubber (N and S for normal and slow, respectively) is followed by 3-digit number; the first one assigns surface area and the followings are arbitrary. Table 4 shows different classification types with the average particle size.

CB can induce several useful properties when compounded with polymer matrices. According to the required application, CB is used to impart reinforcement, UV stabilization, electrical conductance/resistance, opacity, etc. Referring to basic contact theory, the predominance of graphitic structures on CB surface rather than turbostratic structure induces more electrical conductivity [50, 54]. This can be explained by widely spaced planes and high surface porosity induced by the turbostratic structure rather than the graphitic structure [55]. Pantea et al. [54]

Table 4 Abbreviation and average particle size of different CB classes

Series	Common name	ASTM 1765 class	Particle size (nm)
100	Super abrasion furnace (SAF)	N110	20–25
200	Intermediate super abrasion furnace (ISAF)	N242, N220, N231, N219	24–33
300	High abrasion furnace (HAF)	N330	28–36
400	Fine furnace (FF)	N472	31–39
500	Fast extrusion furnace (FEF)	N550	39–55
600	High modulus furnace (HMF)	N660	49–73
700	Semi-reinforcing furnace (SRF)	N770, N772, N774	70–96
800	Fine thermal (FT)	N880	180–200
900	Medium thermal (MT)	N990	250–350

studied the effect of surface chemistry and topology of CB on electrical conductivity using spectroscopic techniques and nitrogen adsorption at low pressure. Results show an intimate relation between graphitic character of CB including dimension of graphitic layers and homogeneity of surface electronic environment and surface topology as well.

5 PVC Reinforced with CF and Carbon Black Nanocomposites

5.1 PVC Reinforced with CFs

Because of the PVC low cost and excellent mechanical properties, it is widely used in a variety of applications. Great interest was directed toward filling PVC with natural fiber materials including wood, coconut, and sisal fibers, rice straw, and bagasse fiber. Composite materials have recently become increasingly important in a variety of industries, including aerospace (plane and space systems), vehicles, pressure vessels, and lightweight cylinders [56]. CFs have exceptional chemical features and mechanical durability which can broaden their applications [57]. PAN-based conversion process quickly became the most popular way to make CFs. PAN is used to make 90% of CFs today. The remaining 10% is made out of petroleum pitch and rayon. PAN-based fiber materials are incredibly strong and lightweight. To manufacture CF reinforced plastic, CFs are filled in the PVC resin including nylon, vinyl ester, and polyester. The behavior of CFs and chemical and physico-mechanical characteristics are based on the employed precursors for making CF nanocomposite. PAN-based CF exhibited 2.7 GPa and 200–600 GPa for tensile strength and modulus experiments, respectively with nearly $30 for each Kg [58]. The expanding applications of CFs based on PAN in the industry are currently hampered by a lengthy stabilization procedure and a relatively expensive CF manufacturing cost [59]. Chlorinated PVC is a low-cost synthetic polymer that contains 62–72 wt.% chlorine content (10 wt.% greater than PVC) prepared via PVC free-radical post-chlorination [60, 61]. Chlorinated PVC has a lot of similarities to PVC in terms of qualities and characteristics, however, it has greater thermal stability, mechanical durability, and resistance against chemicals [62].

CF filler loading, in practice, is a cost-effective approach to improve the stiffness of PVC to any required level, depending on the application. Kim et al. [63] claimed that chlorinated PVC fibers were made at a low cost via wet spinning with several elongation rates (0, 50, 100, and 125%) used to improve the physicochemical properties. PVC with CF reinforcement exhibited excellent mechanical qualities and low density.

Rathy et al. [64] stated the preparation and investigation of innovative PVC/CFs nanocomposites. As CFs have recently become more affordable, they can be used to improve the mechanical qualities of mass-produced PVC (Fig. 3). Increasing the

CFs nanofiller concentrations in the PVC resin can increase hardness and Young's modulus, although tensile stress remained unchanged. Kiani et al. [65] described a new technology of plastic injection to produce PVC/CF-graphene nanocomposite for pipes' coatings. To improve graphene distribution and orientation inside the matrix, preparation cycles and CFs were extruded. The high mechanical durability of the formed PVC/CFs-graphene nanocomposite prepared via melting procedure was caused by the polymer-fibers' strong interfacial interaction.

CFs fillings in thermoplastic polymers (such as PVC) offer various merits, as follows [66]:

1. CFs offer excellent mechanical, thermal, and electrical properties as well as recyclability and corrosion-protection for the developed nanocomposites.
2. They have higher stiffness, strength, electrical and thermal conductivity as well as lower density and friction coefficient than glass fibers.

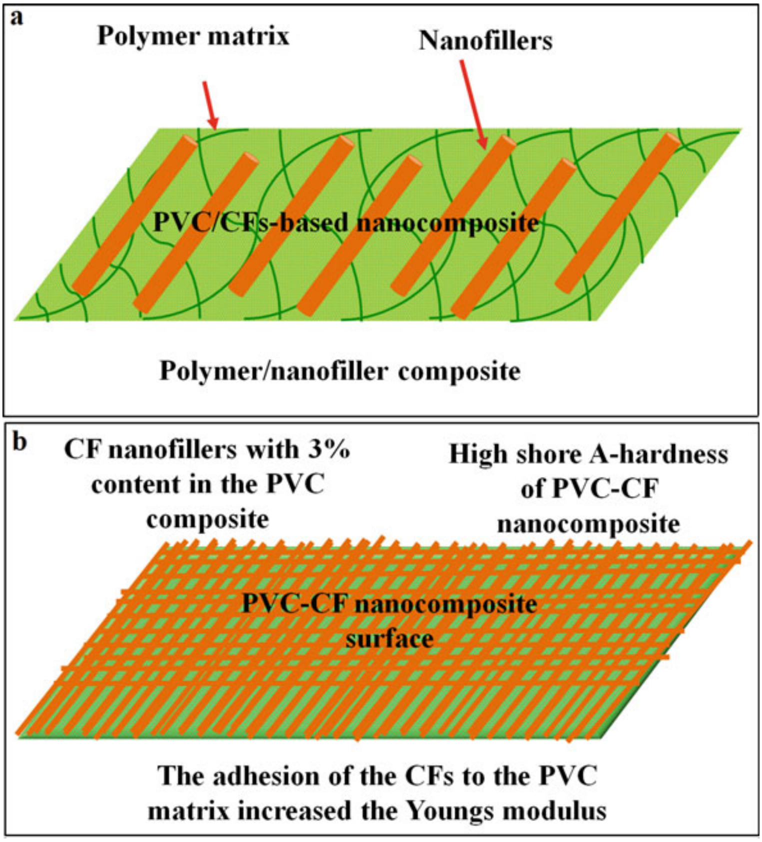


Fig. 3 **a** Schematic illustration of PVC composite reinforced with different CFs contents; **b** PVC–CF composite filled with 3% CF content to achieve high shore A hardness and increased Young's modulus [64]

3. They are extremely conductive, while glass fibers are insulating.
4. CFs-based thermoplastic polymeric composites are recycled through their melting and reconstructing to develop a new structure.

On the contrary, CFs have some drawbacks for using as nanofillers in the thermoplastic resins, as follow [67, 68]:

1. CFs are more expensive compared to glass fibers.
2. The wetting properties and adherence of CFs to the thermoplastic matrix are poor.
3. Under uniaxial tension, CFs-based thermoplastic nanocomposites show the minimal strain.
4. The surface of virgin CFs is nonpolar while PVC resin is polar.

These benefits and drawbacks should be considered before using PVC nanocomposite.

5.2 PVC Reinforced with CB

Polymer composites and recently nanocomposites grasp a great deal of scientific and industrial attention for their unique properties in functional and structural applications [69]. Fillers are usually added to polymers to reduce cost, enhance mechanical properties, facilitate processing and sometimes induce electrical conductivity.

PVC is one of six important worldwide thermoplastics. It is cheap, has good dimensional strength, resisting chemicals and corrosion and importantly having relatively good dielectric constant. However, it is inherently brittle and rigid and suffers from poor heat resistance thus could not find practical application unless formulated with different functional materials. According to scope of application, different ratios of plasticizer, filler, stabilizer, lubricant, UV-absorber, flame retarder, etc. are formulated. Figure 4 shows some application fields and properties of CB/PVC composites and nanocomposites.

Plasticizers make a major contribution in allowing polymer chain mobility and flexibility during processing besides tailoring required properties of the final polymer composites Dioctyl phthalate (DOP) is a common plasticizer for PVC but nowadays, phthalate-free plasticizers become a worldwide need without compromising final product value. Changes in molecular structure and toxicity of plasticized PVC surface and bulk after exposure to short and long wave UV radiation were investigated [70]. Short wave rather than long wave UV radiation was found to produce toxic phthalates on PVC surface. Epoxidized soybean oil (ESBO) was found to be a good choice in enhancing processing and mechanical properties for PVC rather than DOP. It also acts as heat stabilizer for CB/PVC composites [71]. A reported mechanism for limiting dehydrochlorination of PVC during thermal degradation involves reaction of epoxide group in ESBO with HCl produced [72].

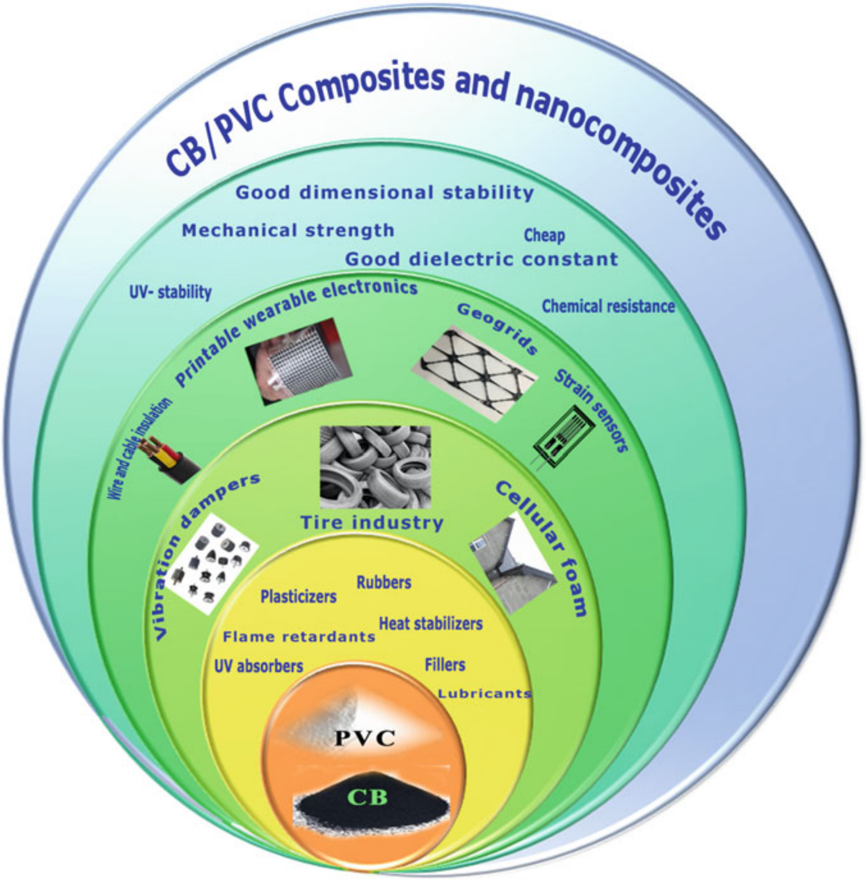


Fig. 4 The industrial applications and properties of PVC reinforced with CB composites and nanocomposites

PVC was widely toughened with rubbers especially poly (butadiene-co-acrylonitril) (NBR) [73] or other elastomers [74]. Different mechanical properties including hardness, resilience and elongation% are improved upon vulcanization [75]. Variation of particle size, specific surface area, structure (low or high), surface activity and loading % of CB besides intrinsic elasticity/viscosity of the rubber in use are main influencers that allow tailoring the required tire properties. Composites of natural rubber, high styrene rubber, nitrile blended PVC (NPVC) and CBs with different classes (ISAF, SAF and SRF) were prepared for heavy duty tire application [76]. It was found that ISAF CB with high surface area and comparative low void volume is optimum filler with regard to curing time, andrate and mechanical properties. In addition, using 20% NPVC shows maximum tear and abrasion resistance against almost all types of rocks and low heat generation upon friction. However, dispersion of small particle sized fillers for good reinforcement is essential but elusive. In this framework, aluminum hydroxide was added to CB/NBR/PVC composites [77]. It was found that it facilitates mixing of CB into NBR/PVC and accelerates vulcanization process.

Swelling, of course, adversely affects mechanical properties of vulcanizates when come in contact with solvents. It was found that increasing the ratio of PVC in CB/PVC/NBR nanocomposites up to 30–40 phr diminishes penetration rate and diffusion coefficient of kerosene that are responsible for enhancement of swelling properties [78]. Swelling resistance of CB/PVC composites was also enhanced by incorporation COOH- functionalized graphene nanoplatelets (GNP) in minute amounts (3–9 phr) [79]. The new CB/PVC/GNP nanocomposites exhibit excellent mechanical performance. Another study found that halloysite nanotube has also beneficial impact on mechanical properties of CB/PVC composite and swelling characteristics [80]. Moreover, mica was reported as a complementary filler with CB for reinforcing NBR/PVC [81] for rubber-based vibration dampers. Increasing the ratio of mica to CB shows decreased swelling and better toughness, elongation and vibration damping at various temperatures.

Recently, in an attempt to replace the necessary CB filler in PVC/NBR, lignin was used as a co-filler. However, the poor compatibility of lignin with rubber is a drawback that would affect mechanical properties of the end product. Metal coordination to different functional groups found in both NBR and lignin opens the door for better compatibility. Wang et al. [82] reported using $ZnCl_2$ for coordination between NBR and lignin through Zn^{2+}. Hybrid composite of lignin/CB/PVC/NBR shows better tensile strength, Young's modulus and oil swelling but lower elongation at break compared with CB/PVC/NBR.

In addition to resilience, further important property was engaged with toughened PVC; electrical conductance. PVC is insulator by nature but composites with electrical conductance find modern applications in electronic and structural materials. CB with different loading percentages was molded by the facile compression mode with PVC [83]. Threshold concentration of 15 wt.% CB was found to enhance electrical properties as well as tensile characteristics. However, elongation at break and thus ductility and toughness were adversely affected.

Enhanced electrical conductivity and dielectric constant of PVC were observed upon irradiating CB/PVC composites with ion beam as well as with increasing CB concentration [84]. Blends of PVC with poly(ethylene oxide) (PEO) and/or poly(ethylene glycol) diglycidyl ether (PEGDGE) as an electrolyte fits good for application in electronic devices. Incorporating conductive CB (CCB) to both blends enhances electric properties of the final composite film. It was found that PEGDGE acts as a good surface modifier for PVC/PEO/CCB composites thus leads to better distribution of CCB on the surface of films but on the other hand lowers tensile strength and thermal stability [85]. Supri et al. [86] also compared CCB with other conducting fillers namely, poly(aniline) (PAni) and poly(pyrrole) (PPy) for PVC/PEO and PVC/PEO/PEGDGE films. Regarding the intrinsic conductivity of PPy, it shows the best conductivity while CCB was the lowest.

Lately, acrylonitrile butadiene styrene (ABS) was used to ensure good dispersion of CCB nanofiller within PVC matrix [87]. CCB/PVC/ABS nanocomposites with segregated network of CCB show enhanced thermal and electrical conductivity in addition to better toughness.

In the field of electroactive materials, piezoelectric polymers have appealing applications as energy harvesters, actuators, transducer, sensors and others [88–91]. Regarding the tensoresistivity of PVC filled with CCB, CCB/PVC composite was used as coating material for developing effective sensor enabled geogrids [92]. The study suggests the suitable concentration and structure (high or low) of CCB, mixing method and coating thickness that would affect the tesoresistivity properties. The established geogrids show excellent sensitivity in sensing strain and could be applied in health monitoring of geosynthetic structures. Sensitivity of tensoresistivity response was further tested upon cyclic tensile loading for the effect of two CCB structures (medium and high) [11]. CCB with high structure composites show minor damage and retrievability in contrast with low structure ones.

Comparing electrical conductivity of CB, CFs and graphite (G) in PVC matrix, it was found that CB/PVC exhibits higher conductivity than PVC/CF and G/PVC for 20% by weight [93]. However, further increase in filler loading CF and G composites show higher conductivity. This behavior was attributed to high surface area of CB with regard to CF or G at low loading.

Application of CB/PVC in the field of strain sensors for wearable flexible electronics is promising for the composite high sensitivity. A new study reveals that micro-crack strain sensor on printable CB/PVC composite exhibits high sensitivity due to preserved morphology of the cracks on the composite surface [94]. Additionally, a flexible temperature sensor was fixed on CB/PVC composite with different weight ratios of CB [95]. The sensor with only 6% CB in the composite shows immediate response with supersensitivity for temperatures between 18 and 44 °C making it a good choice for monitoring human body temperature and respiration rate. It is of interest to mention that a percolation threshold of 10% CB in CB/PVC composite was suggested to be effective for application as positive temperature coefficient composite [96].

Nearly, 60% of polymers used in cable and wire insulation constitute PVC [97] for its inherent flameproof character. Historically, Raychem Corporation, California, USA was the first company to induce crosslinking to PVC by radiation chemistry for enhancing chemical, mechanical and thermal properties at low temperatures. In this context, effect of electron beam on CB/PVC composites was reported by Salem et al. [98]. The study reveals that addition of CB to PVC inhibits degradation up to certain limit of irradiation by introducing more physical and chemical crosslinking. Consequently, tensile strength, elongation at break and thermal stability were improved.

After World War II, it was trending to prepare PVC foam for its water resistance and light weight. In addition, easy processing, durability, low water absorption, low corrosion and fire resistance are attractive characteristics that make PVC foam a good candidate for indoor and outdoor applications. Tensile strength and elongation at break were easily improved by using only 1.5% CB (by weight) to prepare soft low density foam CB/PVC nanocomposite [99]. Moreover, CB is used for UV protection. In this regard, synergistic effect of modified CB with polyacrylic acid and polybenzimidazole as UV-stabilizers for PVC were investigated [100]. Such composite protects PVC against 99% of UV waves.

6 Effect of Nanofillers on the Physico-Mechanical Properties

It was decided to investigate a typical NBR/PVC composite with 70 phr carbon black. In order to reduce the use of Carbon black, melt-blending on a twin roll mill was used to develop new hybrid nanocomposites with a fixed content of 55 phr (Parts by weight per hundred of rubber) CB and a varied content of COOH functionalized graphene nano platelets, which were then tested and compared to conventional composites [79]. Zinc oxide (ZnO) nanoparticles are incorporated into a PVC-based nanocomposite using a gel-like technique. At 2.5–10 wt.% ZnO nanoparticles, tetrahydrofuran solvent was used to make nanocomposites [101]. Controlling the percentages of nanofiller addition is essential to avoid agglomerations, brittleness, and cracking induced by the higher nanofiller concentrations. The structure-folding properties, atomic-scale arrangements, matrix–nanofiller interfacial bonding, surface area, and configurations along the complete nanocomposite building blocks can all be influenced by the nanofillers' concentrations in the PVC matrix. Finally well-dispersion of nanofillers in the PVC matrix can improve thermal stability, hardness, and durability.

7 Conclusion

In this chapter, the history and sustainability of PVC in addition to its structure, additives, polymerization, fusion and processing, formulations, and degradation were discussed in detail. Many PVC polymer nanocomposite materials are considered to be used for industrial applications because of their superior physical and mechanical properties. CFs and CB reinforced PVC composites and nanocomposites were described extensively. Recent researches have been conducted to produce novel PVC/CFs and PVC/CB nanocomposites for plastic applications. To manage the PVC nanocomposites' structure–property relationship, synthesis functions and the addition of nanofillers are critical issues. The physico-mechanical behavior can be altered by suitably spaced CFs or CB nanofillers in nanocomposites. These nanocomposites' benefits include facility, economic, hardness, and recyclability. Conclusively, the effects of dispersing CFs or CB nanofillers in PVC resins influences physico-mechanical properties of the nanocomposites finding advanced applications in various fields.

8 Future Prospective

Although the use of PVC resins in automotive and plastic industries is decades old and well-studied, today's research focuses on modifying these materials to bring innovative nanocomposites with improved performance and environmental friendliness. As a result, efforts must be made to produce low-cost PVC nanocomposites that will result in safe transportation of organic chlorine materials with sustainability awareness. CFs and CB nanofillers have several advantages over microfillers, such as higher strength-to-weight ratio, less filler percentage in the polymeric resin, improved polymer-nanofiller interfacial interactions, and increased mechanical properties. Long-term adverse environmental considerations of organic–inorganic PVC/CFs and PVC/CB nanocomposites are critical issues for future developments. It's unavoidable to investigate the effects of dispersing different concentrations of CFs and CB nanofillers on the hardness and young's modulus capabilities of the PVC resins. Also, it is inevitable to study the wetting properties and adherence of PVC/CFs and PVC/CB nanocomposites. Efforts should be directed toward achieving 100% sustainable carbonaceous PVC nanocomposites, which would provide a number of benefits, particularly for eco-friendly plastic materials' applications. The shortcomings of PVC/carbon filler nanocomposite may be overcome in the future, increasing their efficiency and potential for usage in a variety of novel applications. Such multifunctional PVC nanocomposites will be widely available in the near future, saving billions of dollars in annual plastic costs.

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Mica and Glass Fiber-Filled PVC Composites

Fabiula Danielli Bastos de Sousa

Abstract The in-depth analysis of the keywords used in a given scientific area provides an overview of the area and helps understand it better. Accordingly, in the present work, the analysis of the authors' keywords was the basis and the opening point for discussing the available literature on mica-filled PVC composites and glass fiber-filled PVC composites. Searches in Scopus database were performed to obtain the data inputs and the results were analyzed by Bibliometrix. The Literature concerning the subject was discussed, resulting in an overview of the literature regarding mica-filled PVC composites and glass fiber-filled PVC composites.

Keywords Polyvinyl chloride (PVC) · Mica · Glass fiber · Composites · Authors' keywords

1 Introduction

Polyvinyl chloride (PVC), a thermoplastic polymer, is notable for its extraordinary assortment and extend of properties determined through arranged definitions of each composition for specific purposes. It is always associated with additives, which define its properties and applications [74].

In Europe, PVC accounts for approximately 10% of the estimated European demand for thermoplastic polymers. It is widely applied as a raw material for building materials such as liners, floor coverings, pipes and fittings, cable insulation, doors and window frames, tiles, roofing sheets, profiles, among others [66], being considered an irreplaceable material in these applications [47]. It also has a large use in other sectors of the economy, with applications such as bottles, packaging, medical products, etc. To make electric cables and wires, PVC is the second common polymer used [20] due to its low price and excellent electrical insulating properties [97], being the first the polyethylene.

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Even presenting properties of great interest, these are often insufficient for some specific applications, and it is necessary to add another material to develop a composite with superior properties. In addition, it is more economically viable to join two materials than to develop another molecule in the laboratory.

Composite reinforced with fibers is one of the most used materials. It can be divided into three groups based on the matrix material—polymer, metal, or ceramic. Polymeric composites can be made of thermoplastic or thermoset matrices. It takes advantage of the stiffness and strength of high-performance fibers dispersed in the matrix, acting as a binder and transferring forces to the fibers across the fiber-matrix interface [41].

Fiber-reinforced composites present high strength to weight ratio and anisotropic properties. The high strength of these composites has empowered them to compete with other materials, counting metals. Their anisotropic properties permit the designer to accomplish the wanted properties in the specific locations keeping the same weight [7]. A very high number of researchers have strived to develop advanced composites that have applications in important branches such as aeronautics, marine, and automotive.

Reinforcing fibers may be used in different forms, such as short, long, and continuous [7]. The main task of reinforcing fibers is to make the composite resistant to pressure by transferring force from one fiber to another [43].

Regarding glass fiber and mica, literature depicts the reinforcing character of mica and glass fiber on polymeric matrices [87]. Glass fibers are the foremost broadly used as a reinforcement within the composites industry, and many kinds of them are commercially accessible. Their chemical compounds are distinctive, and each one is appropriate for a specific application. Glass fibers present good strength and hardness. However, their elastic modulus is rather low [7]. Mica is a natural mineral abundant in nature. It has a high aspect ratio and strength, high crystallinity, thermal stability, corrosion resistance, and physical stability [30]. Mica has excellent chemical resistance, good electrical properties, low thermal expansion, and it causes less wear and abrasion to the processing equipment. Its arc resistance and surface resistance improve the mechanical properties of PVC [20]. It also shows significant upgrading in dielectric properties of composites [20].

Bibliometric analysis is a powerful tool in the deep investigation of any research area. It is based on a quantitative analysis of the literature of a given research area [65]. This kind of analysis arose to cope with constantly growing bodies of knowledge and incorporates three main following dimensions (measuring a specific scientific activity, its impacts taken by the total number of article citations, and the associations among articles) [61]. Many different research areas take advantage of the benefits of this tool. Examples of recent publications include different areas such as microfinance [65], medicine [86, 90, 96], infrastructure projects [13], sustainable agrifood supply chains [1], among many others.

By searching in a database such as Scopus or Web of Science, from the obtained result is generated a .bib file, which is analyzed through Bibliometrix, a R-package, being the results revealed through Biblioshiny. All the data can be analyzed such as the keywords, authors, publications, publication countries, affiliations, among others.

According to Zhou et al. [102], “keywords are the core of the paper, which indicates the research direction of the field by abstracting and summarizing the research content of the academic paper”. Through the analysis of the keywords, it is possible to obtain a panorama of the research field, the hotspots, and the future trends [17, 18, 19].

In the present work, due to the relevance of the analysis of the authors’ keywords, this was the initial point and the basis to obtain an overview of the literature about mica-filled PVC composites and glass fiber-filled PVC composites. Searches in Scopus database were performed to obtain the data inputs, being the results analyzed by Bibliometrix. Literature concerning the subject was briefly discussed.

2 Methodology

Two Scopus searches were performed to obtain the data. The first one was performed on April 19th 2022 by using the words “composite*” AND “PVC” AND “mica”. The second one was performed on May 3rd 2022 by using the words “composite*” AND “PVC” AND “glass fiber*”.

In both cases, the obtained results were analyzed by Bibliometrix (from the .bib file generated by Scopus in each search), an R-package. Emphasis in the investigation of the authors’ keywords was given.

3 Results and Discussion

3.1 Glass Fiber-Filled PVC Composites

The Scopus search by using the words “composite*” AND “PVC” AND “glass fiber*” resulted in 192 documents in English, being 189 articles and 3 reviews. The publications are from 1980 up to the search date.

Figure 1 shows the word cloud containing the 50 most popular authors’ keywords, in which the size of the letters represents the number of occurrences in the result of the Scopus search.

Based on the word cloud, an overview of the subject of glass fiber-filled PVC composites can be outlined. According to Shi et al. [70], the word cloud is a clear and entire graphical display of hot topics analyzed in a research area.

Apart from the keywords used in the Scopus search, others more popular in the literature are (number of occurrences in parenthesis) PVC foam (12), sandwich composite (9), sandwich composites (9), mechanical properties (7), composite sandwich panels (6), filled polymer (5), mechanical property (5), mechanical testing (5), modulus (5), damage (4), finite element analysis (4), and frequency (4). These keywords demonstrate both the trends of the research area, as well as some concerns and priorities. The keywords ‘sandwich composite’ and ‘sandwich composites’ can

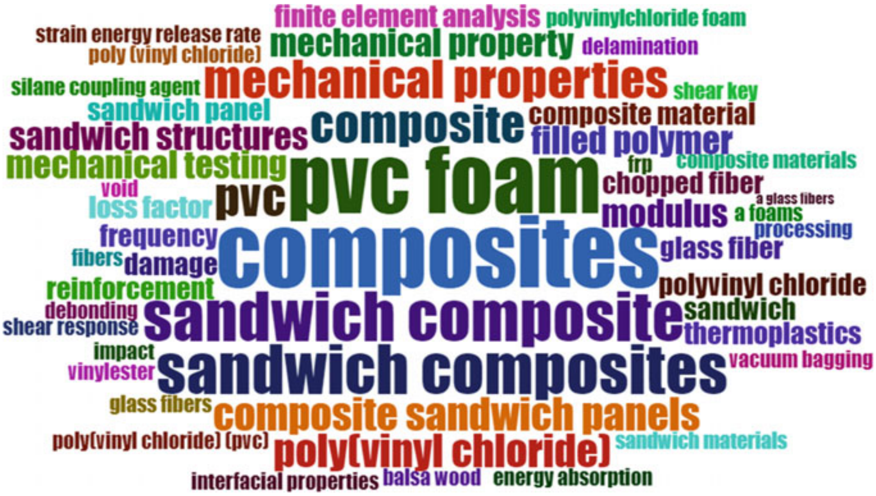

Fig. 1 Word cloud containing the 50 most popular authors' keywords

be merged as 'sandwich composite*', as well as the keywords 'mechanical properties' and 'mechanical property' can be merged as 'mechanical propert*'. So, these keywords have a huge importance in the glass fiber-filled PVC composites research field, being that 'sandwich composite*' obtained 18 occurrences and 'mechanical propert*' 12 occurrences. With this, the authors' keywords 'PVC foam', 'sandwich composite*', and 'mechanical propert*' can be considered hot topics in the research field, as well as top keywords.

Word cloud (Fig. 1) revealed the core of the glass fiber-filled PVC composites literature showing some materials such as silane coupling agent [46], chopped filler [14, 46, 64, 84], thermoplastics [25, 55, 79, 91]; some properties and concerns such as mechanical properties (and mechanical property) [14, 23, 24, 41, 46, 47, 50, 59, 64, 69, 75, 77, 80, 82, 84, 93], energy absorption [2, 39, 40, 52, 72, 98, 100, 101], interfacial properties [14, 54, 59, 73, 84], impact [2, 6, 14, 15, 47, 60, 76, 77, 84, 98, 100, 101], shear response [44, 57], debonding [6, 31–33, 45], damage [5, 6, 9, 11, 12, 38, 53, 59, 60, 67, 71, 73, 75–77], loss factor [9, 31–33], void [41, 64, 81], delamination [44, 45, 68, 85], strain energy release rate [8, 51, 77], modulus [25, 35, 93]; ways used to characterize and model properties such as finite element analysis [8, 32, 57, 88, 101] and mechanical testing [10, 39, 40, 75, 77, 80, 84]; and vaccum bagging, a processing method [22, 23, 24, 29, 54, 76] among many others.

According to Zhao et al. [98], a sandwich structure consists of two stiff face sheets with high-strength combined with a core part made of light-weight materials. Specific properties such as energy absorption, specific stiffness, and strength [39, 72] are responsible for its wide use in various industrial branches, as well as to be cost-effective [72]. Many weight-critical industrial fields take advantage of the lightweight and high flexural stiffness of sandwich structures [80]. Concerning glass fiber-filled PVC composites, it can be observed that literature is focused on sandwich structures. In general, PVC is used in the sandwich core as PVC foam and glass fibers as reinforcing agents.

An overview from literature will be presented in the sequence, in which some publications will be briefly presented.

Concerning PVC foam, it is widely used in naval ships [26, 59, 60, 73], aircrafts [98], and automobiles [98] due to its low density. In particular, sandwich composite structures with the core material being a polymer foam or balsa wood are extensively used in the construction of naval ships [26, 60, 77, 88]. By analyzing these materials, the authors adopt both experimental [24, 26, 32, 45, 52, 76, 98] and numerical investigations [24, 26, 45, 85, 88], such as finite element model [8, 32, 56, 57, 88, 101].

For marine applications is essential to analyze the aging behavior in an environment as real as possible [22, 23, 24]. Concerning experimental investigations, mechanical properties are largely observed [14, 41, 75] (as previously observed in Fig. 1), but some authors examine other properties such as the vibration behavior [9, 31], the energy absorption [2, 95, 101], among others. Literature also seems to be interested in the use of fiber glass as reinforcement in wood/PVC composites [55, 79, 91]. Other applications of sandwich structures are in wave absorbing structures such as radars [3].

As processing methods used, it seems that the vacuum-assisted resin infusion process [8, 15, 24] is the most adopted by literature.

Very relevant in the area is the study of the aging of sandwich composites. Ding et al. [22] examined the behavior of moisture absorption and evolution of various mechanical properties for the sandwich composites immersed in seawater at 30 °C and pure water at 80 °C. Later, the research group [24] studied the same parameters in different harsh environments such as salt-fog spray aging, hygrothermal atmosphere alternating high and low temperature, and solar radiation in combination with water vapor. Toubia et al. [75] analyzed the evolution of various mechanical properties of sandwich panels using foam core with fiber glass/vinyl ester face sheets by exposing them to 100 days of freeze/thaw exposure (−20 to 20 ºC) in the presence of a saline solution.

Ding et al. [24] examined the behavior of moisture absorption and the evolution of various mechanical properties of sandwich composites with ECR glass fiber/vinylester composites faces bonded to PVC foam core. The samples were exposed to different harsh environments such as salt-fog spray aging, hygrothermal atmosphere alternating high and low temperature and solar radiation in combination with water vapor. The results found that the samples exposed to the solar radiation in combination with water vapor deteriorated appreciably in the faces-core interfacial properties.

Other authors [84] examined the reinforcing influence of fibers given by the interfacial bonding between PVC foam core and glass fiber face sheets. The authors found notable improvements in bending strength, energy absorption, and impact strength due to the applied treatment of the fibers: to form a connection between the face and core, one side of the fiber was coated with epoxy extending from the foam, and the other side was embedded into the lower part of the foam layer. Chen et al. [14] used glass fiber to improve the interfacial bonding between PVC core and glass fiber face sheets and observed that the bending strength and energy absorption were enhanced by up to 100% and around 161%, respectively, under three-point bending.

Lee et al. [46] analyzed the reinforcement of chopped glass fiber in PVC containing silane coupling through the mechanical properties. The aspect ratio of the fibers influenced the mechanical properties in different ways, and the presence of silane coupling improved the mechanical properties of the composites, since the compatibility between the phases was enhanced. Mechanical properties were also enhanced in the work by Shanmugasundar et al. [69] due to the presence of graphene in PVC/graphene/glass fiber composites. So, all these publications demonstrate the importance of adequate interaction between the phases in obtaining higher properties.

It is known that sandwich structures are increasingly used in marine applications, wind turbine blades, and spacecraft, and there is a great difficulty in recycling them, being that sometimes their recycling is not possible and feasible. Thus, the study of repairs in these structures is essential. Some authors [4] applied different types of repairs such as the conventional patch repair, extra fiber reinforced repair, splitted fill foam repair, and internal reinforced repair. They observed that extra fiber reinforced repair showed a better performance compared to the conventional patch repair. According to the authors, by reinforcing the discontinuous zones formed in the repair zone, the extra fiber reinforced repair method provides a more robust structure than the conventional patch repair.

In line with the previous work, some authors [47] produced PVC composites reinforced by glass fiber with carbon deposit (GFCD), derived from the recycling of wind turbine blades. It was observed a fine adhesion between the filer and PVC matrix, which resulted in enhanced mechanical properties when using a small concentration of the filler. Additionally, according to the authors, “the percentage of GFCD affects neither the temperature of thermal stability nor the time of thermal stability which is extremely important in the case of PVC composites”. Such results are extremely important since they deal with the use of a material derived from the recycling of wind turbine blades, relevant items in the generation of energy from renewable sources.

Zal et al. [93] evaluated the effects of some processing parameters such as pressure, time, and temperature on the properties of amorphous PVC/fiber glass composite. An elevated processing time and temperature resulted in the degradation of PVC. On the other hand, an increase in the temperature up to 230 °C enhanced the flexural strength. Regarding the processing time, it proved to be relevant at low temperatures since enhanced the wetting, impregnation quality, and mechanical properties. Processing pressures showed a slight improvement in the mechanical properties at low temperatures.

Park et al. [64] produced PVC/fiber glass composites and examined the effect of length and concentration of chopped glass fiber on the composites. It was observed an increase in flexural strength and tensile strength due to the increase of the fiber length, whereas interlaminar shear strength was enhanced due to the increase of the fiber concentration. The authors concluded that the content and length of the chopped fibers act differently on each mechanical property analyzed.

Importantly, some authors [59, 73] examined the influence of interfacial crack size and impact damage size on sandwich composite composed of glass reinforced polymer skins and PVC foam core. All the examined properties were negatively impacted by crack size and impact damage size, bringing implications on the structural integrity of a minehunting ship made of the composite. Other authors also analyzed different types of damages to sandwich structures [5, 6, 9, 11, 12, 26, 38, 44, 53, 60, 56, 59, 60, 67, 71, 73, 75–77].

Gargano et al. [26] examined the explosive blast response of sandwich composite panels with a PVC foam core with polymer laminate facesheets reinforced with carbon or glass fibers. The results showed that the explosive blast resistance of sandwich composite structures was impacted by both the sort of fiber reinforcement used in the laminate facesheets and the kind of core material. Glass fiber showed superior results both for the resistance to out-of-plane deformation and resistance to damage.

In another purpose, Zhou et al. [101] produced tube reinforced PVC foam cores and investigated their energy-absorbing characteristics by using both experimental and numerical investigation (finite element method). The results proved that embedding the tubes in a foam panel enhanced their ability to absorb energy. Additionally, the energy-absorbing capability of tube-based foams was higher than many comparable core systems, highlighting their potential for use in conditions of extreme crushing. The validated models agreed with the experimental data.

Trend topics on the investigated data were also analyzed and are presented in Fig. 2. The top authors' keywords of the last 20 years were chosen to be studied. The minimum frequency of the keywords was 5, and the number of keywords per year 2.

In Fig. 2, the strongest authors' keywords are depicted, i.e., the authors' keywords with the highest number of occurrences in the last 20 years, also known as top authors' keywords. The most popular authors' keywords, apart from the ones used

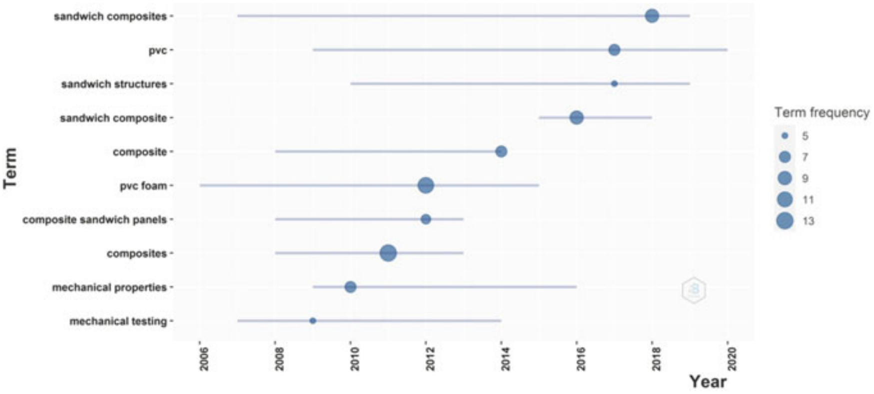

Fig. 2 Trend topics concerning glass fiber-filled PVC composites research field

in the Scopus search are: mechanical testing (2007–2014), mechanical properties (2009–2016), composites (2008–2013), composite sandwich panels (2008–2013), PVC foam (2006–2015), composite (2008–2014), sandwich composite (2015–2018), sandwich structures (2010–2019), and sandwich composites (2007–2019). The strongest authors' keywords in the last years can be considered trends in the research field, i.e., sandwich composites. Considering the merging explained before, in which 'sandwich composites' and 'sandwich composite' become 'sandwich composite*', the strength of this keyword becomes even bigger, which makes it an utmost trend.

Furthermore, according to de Sousa [19], through this kind of analysis, the evolution of the top authors' keywords can be observed over the years. It can be observed that some keywords remain in evidence over a period of time, giving rise to other keywords due to the natural evolution of the literature. So, it can be observed that some keywords such as 'mechanical testing' and 'composite sandwich panels' are no longer in evidence in the literature about glass fiber-filled PVC composites today.

The size of the blue circles means the term frequency. For instance, 'sandwich composites' was the strongest term in 2018, receiving 9 occurrences.

Figure 3 shows the authors' keywords dynamic in the last 20 years. Only the top authors' keywords were analyzed, i.e., 'PVC foam', 'sandwich composite*', and 'mechanical propert*'.

Based on Fig. 3, it can be observed that the three keywords seem to develop with a similar growth rate until 2017. Until 2013, 'mechanical propert*' presented a higher number of occurrences than 'PVC foam' and 'sandwich composite*'. In

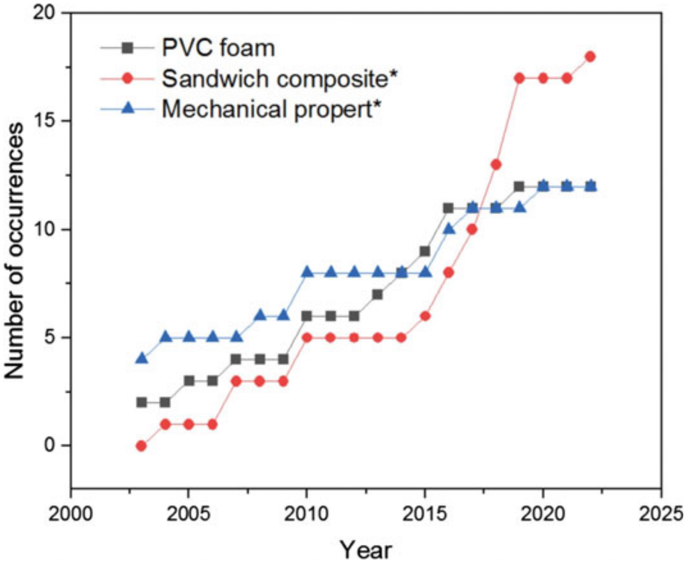

Fig. 3 Dynamic of the authors' keywords 'PVC foam', 'sandwich composite*', and 'mechanical propert*' in the last 20 years

2018, ‘sandwich composite*’ tacked off, presenting since then a higher number of occurrences per year and a higher growth rate than the others.

This result corroborates with the trend topics presented in Fig. 2. ‘Sandwich composite*’ is the strongest authors’ keyword at present by attracting a higher interest of researchers. All the keywords analyzed in Fig. 1 are trend topics in the glass fiber-filled PVC composites research field, but ‘sandwich composite*’ is the most popular authors’ keyword nowadays.

3.2 Mica-Filled PVC Composites

The search in the Scopus database with the words “composite*” AND “PVC” AND “mica” resulted in 21 documents in English, being 20 articles and 1 review, from 1981 to the search date.

Figure 4 brings the word cloud containing the 24 most popular authors’ keywords, in which the size of the letters represents the number of occurrences in the result of the Scopus search.

Apart from the keywords used in the Scopus search, the one with the highest number of occurrences is ‘interface’, with 2 occurrences. The other authors’ keywords present the same number of occurrences. The small number of occurrences is due to the reduced number of documents found in the Scopus search.

The word cloud (Fig. 4) depicts that the literature concerning mica-filled PVC composites is focused on the materials and their characteristics such as PVC foam [34, 41, 89], phlogopide mica [34], filler shape [41], filler aspect ratio [41], rigid PVC foam [34, 41], filler geometry [41], fly ash (and flyash) [41]; properties and behavior of the materials such as thermal properties [41], stiffness [83], thermal degradation behavior, rheology [94], sound transmission loss [83], partial specific compressibility [49], among others; processing ways and characterization techniques such as injection molding and scanning electron microscopy [21]. All these keywords

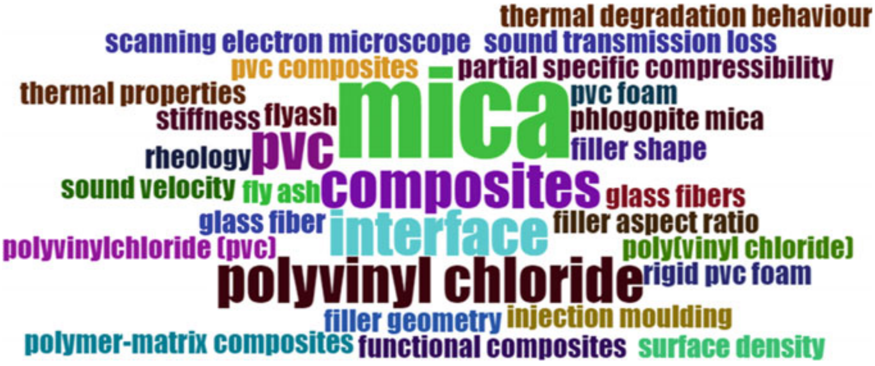

Fig. 4 Word cloud containing the 24 most popular authors’ keywords

outline a panorama [17, 18, 19], concerns of the authors, and the central aspects about mica-filled PVC composites.

According to the results presented in Fig. 4, 'interface' is an important author's keyword in the research field of mica-filled PVC composites [42]. It is known that the mechanical properties of a polymeric composite as a whole depend on the adhesion between the phases, i.e., matrix phase and dispersed phase. In other words, the performance of a given composite is robustly influenced by the matrix-fiber interfacial bonding [28, 37, 63, 92], and the mechanical properties as a consequence. Researchers often use a coupling agent [36], a compatibilizing agent [28], another polymer [62], or even another filler (such as a nanometric filler [69, 99]) in the search of a superior adhesion between the phases. According to Kim and Mai [42], the interfacial strength influences the mechanical and interlaminar fracture properties of composites. Poor wetting of fibers, resulted by the poor fiber/matrix bonding, causes fibers pulled out during the tensile test [92]. Consequently, a concern of the literature on the subject is to study the fracture behavior of these structures [51, 72].

From this point on, literature about mica-filled PVC composites will be briefly presented.

Deshmukh and Rao [20] analyzed the use of mica in different concentrations as filler in PVC matrix. The results demonstrated that, in general, composites presented a slight improvement in the mechanical and electrical properties. The surface treatment of mica improved de arc resistance of composites. Similar behavior was found by Khoshnoud and Abu-Zahra [41], that analyzed the properties of PVC foam composites reinforced with different shape fillers. The tensile strength of the composite containing 10 wt% of mica was slightly improved.

In a previous work, the authors [21] analyzed the influence of particle size, filler concentration, and surface treatment of mica on the mechanical and electrical properties of mica-filled PVC composites. The increase in filler concentration improved the dielectric strength, surface resistance, and Young's modulus. Surface treatment increased the arc resistance of the composites.

Concerning environmental issues and personal unhealthiness, noise pollution has turned out to be one of the major concerns [89]. Given the importance of the subject, the literature seems to be focused on minimizing the problem by using polymeric soundproofing materials as noise control applications. Mica is also used in PVC matrix to improve the sound insulation property of PVC [83], being the PVC/mica composites considered sound absorbers and insulating materials, which are very useful in the reduction of ambient noise [83].

Tripathi et al. [78] studied the effect of grain size on the dielectric properties of PVC/mica composites films. The authors found improved insulating properties of the composites. According to the authors, the reduced grain size of mica increased the intermolecular interaction, while the increase in the grain size increased the plasticizer effect. Correspondingly, some authors [89] sought the increase in sound insulation of the composites lightweight flexible PVC foam-mica. They found that, with a content of mica below 10 wt%, the composites presented good sound insulation properties and maintained ultra-light weight. Wang et al. [83] evaluated the effects of dioctyl phthalate and mica on the sound insulation property of PVC. Based on the results, the stiffness and mass laws can describe the sound insulation property of the composites PVC/mica, and the increase of the amount of mica in the composite influenced the sound transmission loss and resonance frequency.

Liu et al. [48] adopted amino-silane modified microcrystalline muscovite as a filler in PVC matrix, performing acoustic analysis of the composites. The presence of filler improved the processing flowability, which allowed the use of higher amounts of filler and reduced the cost of the polymer matrix.

In another example, Zhang et al. [97] used mica to modify PVC/α-methylstyrene-acrylonitrile copolymer (α -MSAN)/chlorinated polyethylene (CPE) blend. By using mica, the authors obtained improvements in the thermal conductivity, flexural modulus, and overall thermal stability. The authors also found that mica has a superior interfacial interaction with the polymeric matrix. Likewise, some authors [97] examined the thermal conductivity, flexural modulus, and thermal stability of blends PVC/α-methylstyrene–acrylonitrile copolymer/chlorinated polyethylene modified by mica. Mica proved to be efficient in improving the properties analyzed. According to the theoretical modeling results, mica has a more effective potential to increase the thermal conductivity and better interfacial interaction with the polymeric matrix.

Jamel et al. [34] tried to increase the dimensional stability and mechanical properties of rigid PVC foam by adding mica. The authors found that the presence of mica improved the mechanical properties and dimensional stability of the PVC composites.

Maebayashi et al. [49] measured the velocities of longitudinal, transversal, and leaky surface skimming compressional waves of PVC/mica composites. As a result, as the concentration of mica increased, the longitudinal and transversal velocities increased.

In a different purpose, some authors [27] observed the thermal behavior and the aging effect on the ion-selective conduction of the membrane PVC/mica. The results revealed that, as the aging and the temperature increase, the ionic conduction is improved.

Based on the investigated literature, authors seem to be focused on the analysis of the dielectric [78], electrical [20, 21], mechanical [20, 21, 34, 41], and sound insulation [78, 83, 89] properties. The results are obtained by both experimental [83, 97] and theoretical [83, 97] experiments.

In the particular case of mica-filled PVC composites, it could not be a deeper analysis of the authors' keywords, as the number of occurrences of them is small.

4 Discussion and Final Considerations

Even though both are composites, the research areas of mica-filled PVC composites and glass fiber-filled PVC composites are very distinct.

First, what draws attention is the number of publications obtained as a result in the Scopus database. For glass fiber-filled PVC composites (Scopus search by using the words "composite*" AND "PVC" AND "glass fiber*"), the result was 192 documents in English, being 189 articles and 3 reviews. Whereas, for mica-filled PVC composites (Scopus search by using the words “composite*” AND “PVC” AND “mica”), the result was only 21 documents in English, being 20 articles and 1 review. From a particular point of view, the obtained results from the searches in the Scopus database show that there is a great opportunity for growth in both areas.

By analyzing the word cloud, an overview of the analyzed research area can be visualized. In the case of glass fiber-filled PVC composites, some of the most popular authors’ keywords are ‘PVC foam’, ‘sandwich composite*’, and ‘mechanical propert*’. These keywords have a huge magnitude in the literature concerning glass fiber-filled PVC composites and can be considered hotspots. They reveal the main application of the PVC concerning glass fiber-filled PVC composites in the literature: PVC in the form of foam is applicated as a core in sandwich composites (in which glass fiber is used as a property modifier), having as main application the marine branch. Concerning mica-filled PVC composites, some of the most popular authors’ keywords are ‘composite’ and ‘interface’. So, in this case, mica and PVC are used in the production of composites (PVC as matrix phase and mica as filler), including foams as glass fiber-filled PVC, in which the interface between these phases is very relevant. The literature on the subject seems to be focused on examining the influence of mica characteristics (shape, aspect ratio, concentration, surface modification, etc.) on a given property of the composite, such as sound insulation property, mechanical properties, thermal and thermal degradation properties, among others aforementioned in the last section.

While for mica-filled PVC composites the literature analyzes a wide range of different properties of composites, in the case of glass fiber-filled PVC composites the literature analyzes the mechanical properties, in general, more often. Researchers in the two areas use both experimental and numerical investigations, finding in many cases good correlations between them.

As processing methods used, in the case of glass fiber-filled PVC composites it seems that vacuum-assisted resin infusion process is more largely used by literature. In the case of mica-filled PVC, literature seems to adopt processing ways more “conventional” for polymers in the melt state such as extrusion and injection.

Concluding, with this brief discussion and comparison between glass fiber-filled PVC composites and mica-filled PVC composites it could be observed the differences and similarities between the two areas, making it clear that the differences are much greater.

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Metal Carbonate Reinforced PVC Composites and Nanocomposites

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Abstract At first glance, this chapter considers the effects of nano and micro-sized metal carbonate reinforced Polyvinyl chloride (PVC) composites. Initially, this chapter discusses the typical manufacturing processes of metal carbonate/PVC composites; then, the effect of micro and nano-sized metal carbonate was investigated on the mechanical and rheological properties of composites. After that, surface modification and its applications to fire retardancy were considered. Finally, the influence of weathering on composites is discussed.

1 Introduction

Polyvinyl chloride (PVC) is a synthetic polymer that is cost-effective and chemically resistant to solvents, bases, and acids. It also has adequate mechanical and thermal stability, high stiffness, and excellent processability [1]. Fillers have been used in PVC matrix to modify and ameliorate the mechanical and thermal properties. Inorganic fillers, such as aluminum oxide, montmorillonite, metal carbonate, silica, and calcium sulfate, are utilized to improve the mechanical properties of the polymer, like stiffness, toughness, and thermal stability. The mechanical characteristics of composites are significantly influenced by the homogeneous dispersion of fillers and the interfacial contact between fillers and polymer matrix. Metal carbonates are inorganic compounds consisting of a metal cation and a carbonate anion; their reaction products with acid are salt, water, and carbon dioxide. The most often utilized filler in PVC composites among metal carbonates is calcium carbonate.

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The majority of studies investigate how calcium carbonate affects PVC composites since it is cheaper than other carbonates. $MgCO_3$, $BaCO_3$, $LiCO_3$, and other metal carbonates are utilized as fire-retardant materials in PVC.

This chapter includes seven sections as follows: Sect. 2 allocates to the manufacturing processes of PVC composites, Sect. 3 talks about the general impact of fillers, mainly $CaCO_3$, on the characteristics of polymer matrix (PVC), in Sect. 4 the effect of particles size and shape of fillers in the characteristics of the prior section is discussed, Sect. 5 is related to surface modification of fillers used in PVC matrix and it's impacts on the properties of composites, Sect. 6 belongs to the fire retardancy effects of metal carbonates particles in PVC matrix, and the last Sect. 7 is attended the weathering effect of metal carbonate fillers which were composited with PVC matrix.

2 Manufacturing Process

Solution blending, in situ polymerization, and melt blending are the three common addition methods for nanofillers that have all been used for PVC. By adding nanofiller to plastisols, another method can be achieved. With different degrees of effectiveness, the majority of studies have employed melt compounding to disperse nanofillers [2–5].

2.1 In Situ *Polymerization*

In situ polymerization procedures typically include dispersing nanomaterials in a neat monomer (or several monomers) or monomer solution; polymerization takes place in the vicinity of the dispersed particles. Numerous investigations on in situ polymerization techniques have shown that the resultant nanocomposites include covalent connections between the polymer matrix and nanomaterial. In situ polymerization, on the other hand, has been utilized to create noncovalent nanocomposites from diverse polymers such as PE, PMMA, and others [6].

2.2 Solution Blending

Solution blending is a technique that uses a solvent solution to dissolve the polymer or prepolymer and swell the nanofillers. Initially, a solvent, for instance: water, chloroform, or toluene is used to swell the nanofillers. When the polymer and nanofiller are combined in solution, the polymer chains intervene, pushing the solvent out of the nanofiller's interlayer. Then intercalated/exfoliated structure exists when the solvent is removed [7–9].

2.3 Melt Blending

One of the most appealing processes for creating polymer composites is melt blending. This process is environmentally friendly and appropriate for the mass manufacture of polymer composites. This method first begins by melting the polymer at a high temperature, followed by adding the filler under the shear. For thermoplastic polymers, in particular, this technology is the most adaptable and useful. Extrusion and injection molding are used to mechanically combine thermoplastic polymers with nanofiller at high temperatures. The polymer chains diffuse between the aggregated nanofillers during the melting and mixing process to create the nanocomposite [7].

3 General Impact of Filler

The form, concentration, size, agglomeration, surface features, and degree of dispersion of fillers all have an impact on the thermal and mechanical features of composites. The filler aspect ratio was shown to be highly linked to mechanical characteristics. In general, introducing inorganic nanoparticles to polymer matrix may greatly increase the mechanical performance of polymers [10]. As below, we discuss the effects of fillers on tensile strength, toughness, stiffness, thermal stability, and viscosity (during processing).

3.1 Tensile Strength

Composites' tensile strength is affected by the content of fillers and the interfacial adhesion between particles and polymers matrix. If the matrix and particles have poor interfacial adhesion, the cross-sectional area of the polymer that can tolerate load is reduced, and only a minute fraction of stress can be transmitted from the polymer matrix to the filler particles. The polymer's cross-sectional area that can tolerate load diminishes with the incorporation of the $CaCO_3$ particles, and just a minute fraction of stress could be transmitted from the polymer matrix to the fillers if the matrix and particles had weak interfacial adhesion. As a result, the tensile strength of nano-sized $CaCO_3$/PVC composites diminish as the nano-sized $CaCO_3$ particle concentration increases. The interfacial adhesion has a great impact on controlling the composites' tensile strength reduction. Stronger tensile strength is obtained as a result of greater stress transfer from the polymer matrix to the filler particles due to stronger interfacial adhesion [11].

3.2 Toughness

The micro-crack mechanism is the most common toughening method for polymer composites filled with fillers. Cracks are formed in the PVC matrix when $CaCO_3$ particles are distributed in the polymer matrix and function as concentrated stress zones. When cracks reach the surface of another particle, they can be effectively stopped. The toughness of composites would be increased if a substantial number of cracks were produced in the composite; each one absorbed a portion of the impact energy. The interfacial adhesion between filler particles and polymer matrix has a crucial role in increasing the composites' impact strength, and only proper interfacial adhesive would successfully toughen the PVC matrix. For example, micro-cracks may propagate along interfaces between PVC and nano-sized $CaCO_3$ particles if the interfacial adhesion is insufficient, and the capacity of inorganic filler particles to stop crack growth will be diminished. Micro-cracks, on the other hand, are prevented by strong interfacial adhesion. As a result, nano-sized $CaCO_3$ particles can only toughen PVC composite when they have sufficient interfacial interaction with the polymer matrix. The crack pinning process or the crack deflection theory can be used to explain toughening composites by micron-sized inorganic particles. However, applying similar arguments to nano-sized particles does not imply an increase in PVC toughness because the nanoparticles might be too tiny to react with the growing crack effectively [12].

3.3 Stiffness

The influence of filler particle volume fraction (ϕ_P) on yield stress $\sigma_{c,y}$ of a composite filled with particles can be calculated using Eq. (1).

$$\sigma_{c,y} = \sigma_{m,y}(1 - \phi_P)exp\frac{\beta\phi_P}{1 + 2.5\phi_P} \tag{1}$$

where $\sigma_{m,y}$ denotes the matrix yield stress, and β denotes an interfacial parameter defining the matrix-nanoparticle interaction. Composites with high volume fractions of particles have a lower β value, which translates to a lower tensile strength.

For rigid micron-sized particles, an alternative relationship (2) is used

$$\sigma_{c,y} = \sigma_{m,y}\left(1 - 1.21\phi_P{}^{2/3}\right) \tag{2}$$

Because nano-sized particles have a greater surface area than micro-sized particles, they are thought to enhance better particle–matrix phase bonding, requiring more stress to generate cavities.

Also, the iso-stress rule of mixtures Eq. (3) can be used to explain the rise in elasticity modulus, E, and storage properties of the composite filled with rigid inorganic filler particles:

$$E = \left(\frac{E_P E_m}{(1 - \phi_P)E_P + \phi_P E_m} \right) \tag{3}$$

The p and m denote the particle phase and polymer matrix phases, respectively, and ϕ denotes the volume fraction.

However, the rule of mixture does not address the particle size distribution, making it more appropriate for laminate constructions than composites reinforced with particles, elasticity modulus of composites based on shape and packing fraction of fillers can be calculated by Nielsen's modified Kerner's formula which is shown in Eq. (4)

$$E_c = E_m \left(\frac{1 + AB\phi_P}{1 - B\psi\phi_P} \right) \tag{10-4}$$

A and B are constants determined by filler phase geometry and the matrix's Poisson's ratio, and relative stiffness of the particles and the matrix, respectively, and ψ is a constant determined by the filler's packing fraction [11].

3.4 Thermal Stability

Thermal decomposition of PVC happens in two stages, followed by mass loss when it is under nitrogen. A dehydrochlorination sequential reaction is carried out in the initial stage of the process. This stage includes three steps: initiation, growth, and termination. In the initiation stage, the process is started by structural flaws in the PVC backbone, like tertiary and allylic chlorides generated in the polymerization stage, which result in hydrogen chloride (HCl) release and double bond formation; in the propagation stage, these groups quickly elongate into allylic chains and polyene sequences. Both the initiation and growth processes include ion pairs or a quasi-ionic concerted mechanism. The mechanism for the last stage has yet to be identified. The autocatalysis of the dehydrochlorination reaction, which most likely happens through a radical-cation mechanism, is a significant feature of the PVC's thermal degradation; when HCl and polyenes concentrations reach a particular point, they react to generate polyenyl cation radicals, resulting in autocatalysis [13].

Many attempts have been undertaken to address structural faults caused during the polymerization process to increase the thermal stability of PVC. Even though eliminating these abnormalities by changes in the polymerization process or particular treatments of the matrix might increase the thermal durability of PVC, decomposition takes place at low temperatures from monomers, necessitating the employment of specific stabilizers. As a result, PVC thermal stability may be improved in two ways: by increasing barrier qualities or by trapping HCl. To restrict or postpone the dehydrochlorination process, metallic carboxylates and other compounds like basic, organotin, epoxy and completely organic chemicals are some of the most frequent additives employed. Nonetheless, some of them are harmful and contribute to environmental issues since the majority of them leave toxic wastes after their decomposition. Recently, numerous alternatives have been investigated, such as binary blends, including poly (vinyl butyral) (PVB), poly(methyl methacrylate butadiene styrene), poly(acrylonitrile butadiene styrene), poly(methyl methacrylate) (PMMA), and copolymers of poly(vinyl chloride-co-vinyl acetate), or insertion of nano charges such as layered silicates or $CaCO_3$ [13].

During processing, the low thermal stability of PVC polymer is the main factor that leads to degradation. Dehydrochlorination forms conjugated double bonds in the backbone of PVC polymer chains and cause thermal degradation during processing. This degradation decreases mechanical properties and changes the color of PVC. Different heat stabilizers have been employed to solve the issue of PVC thermal stability. The majority of stabilizers are lead-based, organotin chemicals, and mixed metal soaps. In this process, calcium carbonate, metal hydroxides, and metal oxide absorb HCL that liberate from PVC during thermal degradation; as a result, HCL is not available for autocatalytic dehydrochlorination; therefore, thermal degradation of PVC polymer decreases [14].

Layered double hydroxides (LDH), inorganic and non-toxic heat stabilizers, can use as HCL scavenging to improve PVC thermal stability. The cooperative effect of micro and nano-sized $CaCO_3$ and LDH on the thermal stability of PVC was investigated. The Brabender plastograph was used to make PVC composites, and the PVC samples were fabricated by a compressive molding device. LDH with nano-sized $CaCO_3$ showed better synergism than LDH with micro-sized $CaCO_3$ on the thermal stability of PVC [14]. In using the solution blending approach, Liu et al. investigated the thermal stability of $CaCO_3$/PVC composites incorporated with micro/nanosized $CaCO_3$. The results illustrated that the inclusion of $CaCO_3$ fillers increased the polymer's thermal stability. It was also observed that the nano-sized $CaCO_3$ fillers gave superior thermal stability to the micro-sized $CaCO_3$ particles, even when used in smaller amounts. The $CaCO_3$ fillers' stabilizing effect is due to HCl absorption and the better impact of the nano-sized $CaCO_3$ filler as a result of a larger surface area [15].

In 2012 Tuen et al.'s study, talc and uncoated ground $CaCO_3$ and the hybrid filler consisting of both were incorporated with the PVC matrix; the result showed that adding talc and $CaCO_3$ to PVC did not considerably increase its thermal stability, incorporating fillers had no significant impact on the beginning and range of thermal degradation onset and decomposition temperatures of PVC hybrid composites, but fusing time of the PVC was dramatically enhanced by talc and calcium carbonate [16].

Some research reported that micro-sized inorganic filler could reduce the thermal stability of the composites. According to Chen et al. the presence of micro-sized $CaCO_3$ particles impeded the fusion process of the PVC molecules, resulting in a reduction in PVC thermal stability. They also came to the conclusion that $CaCO_3$ particles size had a more significant influence on the commencement of thermal degradation than $CaCO_3$ addition. Based on findings, the onset temperature (T_{onset}) of the micro-sized $CaCO_3$/rigid PVC composite was 7.5ºC, lesser than pure PVC. The glass transition temperature $\left(T_g\right)$ of the micro-sized $CaCO_3$/rigid PVC composite, meanwhile, was slightly identical to the pure PVC. The nano-sized $CaCO_3$/rigid PVC composite T_{onset} and T_g, however, raised by up to 30 and 4.4 percent, respectively. Also, the fusing time of PVC was dramatically slowed by the addition of nano or micro-sized $CaCO_3$. The increased fusing time shows that the composites' PVC particles required more heat energy to fuse than without the inclusion of filler [17].

3.5 Viscosity

In polymer composites, there are several variables that might impact viscosity. Wu et al. investigated the possibility of toughening PVC that has been loaded with nano-sized $CaCO_3$ particles. The research showed that adding nano-sized $CaCO_3$ particles to the PVC system increased its viscosity. They also found that when the amount of nano-sized $CaCO_3$ in PVC/$CaCO_3$ nanocomposites decrease, the viscosity rises. They explained this outcome by claiming that adding a stiff filler to PVC decreased its flowability and made it more difficult for its molecular chains to disentangle [18, 19]. In other work, the viscosity of $CaCO_3$/PVC nanocomposites was diminished using in situ polymerization with spherical nanoparticles, as reported by Xie et al. They claimed that the spherical nanoparticles dispersed equally between the extended PVC chains acted as "ball bearings," lowering interlayer contact and thereby lowering the viscosity of nanocomposites made of PVC/$CaCO_3$ [20].

3.6 Particle Size and Shape Effect

In nanocomposites, particle size affects mechanical characteristics dramatically because the interparticle distance and interfacial area fall and rise correspondingly when particle size decreases at constant particle content [21]. For PVC, the most frequent filler is calcium carbonate [2], as well as using magnesium carbonate [22].

3.7 Effect of Particles Size and Shape of $MgCO_3$

Synthetic $MgCO_3$ fillers often have well-managed morphologies, and the size of particles has a substantial impact on dispersion, flame-retardant efficacy, and thermal properties of inorganic–organic composites. It is necessary to note that the interfacial interaction and the shape of particles have a significant impact on boosting the mechanical behaviors of PVC composites. Among four various morphologies (cubic, spherical, corncob, and block shape), which are treated in PVC matrix, the cube-like morphology with a mean particle size of 4 mm showed the best interaction and raised the impact strength, yield strength, breaking, and flexural strength of $MgCO_3$/PVC composite at about 77.4%, 24.4%, 25.3%, and 4.5%, respectively compared to pristine PVC due to the fine particle size that caused good dispersity to result in stronger interfacial interaction and it takes a lot of energy to debond filler from PVC matrix [23]. Lu et al., in another study, considered the effect of different morphologies like hydrangea, dumbbell, and cubic shapes on nanostructured anhydrous $MgCO_3$ fillers in PVC/$MgCO_3$ composites. The findings revealed that directly integrating a minute fraction of $MgCO_3$ into the PVC matrix will considerably strengthen and toughen the PVC matrix and significantly increased the thermal stability of PVC composites. As a consequence, the impact strength of PVC composite with just 4wt% dumbbell-like morphology of $MgCO_3$ was 11.5 kJ/m^2, an increase of 117% over pristine PVC, whereas the flexural modulus of composite with 4 wt% hydrangea-like $MgCO_3$/ PVC is 5771 MPa, an increase of 106%, and also for the same compound, 269 °C was reported the first degradation temperature, 12 °C over pristine PVC [22].

3.8 Effect of Particles Size and Shape of $CaCO_3$

Due to weak particle–polymer interaction, micro-sized $CaCO_3$ has a finite influence on the properties improvement of PVC composites. Nanocomposites, on the other hand, have exceptional characteristics. The small size of particles, high surface energy, huge interfacial area, and nanoparticles are responsible for this condition, which results in significant interfacial adhesion. The nano-sized $CaCO_3$ exhibited a greater toughening impact on the PVC in contrast to the micro-sized $CaCO_3$. Conversely, nanoparticles have a great propensity to agglomeration, and the impact of agglomerates on composite characteristics is adverse. $CaCO_3$ nanoparticles were more likely to agglomerate than their micro-sized counterparts, and the number of agglomerates escalated as the particle concentration rose [24]. Depending on the particle size of filler, the mechanical characteristics of composites might vary. Submicron $CaCO_3$ may be utilized to modify impacts; however, too coarse $CaCO_3$ can reduce the impact performance [25]. Sun et al. [26] found that the tensile and impact strength of $CaCO_3$/PVC composites improved dramatically as the particle size of $CaCO_3$ decreased, a finding attributable to greater interfacial interaction between fillers and the PVC matrix. A study by Xie et al. found that nano-sized $CaCO_3$ particles simultaneously could be strengthening and toughening the PVC matrix. $CaCO_3$ nanoparticles operated as stress concentrators in the study, causing interface debonding, as well as matrix deformation [20].

In some content, particle size may impact fusion processing and serves as a processing assist. The effects of particle size of $CaCO_3$ on the fusion of rigid PVC composites were fabricated by Haake torque rheometer was studied by Ari et al. In this study, rising in the number of particles in a mixture with the identical volume by lowering the size of particles increased the frictional forces, resulted in greater fusion torque as well as a reduction in fusion time and temperature [18].

Precipitated calcium carbonate (PCC) is synthetic calcium carbonate with a very small particle size, excellent purity, and finite-size distribution. Ultra-fine PCC grades typically have initial particle sizes of 50–70 nm, agglomerated to clusters with a diameter of 0.7–2.0 μm. The surface coating hydrophobics the PCC particles, lowering surface energy and facilitating polymer mixing, e.g., stearic acid is frequently used to coat PCC particles at a 1–2% concentration. Furthermore, the tiny PCC particles, which are smaller than primary PVC particles, may cause interparticle friction in PVC, raising shear and facilitating fusion. As a result, PCC may use as a processing aid in PVC composites [27].

50 nm PCC has been studied for its influence on the mechanical and fusion behavior of Ca/Zn stabilized PVC. The findings show that ultrafine PCC may significantly increase single-notch impact strengths. There was also a considerable rise in fusion stages, but no influence on the samples' tensile strength [27].

4 Surface Modification

The surface of most particle fillers, including calcium carbonate, is not suitable for optimizing the process and functionalities of the polymer-based composites in which they are employed. The processability and performance of composites are extremely affected by the interface between calcium carbonate and the polymer matrix. They have inadequate interaction with the polymer surface to address this issue; hence surface modification is typically performed to increase wetting ability and interaction with the polymer surface. Calcium carbonate Surface modification can ameliorate tensile strength, impact strength, and toughness of composite in comparison with unmodified calcium carbonate composites. Also, a rise in Glass Transition Temperature (Tg) has been seen by using well-coated $CaCO_3$ in $CaCO_3$/PVC composites. In addition to improving mechanical characteristics, composites' processing behavior and characteristics are greatly influenced by the interaction of the interface of calcium carbonate particles and the polymer matrix. The interplay between calcium carbonate and the polymer is influenced by two factors: wetting and adhesion. The efficiency with which the polymer wets its surface determines how quickly they may be interacted and be dispersed. However, in nano-scale $CaCO_3$, nanoparticles have a significant propensity to agglomerate due to the vast surface area and energy. Because of the agglomerates, dispersing the nanosized particles in the matrix might be problematic. In particle–particle interactions, Van der Waals and electrostatic forces play an important role in attraction and repulsion. Reduced particle size decrease repellent electrostatic forces much more than Van der Waals does; thus, the attraction takes over at the interface and leads to agglomeration of the particles. To solve this problem, most filler producers treat the particle surface with inexpensive surfactants like stearic acid to increase filler dispersion and integration by decreasing interparticle interaction and enhancing the interaction of particles-matrix. Furthermore, particle dispersion is improved by surface modification because they make the particle surfaces hydrophobic and enable water to be eliminated from hydration and voids, leading to deagglomeration. As a result, calcium carbonate being well dispersed and interacting with polymer matrix minimizes the differences between calcium carbonate and PVC characteristics. So, the composite characteristics will improve significantly. In addition to mechanical and end-use properties improvements, applying surface treatment can add other beneficial effects on calcium carbonate filler in PVC composites, including decreasing plasticizers adsorption. Moreover, using surface modification may influence filler handling characteristics, including bulk density, particle flowing, and dustiness. However, increasing the price of fillers by surface treatment is a disadvantage of surface modification of calcium carbonate, making composite producers not use this treatment for any PVC/$CaCO_3$ application [28].

Surface modification of calcium carbonate could be applied before the mixing stage of calcium carbonate with polymer or as an additive introducing the mixing stage. It is generally done by reacting an appropriate organic modifier with the filler surface chemically. Depending on which organic group is applied, there are two types of surface modifiers: coupling and non-coupling. Both types interact well with the filler surface, whereas just the coupling type has a chemical interaction with the matrix [28].

4.1 Silane Coupling Agent

The most frequent non-coupling treatment is fatty acids, while the organo-silanes are the most ubiquitous coupling treatment, but organo-silanes interact with fillers that have oxide or hydroxide groups. So, this type of coupling agent does not usually work for calcium carbonate composites [28]. Based on a report by Jiang et al., pretreatment of ground calcium carbonate (GCC) particles using NaOH could enhance development of hydroxide ions on their surfaces, which facilitated the graft of aminopropyltrimethoxysilane (APS) on GCC surfaces and improved the interfacial interaction between fillers and PVC matrix [29]. In another report by Jazi et al., by treating 3-mercaptopropyl trimethoxysilane (MPTS) and polymethylhydrogensiloxane (PMHS) on nano and micro-size calcium carbonate, a monolayer of coverage was founded on the surface of calcium carbonate and make it hydrophobic. Then PVC and treated $CaCO_3$ with various weight fractions of micro and nano-sized particles were fabricated using the Brabender torque rheometer in the melt blended method; because of the interfacial connection between the filler and the matrix. The result was the enhancement of mechanical characteristics over pure PVC [30].

4.2 Titanate Coupling Agent

Despite of organo-silanes, coupling agents with titanate functional groups interact properly with surface protons through solvolysis or coordination without the requirement for water condensation, forming a monomolecular layer on the organic surface capable of reacting with an organic polymer. Furthermore, the titanate coupling agents may be used as plasticizers, allowing for greater filler loadings and catalysts for various polymer processes. Also, in situ coupling is a typical technique for pretreating nano-sized calcium carbonate with a coupling agent that is utilized in industry. In this approach, polymer, coupling agent, and filler are combined before melt compounding. Some alternate methods for treating nano-sized calcium carbonate with titanate, including spraying it directly onto the particles or immersing them in a solution that contains the coupling agent, have also been approved. This procedure, however, takes more time and raises the total cost due to the additional processing [31].

With an in-situ approach, nano-sized $CaCO_3$ was treated with a titanate coupling agent and filled in a PVC matrix by varying volume fractions; composites were made with a compression molding and two-roll mill. The introduction of nano-sized $CaCO_3$ particles reduced the tensile strength somewhat but enhanced the composite's impact strength, storage modulus, and fracture toughness. When titanate coupling agent was used, the polymer matrix became softer, and its modulus decreased. In Chetanachan et al.'s study, the impact strength and weathering improvement of an 80 nm $CaCO_3$/PVC composite treated with a titanate coupling agent were superior to those of a 40 nm $CaCO_3$/PVC composite treated with fatty acid. Improved dispersion of nano-$CaCO_3$ was achieved by using the titanate coupling agent, which inhibited calcium carbonate aggregation and gave excellent adherence to PVC, resulting in a notable increase in strength and weathering improvement [32].

4.3 Non-coupling Treatment

The most frequent and well-known surface modification of $CaCO_3$ is an adjustment of fatty acids. They have known as "fatty acids" because of their appearance in fats resources. Their long chain of saturated aliphatic, with even carbon numbers from 4 to 28, is the reason they have known as fats, and they are named "acids" because of their carboxylic acid group in their structure. Their acid group can interact with the basic surface of calcium carbonate and form a slim layer of calcium stearate at the surface of calcium carbonate particles. The most known fatty acid is stearic acid which has 18 carbons in its structure. The primary recourse of these materials is herbal oils, but separating components in high purity by their carbon number is expensive, and purification is done by far that most of the blend would be made of fatty acids with close carbon number. Also, producing them in a chemical way is a more expensive route, and it is not common in the industry. The blend frequently used for surface modification of calcium carbonate is often known as "stearic acid." Although, the purity of stearic acid may not exceed half of the blend [33].

In industry, the term "coated calcium carbonate" usually refers to the calcium carbonate surface modified by fatty acids. Fatty acids are generally precoated onto calcium carbonate using one of two coating methods: dry blending or wet coating. The dry blending is commonly utilized for producing "coated GCC, while the wet coating is often used in PCC." In the wet coating technique, a solution containing water-soluble salt of fatty acid is mixed with an aqueous slurry of calcium carbonate. If an alkali metal salt of the acid is used (e.g., sodium stearate), the residue of its generated and unreacted salts must be eliminated from the solution. Due to the low solubility of calcium carbonate in water, despite alkali metal salts, the elimination could be done by washing and filtering the solution. By using ammonium stearate, due to instability of ammonium group elevated temperature and mixing and its decomposition to ammonia gas, the washing and filtering stages could be eliminated, and ammonia gas could be used absorbed for regenerating ammonium stearate [33]. In the dry coating method, fatty acid and calcium carbonate are entered in a high-shear mixer. Since plenty of fatty acids are solids that must be melted to distribute and react with particle surface, the shear force of the mixer may provide sufficient heat in certain circumstances; perhaps additional heating may also be required to proceed with the reaction. The usage of fatty acid is between 0.5–1.5wt% of calcium carbonate, which depends on the active surface of the filler [34].

In the coating process, there would be three chemical components as follow:

1. Calcium mono-stearate is produced by not completing the reaction of stearic acid and calcium carbonate. This component is attached to the filler and enhances the filler surface hydrophobicity. It would be the main product of the process and make the calcium carbonate surface modified.
2. Unreacted stearic acids, some of them are trapped between calcium mono-stearate chains, and some of them are in bulk, known as an impurity.
3. The product of the complete reaction of calcium carbonate and stearic acid, calcium stearate ($CaSt_2$), is the undesired product in this process because it consumes the stearic acid and is not attached to the filler. Although this substrate is used as a processing aid in the plastic industry, in the coating process, it precipitates in bulk [33].

In a surface modification, the less unreacted stearic acids and calcium stearate substrates make the process more efficient [33].

5 Fire Retardancy

Pure PVC has a comparatively enormous chlorine content (56.7wt%), making it more immune to burning than other organic polymers. Because the emission of halogen gas during burning leads to a 'flame poisoning effect,' or the deceleration of the free radical chain reactions in the flame, the release of HCl by the decomposing PVC prevents flame combustion. HCl concentrations are reduced quickly, unlike carbon monoxide, since it is easily absorbed on material surfaces. In addition, burning of PVC produces an isotropic carbon char residue which aids in flame retardancy. With these features, when the flame or heat source is extinguished, PVC will stop burning. Whereas traditional plasticizers used in the manufacturing of plasticized PVC, like diisodecylphthalate (DIDP), dioctylphthalate (DOP), and polyester plasticizer (PEP), diminish the excellent fire resistance feature of pure PVC. These additives also enhance the combustion process, resulting in a massive volume of thick, black smoke. To address these issues, smoke suppressants and flame retardants could be added to PVC systems to lessen the risk of fire. Many additives have already been introduced to diminish the smoke originating from the combustion and ameliorate the fire resistance feature. Metal carbonates like $CaCO_3$, $MgCO_3$, and $ZnCO_3$ can be used as one of these additives [35].

Generally, the fire-retardant qualities of hydroxides and group II or III carbonates could be divided into three parts.

1. Endothermic degradation of fillers, absorbing heat and maintaining the surrounding polymer at a lower temperature.
2. By providing inert diluent gases such as carbon dioxide and water, fillers decrease free radicals' concentration which is responsible for self-sustaining flame, thus extinguishing the fire.
3. An inert layer forms on the surface of the decomposing polymer, protecting it from incoming radiation and serving as a shield against oxygen entering the fuel, flammable pyrolysis products entering the gas phase, and radiant heat entering the polymer.

According to the literature review, the metal carbonates $CaCO_3$, $MgCO_3$, $ZnCO_3$, $BaCO_3$, and Li_2CO_3 listed below have been utilized to reinforce PVC as a fire-retardant [36].

5.1 $CaCO_3$ *as an Additive*

$CaCO_3$ Is a popular PVC additive that makes the polymer easier to produce and reduces costs. It serves as an HCl absorber during PVC burning to create calcium chloride ($CaCl_2$), which wraps the peripheral of the composite materials, preventing oxygen from reacting with the PVC matrix and resulting in a high limiting oxygen index (LOI) for combustion; although, in some researches reported that it has little or no flame retardance [35]. Much research has been conducted to find a flame retardant with extremely effective flame retardance capabilities. The results demonstrate that using filler powders, including an inorganic filler particle with a coating of a tin compound on the particles, improves flame retardant properties [36]. Xu et al. studied semi-rigid PVC treated with a mixture of $SnO_2/CaCO_3$ and $CaCO_3$ coated with SnO_2, resulted that SnO_2-coated $CaCO_3$ had higher flame retardant and smoke suppression qualities than SnO_2 and the mixture of $SnO_2/CaCO_3$. The char of semi-rigid PVC treated with SnO_2-coated $CaCO_3$ had a more compact and nonflammable morphology than the char treated with the combination of $SnO_2/CaCO_3$ [37].

Semi-rigid PVC incorporated with $CaCO_3$, calcium carbonate coated with zinc hydroxystannate, and calcium carbonate coated with zinc stannate have been examined for flame-retardant, and smoke suppression qualities by Xu et al. According to the findings, the semi-rigid PVC treated with zinc hydroxystannate-coated calcium carbonate or zinc stannate-coated calcium carbonate has a greater limiting oxygen index and anaerobic char output. There are two ways to explain it:

1. Zinc hydroxystannate and zinc stannate disperses on the surface of $CaCO_3$, catalyze dehydrochlorination, and advance early cross-linking, resulting in quick charring, primarily due to the Lewis acid mechanism in the condensed phase.
2. The compact structure of the char of calcium carbonate coated with zinc hydroxystannate or zinc stannate can prevent heat and combustion gases from entering the PVC bulk [37].

Soft PVC treated with the $CaCO_3$ coated with hydroxystannates had a better flame retardant effect among magnesium hydroxystannate [$MgSn(OH)_6$], zinc hydroxystannate (ZHS), strontium hydroxystannate [$SrSn(OH)_6$], calcium carbonate ($CaCO_3$), ZHS–$MgSn(OH)_6$, $CaCO_3$ coated with $MgSn(OH)_6$, ZHS–$SrSn(OH)_6$, $CaCO_3$ coated with $SrSn(OH)_6$, and ZHS–$MgSn(OH)_6$-coated because of the better dispersion of the hydroxystannates on the surface of the $CaCO_3$ [38].

5.2 $MgCO_3$ *as an Additive*

As a novel inorganic flame retardant, $MgCO_3$ has earned a lot of interest. It has the benefits of high heat absorption and fire extinguishing capability without emitting CO_2 and is non-toxic compared to traditional flame retardants [38].

Basic and hydrated magnesium carbonate accounts for most of the magnesium carbonate on the market today. Furthermore, impurities such as Fe^{2+} and Mn^{2+} are constantly present in various amounts in natural magnesite. There are several hydrated double salts of magnesium hydroxide ($Mg(OH)_2$) and $MgCO_3$ that have been used as flame retardants in the past. Hydromagnesite ($4\ MgCO_3.\ Mg(OH)_2.\ 4\ H_2O$) is the only one of any relevance today, and it is used in both synthetic and mineral forms [39]. The first application of hydromagnesite as a flame retardant was mentioned in a patent issued to Bakelite Xylonite Limited in 1967 [40]. Initially, the synthetic version piqued people's imagination, and it was commercially produced in the United States. This shape provides a large specific surface area and absorbs a lot of oil; hence it can't be used at extremely high loadings. As a result, it is mostly used as a smoke suppressor in PVC formulations. Mineral resources have been excavated and utilized in recent years, mostly in Turkey and Greece. These deposits contain a mixture of hydromagnesite and another mineral (huntite $MgCO_3.\ CaCO_3$); the resulting blends are used as flame retardants [39].

A synergistic flame-retardant effect of flexible PVC treated with the combination of magnesium carbonate ($MgCO_3$) and $2\,ZnCO_3 \cdot 3ZnO \cdot 4\,H_2O$ (AZC) was identified by Qu et al. The continuous and dense structure of the char produced in PVC treated with $MgCO_3$ and AZC may be employed as a barrier to prevent the volatilization of flammable gases and the heat transfer to the PVC matrix which improves flame retardancy [41].

5.3 $ZnCO_3$*As an Additive*

In the industry, antimony trioxide (Sb_2O_3) is a conventional flame retardant for flexible PVC. Because of the synergistic interaction between halogenated compounds and antimony trioxide, it provides good flame retardancy to halogen-containing polymers like PVC. Antimony, on the other hand, is a poisonous substance that causes considerable damage to human health, and antimony compounds emit toxic or irritating gases when burned. More studies are focusing on the synergy between inorganic zinc compounds and Sb_2O_3, with the goal of partially replacing Sb_2O_3 while maintaining flame retardancy [42].

There are multiple processes involved in making zinc carbonate hydroxide [$Zn(OH)_2$. x $ZnCO_3$]. Nevertheless, due to the presence of hydroxyl, its decomposition temperature began at around 150 °C, which is lower than the processing temperature for flexible PVC (170 ºC) [42].

A hydrothermal process using zinc nitrite and urea as starting ingredients was used to produce nanometric zinc carbonate powder and used in a flexible PVC composite blend by Pan et al. The findings showed that nano $ZnCO_3$ was an effective flame retardant for flexible PVC. Also, the flame-retardant efficacy of flexible PVC was significantly increased by mixing with Sb_2O_3. Moreover, the flame retardant Sb_2O_3/$ZnCO_3$ with a weight ratio of 1:3 had the maximum efficiency, with a limiting oxygen index (LOI) rising from 25 to 36.7% [42].

5.4 $BaCO_3$ *as an Additive*

Barium carbonate ($BaCO_3$), like calcium carbonate and magnesium carbonate, are members of the IIA group of metal carbonates and zinc hydroxystannate (ZHS) or Zinc Stannate (ZS), coated this group of metal carbonates, exhibited significant flame-retardancy in PVC. Zinc hydroxystannate coated one-dimensional dendritic fibrillar barium carbonate (ZHS/$BaCO_{3-F}$) was prepared by ultrasonic-assisted technique at room temperature. Introducing one-dimensional structural materials into a polymer as filler might significantly boost the polymer's mechanical characteristics due to the high aspect ratios. Consequently, one-dimensional inorganic flame retardants have the potential to overcome the drawbacks of conventional inorganic flame retardants. The PVC sample was incorporated with 5 phr ZHS/$BaCO_{3-F}$ exhibited the most outstanding integrated characteristics like LOI and tensile strength. ZHS/$BaCO_{3-F}$ plays a vital function in the initial stage of PVC degradation, improving thermal degradation rate, thermal stability, and char residue. Furthermore, the HCl emitted by the thermal degradation of PVC could react with ZHS and $BaCO_{3-F}$, resulting in the generation of CO_2, H_2O, $BaCl_2$, $ZnCl_2$, Zn_2SnO_4, $SnCl_4$, and also reducing HCl release [43].

5.5 Li_2CO_3 *as an Additive*

According to a patent, Lithium-containing compounds, like lithium carbonate (Li_2CO_3) and lithium hydroxide (LiOH), are more effective than $CaCO_3$ in absorbing HCl. LiOH has too much alkalinity and is too hygroscopic to be utilized as a PVC filler, but Li_2CO_3 is generally stable in air, allowing it to be used at high loading. Using both $CaCO_3$ and Li_2CO_3 as a filler simultaneously could reduce HCl generation even more than using just one of them [44].

6 Weathering Effect

Moisture, mechanical stress, harsh environment, and ionizing radiation play key role in the deterioration of PVC. Also, weathering causes pure PVC to degrade by a free radical mechanism that begins with the absorption of enough energy to disrupt chemical bonds. Exposure to sunshine causes fast dehydrochlorination of PVC materials applied for outdoor uses; as a result of the production of conjugated polyene sequences and material discoloration cause PVC's mechanical properties decrease. Inorganic fillers like TiO_2, ZnO, and $CaCO_3$ fillers are often used as UV light screening agents in PVC. In conclusion, the inorganic fillers serve as a shield between the polymer and light source by either absorbing or reflecting UV radiation, so the polymer matrix is protected from the sun by an inorganic barrier that blocks UV radiation from entering the polymer. Additional factors that affect PVC resins' anti-aging characteristics are the dispersion of inorganic fillers inside the PVC matrix. Uniform dispersion of inorganic fillers in the PVC matrix allowed them to efficiently absorb or reflect UV light. Furthermore, many flaws in the PVC matrix are caused by the agglomerated inorganic fillers. The anti-aging properties of nanosized $CaCO_3$ and nano-sized $CaCO_3$ coated with macromolecular modifiers were evaluated by Liu et al., and the anti-aging effects of PVC were shown to be enhanced by nano-sized $CaCO_3$ particles. Moreover, the macromolecular modifier (MP) increased the compatibility of nano-sized $CaCO_3$ particles and PVC matrix, resulting in a more homogenized dispersion of fillers. Therefore, PVC/$CaCO_3$/MP composite was shown to have superior anti-aging qualities to $CaCO_3$/PVC composite [45].

Mechanical properties can be improved or diminished by exposure to heat and water in specific ways. The mechanical behaviors of $CaCO_3$/PVC were investigated by Guermazi et al. before and after exposure to the water. Five samples with different concentrations from 20wt% to 40wt% of $CaCO_3$ were provided, and all samples were exposed to water at different temperatures. However, the addition of $CaCO_3$ filler to the PVC matrix had only a little effect on water absorption; stiffness and thermal stability are enhanced, whereas elongation at break and tensile strength decreased. With adding fillers up to 35wt% of $CaCO_3$, flexural modulus and strength were increased, then dropped. As a result, regarding the influence of the filler, it can be concluded that careful choice of an appropriate quantity of fillers permits to gain of good functional qualities of composites. In the aging process, time and temperature straightly affect the properties of PVC composites. Most mechanical properties increase with increasing temperature from ambient to 70 °C, while they decrease at 90 °C. On the contrary, the elongation at break diminishes at 70 °C but rises at 90 °C [10].

7 Conclusion

Metal carbonates significantly impact the mechanical and thermal properties of PVC composites. Among them, calcium carbonate is the most typical carbonate utilized in the industry because it is much more cost-effective rather than the other metal carbonates and can diminish the cost of production. Adding metal carbonates to the PVC matrix improves mechanical properties like tensile strength, toughness, stiffness, and thermal properties. Metal carbonates, in some ways, modify the rheological properties of the composites. Metal carbonates' particle size and shapes play a crucial role in interfacial adhesion; consequently, nano-sized metal carbonates show better characteristics than micro-sized metal carbonates. Metal carbonates like $CaCO_3$, $MgCO_3$, and $ZnCO_3$ can be used as a smoke suppressant agent and enhance the fire retardancy effects of metal carbonates/PVC composites.

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POSS Reinforced PVC Nanocomposites

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Abstract Over the past few years, research into polymers containing polyhedral oligomeric silsesquioxane (POSS) has grown, emphasizing new categories of polymer/polyhedral oligomeric silsesquioxane nanocomposite materials as well as previously unidentified uses. Due to the nano-scale size of polyhedral oligomeric silsesquioxane, these hybrids provide exceptional structural and functional qualities (strength, thermal stability, optical characteristics, low toxicity, and biocompatibility). This book chapter reviews the current development of polyhedral oligomeric silsesquioxane-reinforced poly(vinyl chloride) (PVC) systems. Chlorine atoms in PVC make it a more rigid and stiffer material by increasing the intermolecular attraction between polymer chains. These hybrid POSS nanofillers were found to be simple to incorporate into PVC and may be able to construct, reinforce, and stabilize materials more effectively than conventional ones. The key focus of this chapter was the morphological, thermal, mechanical, and rheological properties of the POSS reinforced PVC nanocomposites.

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1 Introduction

Poly(vinyl chloride) (PVC) is a commodity synthetic polymer produced in second large amounts after polyethylene (PE). PVC is a thermoplastic polymer and is one of the three (PE, polypropylene (PP), and PVC) most important polymers currently used in the worldwide. PVC is one of the most economical polymers to make and has an extensive range of properties so that it can be used for hundreds of applications. PVC is polar in nature, and it is resistant to nonpolar solvents. Also, it is a flame-retardant and self-extinguishing polymer. Pure PVC is a white, brittle solid (although different PVC variants are designed to be very flexible) and strong. PVC is obtained by polymerizing vinyl chloride (chloromethane) monomer units, as can be seen in Fig. 1 [1–3].

Vinyl chloride is a colorless, combustible, and narcotic gas created by synthesizing ethylene and chlorine from petroleum thermal cracking and membrane electrolysis of rock salt. The membrane process produces caustic soda and hydrogen, used as raw ingredients in various processes. In different polymerization procedures, stabilizers and plasticizers are added to the monomer vinyl chloride to produce PVC (radical or ionic).

Synthetic resin is made by reacting vinyl chloride and other monomers in agitated pressure vessels in the presence of catalysts and then converting the liquids and/or gases to solid resin. The reaction produces a significant amount of heat, and the vessel is cooled to remove this. The rate of reaction slows as the monomer is converted to polymer; hence, after an optimum reaction period, the unconverted residual monomer is removed from the reacting mass by heat and vacuum, and the resin (PVC) is recovered as a dry white powder, liquid latex, or solution. This polymerization reaction can occur in a pure monomer, a solution, a water-monomer emulsion, or a monomer water suspension. The type of polymerization process determines the type of recovery method and resin particles produced [4]. Vinyl chloride (VC) is produced via four processes; bulk polymerization process [5], suspension polymerization process [6], emulsion polymerization process [7], and solution polymerization process [8]. Suspension polymerization and emulsion polymerization have been the most widely used processes for many years. Suspension polymerization (Fig. 2) is the most common method for producing PVC resins, accounting for 82–85% of output produced in the United States. It comprises charging an agitated reactor with one or two parts water and one-part vinyl chloride monomer or comonomer combination, as well as initiator and suspending agents such poly(vinyl alcohol).

The mass is reacted at 50–65 °C until around 85–90% of the monomer is transformed into the resin. The unconverted monomer is removed from the resin water

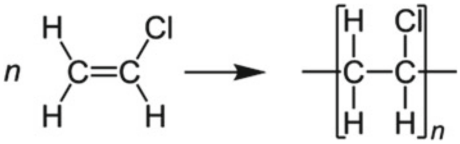


Fig. 1 Polymerization of vinyl chloride

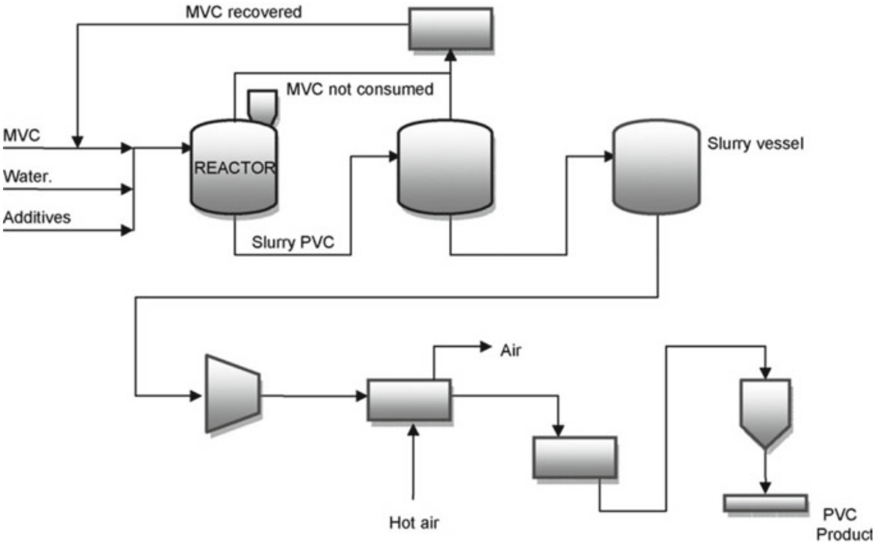


Fig. 2 Simplified flowsheet of the PVC production process by suspension [9]

mixture by heating it, often under a vacuum. The resin is subsequently taken from the water and dried by exposure to warm air in rotary, flash, or fluid bed driers before being delivered to storage silos. The high productivity per unit reactor volume, flexibility in polymer composition and resin particle properties, and granular nature of the product are all advantages of the suspension resin process. The problem with this process is the larger resin particle size (50–150 μm), making it challenging to remove unconverted vinyl chloride monomer [4, 9, 10].

Emulsion polymerization is the second most common method for producing PVC resins, accounting for 10–12% of total output in the United States. One of the most critical parts of emulsion polymerization is that it is a diverse range of processes that each produce specialized products that are defined or specified in terms of performance in a particular application. In addition to the reactor fouling issue described for suspension polymerization, the emulsion polymerization process provides less flexibility in terms of changing process variables. Furthermore, emulsion process resins are costly to produce, and plant operators are more conservative regarding process modifications. Also, more vinyl chloride monomer is emitted in this process, which affects workers' health as well. Bulk and solution polymerization account for 5–7% of total PVC output in the United States [4, 11–13].

The presence of a chlorine atom increases intermolecular attractions between polymer chains, making PVC a more rigid and stiffer material. Window frames, drainage pipe, water service pipe, medical devices, blood storage bags, cable and wire insulation, resilient flooring, roofing membranes, stationary, automotive interiors and seat coverings, fashion and footwear, packaging, cling film, credit cards, vinyl records, synthetic leather, and other coated fabrics are just some of the applications for PVC [1, 2, 14–20]. PVC that has not been compounded is colorless and hard, with poor heat and light stability. However, by using additives/stabilizers, we can adjust the qualities of PVC to our requirements and applications. In recent years, the blending of polymers has been deemed the most suitable approach for obtaining balanced and needed qualities in hybrid polymeric materials. Because these required features cannot be acquired from a single polymeric component, blending two or more polymers has emerged as a new technique for achieving innovative and desirable uncommon properties, such as mechanical, thermal, morphological, rheological, and chemical properties. Polymeric hybrids/composites are widely employed in a wide range of items, including footwear, medical equipment, automobiles, packaging, and space transportation [21–24]. Researchers have recently considered nanoparticles for incorporating into polymer blends because of their extraordinary physical and chemical properties, notably their nano size ranges of 10 nm to 1 μm. Their applications can be found in various industrial, commercial, and consumer products. Because of these applications, nanoparticles must be analyzed precisely and thoroughly based on their nanostructure.

To give maximum mechanical and thermal benefits, polyhedral oligomeric silsesquioxane (POSS), a nanostructured chemical, is used as a building block in polymer matrices of blends [13, 25]. In recent decades, polyhedral oligomeric silsesquioxanes (POSSs) have been employed as filler, nucleating agent, crosslinker, and adhesion promoter [26–32]. POSSs are a new generation of hybrid nanofillers that combine organic and inorganic nanoscale structures. These hybrid nanofillers (POSSs) are expected to be easy to incorporate into polymers, including PVC. They may be able to build, reinforce, and stabilize materials compared to traditional ones [29, 32–35]. POSS is a nanosized hybrid with a chemical composition that is intermediate between silica (SiO_2) and silicon (SiO_2) (R_2SiO). A silsesquioxane is an organosilicon compound having the chemical formula $[RSiO_{1.5}]_n$, where R is an organic functional group (aryl, alkyl, or alkoxyl) with reactive and/or non-reactive groups. Silsesquioxanes are colorless solids with Si–O-Si connections that form cages or polymeric structures. Silsesquioxanes have two types of molecular structures: caged and non-caged [22, 29, 36]. Figure 3 illustrates the chemical structures of various functionalized POSS types. Researchers are attracted to them because of their unique structure, which has an organic shell and an inorganic silicate core. The inorganic silicate core provides a significant improvement in thermal characteristics and stiffness of materials, among other things. Unlike silica, POSS molecules, made up of reactive functional groups linked covalently, are suitable for polymerization and integration into different polymer blend systems. Because the POSS technology is chemically versatile, several POSS monomer and polymer systems are being developed or have already been produced. POSSs come in various molecular structures, including 6, 8, 10, and 12 Si vertices denoted T_6, T_8, T_{10}, and T_{12} (T = tetrahedral vertex). POSS molecules with a T_8 cubic inorganic core composed of silicon-oxygen ($R_8Si_8O_{12}$) are the most often studied structures in POSS molecules [37–40].

Furthermore, the hybrid organic–inorganic framework makes POSS thermally and chemically robust. One of the most promising uses for POSS-based polymers

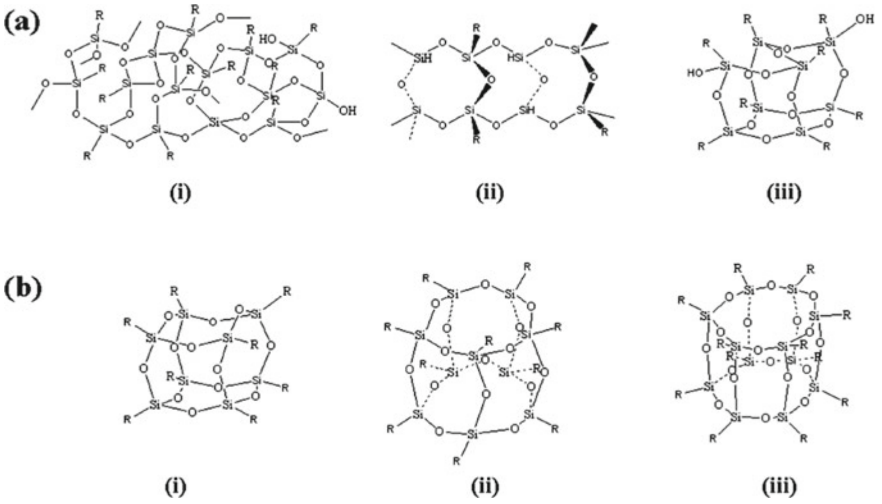


Fig. 3 Chemical structures of silsesquioxanes. **a** non-caged silsesquioxanes: (i) random, (ii) ladder; (iii) partial caged structures, and **b** caged silsesquioxanes: (i) T_8, (ii) T_{10}, (iii) T_{12} structures [40]

is in the highly oxidizing environment of orbiting spacecraft. POSS can improve polymers' oxidative stability and flame retardance in terrestrial applications, similar to the atomic oxygen resistance trend [41–43].

This chapter has comprehensively discussed the impact of POSS incorporation on the mechanical, thermal, rheological, and morphological properties of PVC and its nanocomposites.

2 Mechanical, Dynamic Mechanical, and Morphological Properties of POSS Reinforced PVC Nanocomposites

As a significant commercial polymer, PVC has been studied extensively in industrial applications for many years. PVC and its composites, on the other hand, are limited in several applications due to underlying deficiencies such as lower heat softening temperature and high brittleness (low toughness). Therefore, new PVC products with high quality must be developed to generate high added values and expand PVC applications. Some studies have been conducted to improve the mechanical properties of PVC using nanoscale reinforcement additives. The main goal is to use molecular or nanoscale reinforcements to enhance the strength and toughness of polymeric components [44–46]. This section presents the mechanical, dynamic-mechanical, and morphological findings from studies involving PVC matrix and several types of POSS nano additives.

In a study by Du et al., PVC/ octyl-POSS (O-POSS) composites containing O-POSS at 0, 1, 1.5, 2, 2.5, and 3 wt% were prepared using a two-roll laboratory mill.

Then, to observe the mechanical properties, 1 mm and 5 mm thickness nanocomposite plates were obtained by pressing these mixtures at 180 °C. The resultant composite samples were then subjected to various analyses such as tensile, impact strength, and dynamic mechanical analysis (DMA). Figure 4 shows that as the weight content of O-POSS in the PVC matrix increases, the tensile strength drops constantly. Moreover, according to the impact strength results, an increment in impact strength values was observed up to 1.5 wt% O-POSS content, while the impact strength value was decreased as the O-POSS contents were increased from 1.5 wt%. When O-POSS content exceeds 1.5 wt%, phase separation occurs, and impact strength drops. This is because adding O-POSS reduces the molecular frictional force or entanglement of PVC chains or particles, resulting in a reduction in tensile strength. This phase separation was proved via SEM images, as seen in Fig. 5.

As a result of the scanning electron microscopy (SEM) observations performed on the impact test samples, it was observed that the samples without O-POSS exhibited a brittle fracture behavior (Fig. 5 P1). In contrast, the samples containing 1%

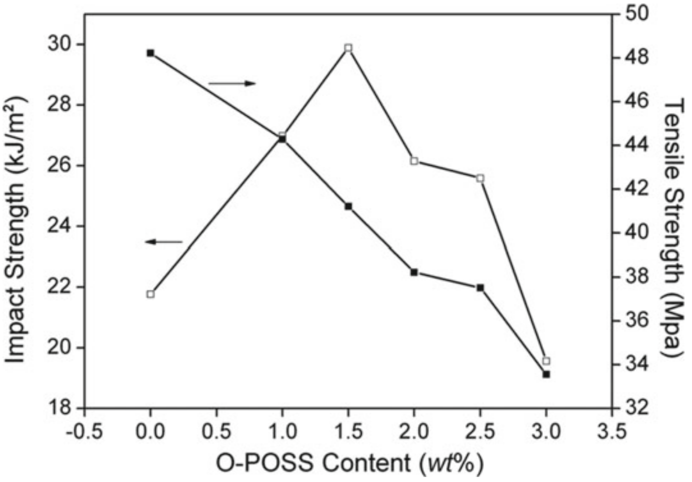


Fig. 4 Relationship of impact strength, tension strength, and O-POSS content [47]

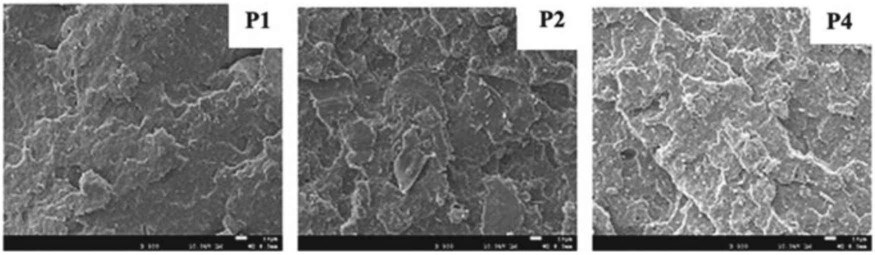


Fig. 5 SEM photographs of impact breaking surface of P1, P2 and P4 sample [47]

(Fig. 5 P2) by weight of O-POSS showed a toughness characteristic because of the plasticizing effect. An obscure structure was noticed due to poor compatibility in the morphological observation of the samples containing 2 wt% O-POSS, and it was assumed that there was a fall in impact strength due to phase separation. The DMA test was applied to the $20 \times 5x0.8\ mm^3$ samples; extremely small variations in glass transition temperature (T_g) values were obtained due to the small amounts of O-POSS additive used [47].

In another study, Du et al., using similar production methods, produced PVC/chlorinated polyethylene (CPE) blends in different mixing ratios and nanocomposites by mixing 3, 5, 7, and 10 wt% methylacryloylpropyl-POSS (MAP-POSS) into 90–10 wt% PVC/CPE blend. Then, nanocomposite sheets of 1 mm and 5 mm thickness were subjected to tensile, impact, and DMA tests. Table 1 summarizes the mechanical test results, revealing that the blend with the highest impact strength is C20 coded blend containing 20 wt% CPE, and the nanocomposite with the highest impact strength is C10M10 containing 10 wt% MAP-POSS. Furthermore, the impact strength of nanocomposites was shown to rise as the amount of MAP-POSS increased in the blend systems. As a result of the SEM observations made on the impact samples, it was deduced that the C10M0 sample without MAP-POSS showed toughness characteristics.

In contrast, the samples containing 7 wt% MAP-POSS showed a layered and uncertain structure. Contrary to the impact strength results, it was concluded that the amount of MAP-POSS decreased the tensile strength. DMA tests revelaed that the storage module increases when a small quantity of MAP-POSS is added but drops when the amount of added MAP-POSS is increased. This was due to the low amount of MAP-POSS filling the free space between PVC and CPE and even partially crosslinking with PVC and CPE molecules. Due to filler effects and the crosslinks they form, the low amount of MAP-POSS addition improves the modulus value by preventing chain movements and increasing the friction force between the PVC and CPE chains. It was concluded that when the number of MAP-POSS in the nanocomposite increased, MAP-POSS molecules that could not crosslink with the matrix developed, lowering the modulus through a plasticizing effect [48].

Gao et al. produced six different nanocomposites using PVC and 3-chloropropyl-POSS (CP-POSS). In the PVC matrix, the CP-POSS content was 3, 5, 7, 9, and 11% by weight. The T_g values and mechanical properties were investigated via DMA and electronic tensile machines, respectively. At the same time, an XCJ-40 impact tester

Table 1 Data of impact strength and tensile strength of blends [48]

Sample no	C0	C5	C10	C15	C20
Impact strength (kJ/m^2)	2.04	3.86	6.90	11.45	26.37
Tensile strength (MPa)	23.48	22.45	20.36	19.02	16.84
Sample no	C10M0	C10M3	C10M5	C10M7	C10M10
Impact strength (kJ/m^2)	6.90	8.01	8.91	11.42	12.28
Tensile strength (MPa)	20.36	14.28	11.58	10.44	9.55

was used to perform the notch impact test. DMA results showed that T_g values of CP-POSS/PVC blends increased upon addition of CP-POSS to PVC, but this increment was only by 2–3 °C, with the maximum T_g being 73.3 °C for the P3 sample having 3 wt% CP-POSS. The molecular interaction of PVC and CP-POSS accounts for the little increase in T_g. PVC molecules can generate physical crosslinks with the multi-polar groups of the CP-POSS molecule. However, because the CP-POSS has a lower melting point and plasticizes PVC, the T_g only increases slightly. Mechanical test results shown in Fig. 6 depicts the impact strength and elastic modulus data. When the CP-POSS content is 3–11 wt%, the blends have superior impact strength and have the best value at 7 wt%, but the elasticity modulus has the lowest value at 7 wt%. As a plasticizing agent, the CP-POSS can raise the impact strength of pure PVC, but it also has some activity to increase elastic modulus when the content is greater than 9 wt%. Figure 7 shows SEM images of P0 (pure PVC with 0 wt% CP-POSS) and P7's impact cracked surfaces. Figure 7 shows that the P0 has a smooth fracture surface and a brittle break; this is the brittle material's breaking feature. P7's fracture behavior reveals several toughness traits, such as a rough fracture surface and numerous holes, which is the breaking character of tough materials.

The plastic activity of CP-POSS in blends and physical cross-connections between PVC molecules and CP-POSS are also compatible with their findings. The plasticization effect is predominant when the CP-POSS content is less than 7 wt%, and the impact strength increases.

Based on the analysis of the mechanical and morphological features of CP-POSS/PVC blends, it has been determined that 3-chloropropyl-POSS (CP-POSS) has good compatibility with PVC and has a plasticizing impact on PVC. When the content of CP-POSS is 7 wt %, it can strengthen impact strength and has the best value. However, when the CP-POSS content exceeds 7 wt%, the impact strength drops, and

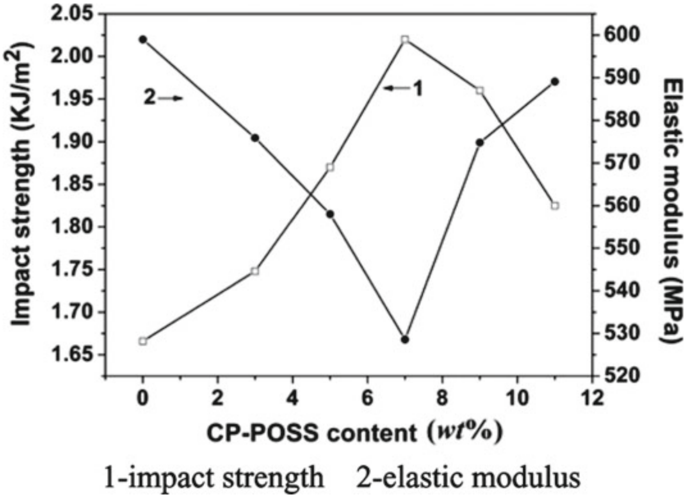


Fig. 6 Relationship between impact strength, elastic modulus and CP-POSS content [49]

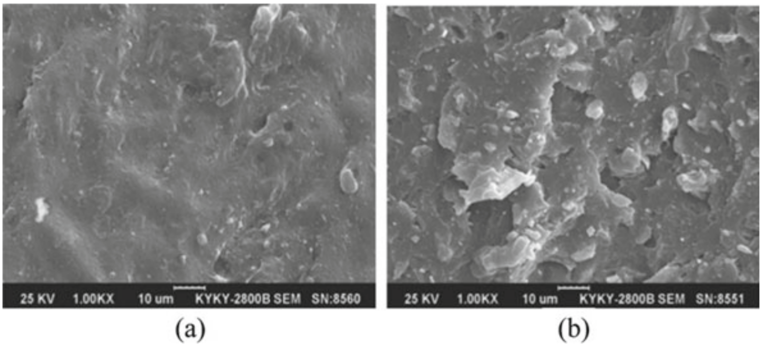


Fig. 7 SEM photographs of impact breaking surface of P0 and P7 **(a)** P0, and **(b)** P7 [49]

the elastic modulus increases. For PVC, the CP-POSS can be utilized as processing support and an impact-resistant aid [49].

Yang et al. used a mixer and a laboratory two-roll mill to make nanocomposites of PVC/acrylonitrile chlorinated polyethylene styrene (ACS)/methylacryloylpropyl-POSS (MAP-POSS) containing 0, 1, 2, 3, 4, 5, 6 wt% MAP-POSS. PVC, ACS, and MAP-POSS were combined in a mixer before being milled at 185 °C on a laboratory two-roll mill. To determine dynamic rheological behavior and mechanical properties, 1 mm and 5 mm thick plates were pressed at 185 °C and subsequently cold-pressed for 10 min at 5 MPa. The researchers examined the mechanical and dynamic mechanical properties of these nanocomposites. Figure 8 depicts the relationship between the mechanical properties of PVC/ACS/MAP-POSS nanocomposites and their MAP-POSS content. According to Fig. 8, increasing the MAP-POSS ratio by up to 2% increases tensile strength, whereas increasing it by more than 2% drastically diminishes it. The impact strength results followed the same pattern as the tensile strength data. While the highest impact strength was attained at 3 wt% MAP-POSS ratios, there was an increase up to this rate before a decline. The cracked impact samples revealed that 3 wt% of the MAP-POSS additive made the structure ductile; however, when the ratio was increased to 6 wt%, the structure became brittle and had the reverse effect. The explanation was that the number of crosslinking increased as the amount of MAP-POSS increased. The maximum T_g value was obtained by DMA tests at a rate of 2 wt%, which was identical to the tensile test findings. T_g has developed a rising trend below 2 wt% and a falling trend beyond 2 wt%. In the storage modulus, comparable results were seen. Yang et al. concluded that the plasticizing action of free MAP-POSS and the balance of hydrogen bonds between MAP-POSS and PVC/ACS were responsible for the trend difference [50].

Palin et al. investigated the impact of POSS on a PVC matrix using two closed cages POSS types (Octvinyl POSS, VyPOSS, and glycidyl POSS, GlyPOSS) and two open cages POSS types (trisilanol heptaphenyl POSS, PhPOSSOH and trisilanol heptaisobutyl POSS, IBuPOSSOH). Nanocomposites were obtained independently and in an equal mixing ratio with all POSSs as a preliminary investigation

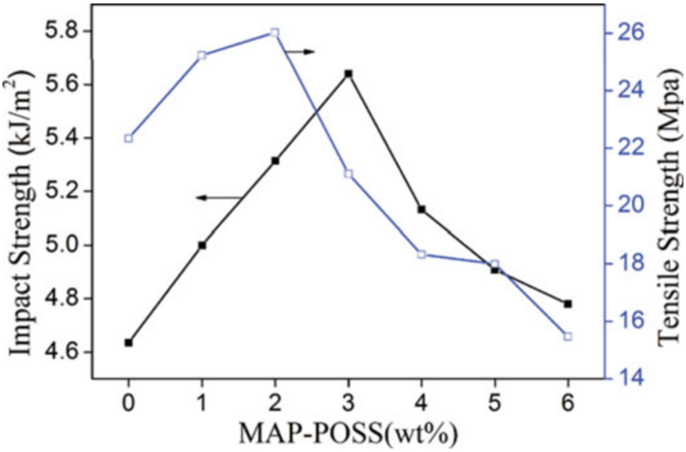


Fig. 8 Relationship of impact strength, tensile strength and MAP-POSS content [50]

to discover the optimal nano additive. As a result, VyPOSS and GlyPOSS were selected as outstanding contributions and are being explored further. VyPOSS and GlyPOSS were combined with X-type zeolite and carbonate-substituted hydrotalcite (CO_3-HTLC) nanoparticles. Hardness and mechanical properties were investigated to emphasize these additives' implications in final industrial applications. Mechanical test results showed that nano additives have almost no effect on properties like tensile strength and elastic modulus. On the other hand, the POSS improved the thermal stability of the nanomaterial-added samples without compromising their mechanical properties [51].

Silva et al. studied the tensile and dynamic mechanical properties of PVC/POSS nanocomposites containing 1 and 5 wt% chlorobenzylethylisobutyl POSS. Tensile test results are shown in Fig. 9, and it was found that the tensile strength of POSS modified samples was found lower than plasticized PVC compound. However, the addition of 1 wt% POSS improved the elongation at break value as compared to plasticized PVC compound. Furthermore, the weak interaction of POSS in the PVC matrix was observed due to the lack of the theoretically predicted increase in elastic modulus [52].

A research study was conducted by Soong et al. to investigate the application of polyhedral oligomeric silsesquioxanes to plasticize PVC. Traditional organic plasticizers for PVC, such as dioctyl phthalate (DOP), are relatively volatile, resulting in plasticizer loss and undesirable material degradation over time. Previous experiments have shown that methacryl-POSS (mPOSS) can plasticize PVC despite its low volatility due to its hybrid organic–inorganic composition. Using a lab-size extruder (DACA Instruments), melt blending was used to prepare various PVC/mPOSS and PVC/DOP binary blends, as well as PVC/mPOSS/DOP ternary blends. TA Instruments Q800 DMA was used to describe the thermomechanical behavior of the materials, and the results of DMA investigations are shown in Fig. 10. The

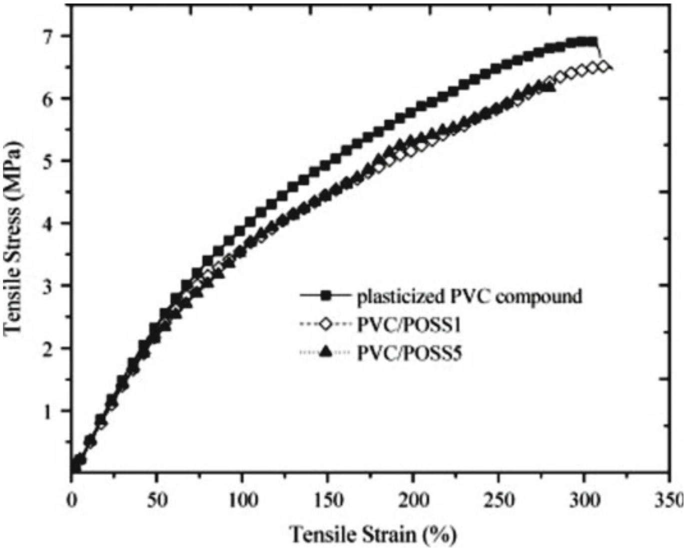


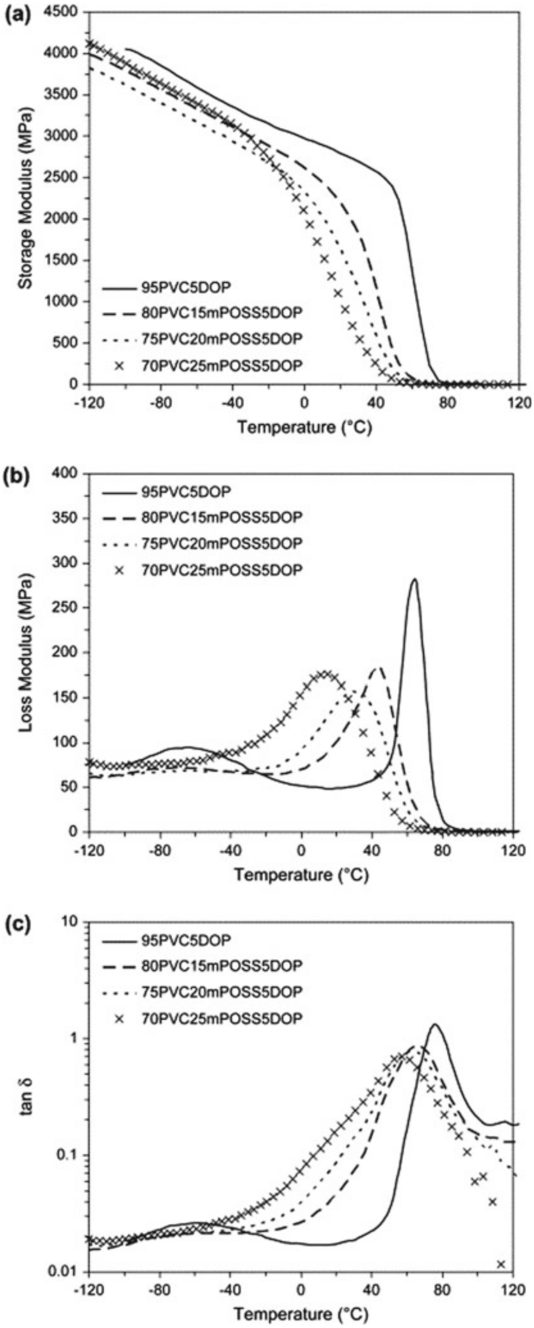
Fig. 9 Stress/strain curves of plasticised PVC compound and PCV/POSS1 and PVC/POSS5 nanocomposites [52]

storage modulus, loss modulus, and tan δ curves for PVC/5 wt% DOP and ternary PVC/mPOSS/5 wt% DOP blends are shown in Fig. 10. PVC becomes more plasticized as its methacryl-POSS composition rises. Based on the tan δ peak value at 1 Hz, the addition of 25 wt% methacryl-POSS lowers the α-transition temperature of the PVC/5 wt% DOP from 77 to 59 °C. In DMA results, ternary blends produced with 20 wt% POSS and 20 wt% DOP showed lower α-transition temperature compared to pure PVC sample but higher value compared to 60 wt% POSS/40 wt% DOP binary blend produced without POSS. Also, DMA results revealed that the T_g of well-formed ternary PVC/POSS/DOP compounds could be decreased to near room temperature, and these materials have good ductility.

Figure 11 shows the uniaxial compression true stress–true strain curves of the ternary blends PVC/mPOSS/5 wt% DOP containing 5 wt% DOP at a strain rate of 0.001/s, which were tested using a Zwick mechanical tester (Zwick Roell Group). The compounds get more plasticized as the amount of methacryl-POSS in PVC increases. The materials change from glassy to leathery behavior, significantly reducing yield and flow stress. The mechanical characteristics of binary (PVC/DOP) and ternary (PVC/POSS/DOP) compounds formed with identical T_g values differed significantly. These findings suggest that POSS could be used to modify the mechanical properties of plasticized PVC [53].

Tomaszewska et al. investigated the modification of poly(vinyl chloride) (PVC) by polyhedral silsesquioxane containing both methacryl and octyl groups in another work (MeOctPOSS). Melt mixing was used to make PVC nanocomposites with

Fig. 10 Storage modulus (**a**), loss modulus (**b**), and tan δ (**c**) curves of PVC/mPOSS/5 wt% DOP blends as a function of temperature at 1 Hz [53]



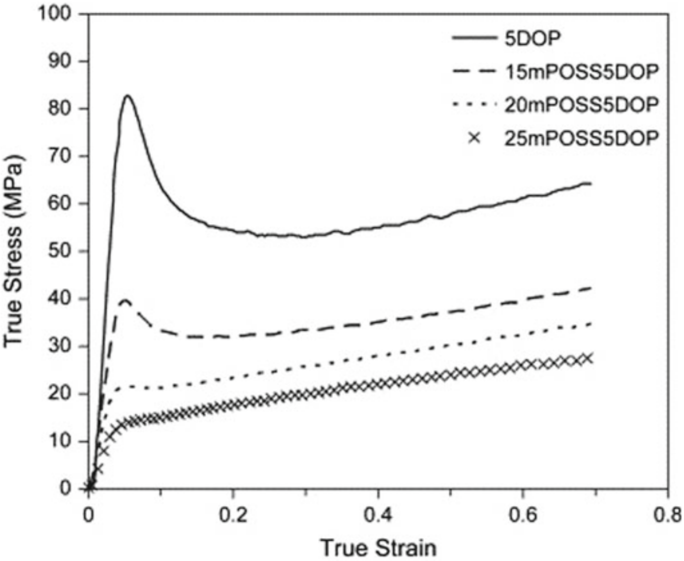


Fig. 11 True stress–true strain curves of compounds containing 5 wt% DOP and various amounts of methacryl-POSS. Testing was done in uniaxial compression at 0.001/s [53]

MeOctPOSS. MeOctPOSS concentrations ranged from 1 to 10 wt%. Scanning electron microscopy and energy dispersive spectroscopy measurements were performed to analyze the homogeneity of MeOctPOSS dispersion in the polymeric matrix. SEM pictures revealed that POSS dispersion in the PVC matrix was homogeneous. Based on the SEM findings, it is possible to conclude that the MeOctPOSS is equally distributed in the PVC matrix, regardless of additive concentration, and no agglomerates are present. The dispersion of silicon atoms in the PVC matrix was confirmed using EDS. As shown in Fig. 12a–d, all samples have a homogeneous Si-atoms distribution, which indicates the MeOctPOSS. Furthermore, no nano additives aggregates were visible to the naked eye, indicating that the nanocomposite production was proper.

The more concentrated the POSS additive, the denser the Si-atom distribution in the matrix, resulting in a brighter image. The mechanical analysis (tensile tests) was performed on an Instron 5985 universal tensile machine controlled by the BlueHill 2 program. The purpose of the tensile testing was to see if adding POSS to the PVC compounds changed their elastic characteristics. The plasticizing effect of the MeOctPOSS long chains was validated by uniaxial stress–strain tests that measured the elastic modulus of the PVC matrix as a function of the POSS content (Fig. 13). Moreover, the authors stated that adding POSS with long chains connected to the Si-cage lowers the modulus, especially at POSS concentrations over 2.5 wt%, with the most apparent consequence at 5 and 10 wt% [54].

Wang et al. investigated the influence of methacryl-functionalized polyhedral oligomeric silsesquioxane (MA-POSS) nanoparticles for a PVC homopolymer and a

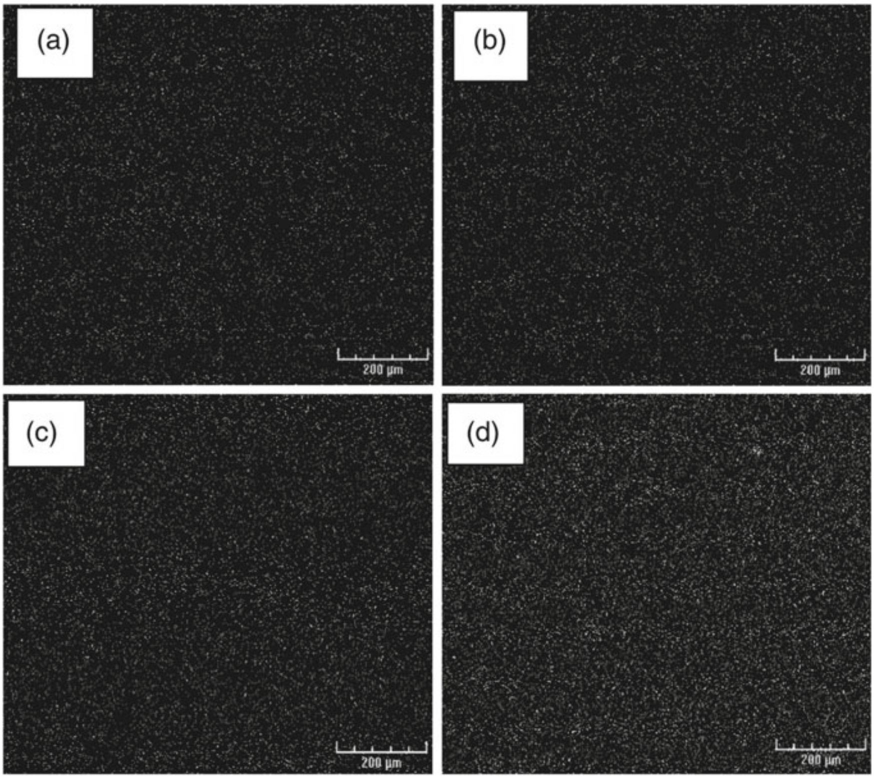


Fig. 12 Mapping of silicon atoms distribution of PVC composite: **(a)** PVC/1POSS, **(b)** PVC/2.5POSS, **(c)** PVC/5POSS, **(d)** PVC/10POSS [54]

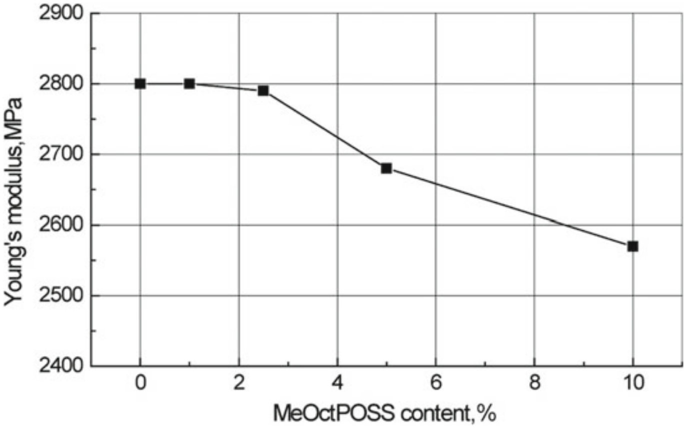


Fig. 13 The Young modulus of PVC nanocomposites as a function of MeOctPOSS contain [54]

PVC/dissononyl cyclohexane-1,2-dicarboxylate (PVC/DINCH) binary blend. They used MA-POSS as a plasticizer and thermal stabilizer. The PVC binary blends were prepared with 10, 20, 30, 40, and 50 wt% MA-POSS. On the other hand, ternary blends were prepared with 5, 10, and 15 wt% MA-POSS and PVC/DINCH blends. In this study, annealing at 100 °C for seven days was applied to the ternary blends. And the effect of MA-POSS amount of ternary blends on tensile properties before and after annealing was investigated. All the PVC/DINCH/MA-POSS ternary blends were found transparent and flexible; however, as the MA-POSS concentration was increased, their modulus and tensile strength both declined. Moreover, elongation properties increased both before and after thermal annealing. After seven days of thermal annealing at 100 °C, the elongation dropped, but the modulus and tensile strength increased (Fig. 14).

The DMA test results of ternary blends show that the T_g value increased with the increase in the amount of MA-POSS. Both DMA and tensile test results confirmed that MA-POSS nanoparticles were incorporated into the blends with complete miscibility. MA-POSS promises to be a viable candidate for substituting traditional plasticizers, such as di-(2-ethylhexyl)phthalate (DEHP), in PVC matrices [55].

3 Thermal Properties of POSS Reinforced PVC Nanocomposites

For many years, PVC has been investigated and used widely in industrial applications as an essential commercial commodity polymer. PVC and its composites, on the other hand, are limited in several applications due to intrinsic drawbacks such as low-temperature stability and brittleness. As a result, new PVC products with high quality and good qualities must be developed to generate high added values and boost PVC applications [58, 59]. Researchers have been working on enhancing the thermal stability and thermal behavior of PVC-based nanocomposites for a long time.

3.1 Glass Transition Temperature of POSS Reinforced PVC Nanocomposites

A differential scanning calorimetry (DSC) is one of the most effective methods for determining a material’s thermal behavior. Different data can be collected as a result of DSC evaluation, such as melting temperature (T_m), crystallization temperature (T_c), and glass transition temperature (T_g). Glass transition temperature is among the specific properties of polymers. PVC is a polymer in amorphous structure due to the chlorine atom in its molecular structure, and its T_g value varies between 75–85 °C. A polymer’s glass transition temperature is associated with its processability, whereas plasticizers make the processibility of polymers easier by reducing the glass transition

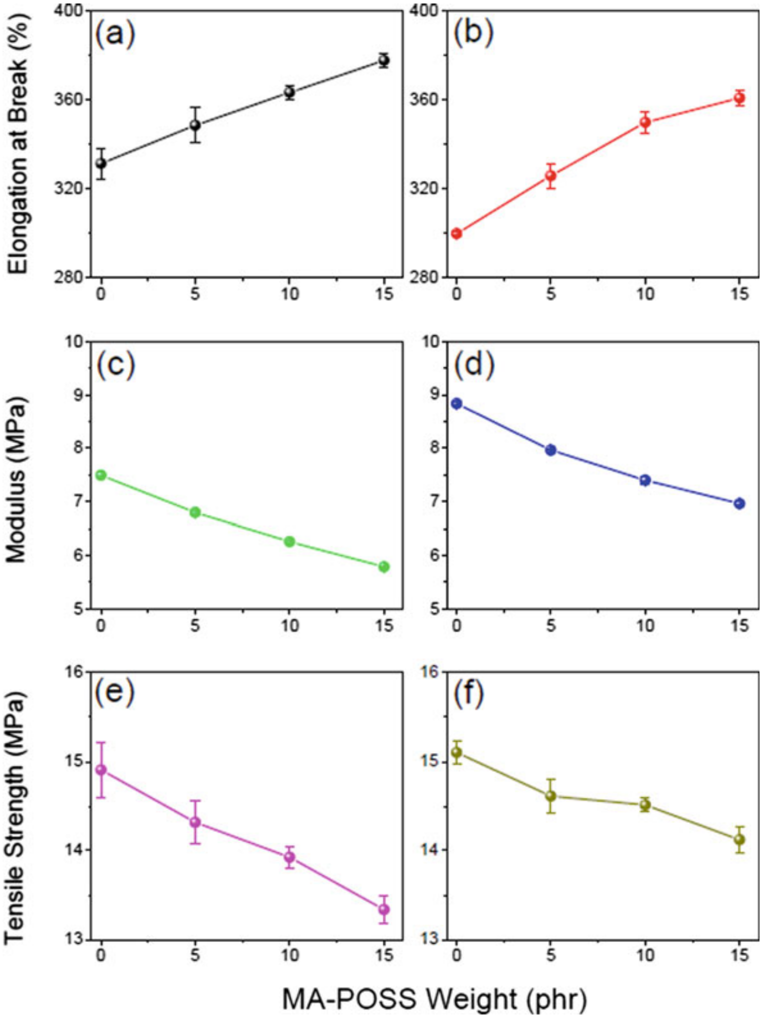


Fig. 14 Mechanical properties of PVC/DINCH/MA-POSS blends at various MA-POSS content **(a, c, e)** before and **(b, d, f)** after thermal annealing at 100 °C for 7 days: **(a, b)** elongation properties, **(b, d)** moduli, and **(c, f)** tensile strengths [55]

temperature. The literature shows that POSS nanoparticles added to PVC can reduce the plasticization time and balance torque values [50]. DSC analyses were carried out in many investigations to assess the Tg value of the nanocomposites. As can be seen from Table 2, PVC nanocomposites were prepared using various functional POSS nanoparticles, and the researchers used several DSC test methods to evaluate their T_g values. PVC/POSS nanocomposites with different POSS ratios were prepared using various methods, and the plasticizing effect of various functional POSS types on the PVC performance was investigated.

Table 2 Research studies using different POSS types and DSC test methods

Nanocomposites	Nanoparticle ratio (%)	DSC Method	References
PVC/PEG-POSS	0 20 40 50	• 25 °C−130 °C/10 °C/min 130 °C –5 min 130 °C−(−100 °C)/10 °C/min • Under a nitrogen atmosphere • Samples of approximately 10 mg	Yang et al. [58]
PVC/MA-POSS	0 10 20 30 40	• 25 °C−150 °C/20 °C/min 150 °C−(−90 °C)/20 °C/min −90 °C−200 °C /20 °C/min • Under a nitrogen atmosphere	Wang et al. [55]
PVC/ MeOctPOSS	0 1 2.5 5 10	• 30 °C−120 °C/5 °C/min • Samples of approximately 10 mg	Tomaszewska et al. [54]

The plasticizing impact of poly(ethylene glycol)–polyhedral oligomeric silsesquioxane (PEG-POSS) on PVC was studied by Yang et al. [58]. As the PEG-POSS ratio increased in the nanocomposites, PVC became more flexible, and T_g values decreased, as seen in Fig. 15. The T_g value of pure PVC was found at 72 °C, and T_g values were reduced to 57.6, 47.6, and 44.3 °C as PEG-POSS was added in amounts of 20, 40, and 50 wt%, respectively. This significant decrease in T_g values suggests that PEG-POSS has a specific plasticizing impact on PVC. These observed behaviors suggest that PEG-POSS is a potential plasticizer for PVC, especially at high PEG-POSS contents (50 wt%), consistent with prior literature [59]. The formation of hydrogen bonds was confirmed via FTIR analysis. The presence of hydrogen bonds would result in a substantial restriction on the mobility of polymeric chains, causing a drop in T_g values. PEG interacts with PVC polar groups when PEG-POSS is added, which is unfavorable for polar site interactions. PVC molecule chains would be separated from one another by the enormous bulk characteristic of POSS to a certain extent, giving them extra free volume. As a result, T_g value of PVC shifts to a lower temperature [58].

In another study by Wang et al., the plasticizing effect of methacryl-functionalized polyhedral oligomeric silsesquioxane (MA-POSS) nanoparticles on PVC homopolymer was investigated. PVC/MA-POSS mixtures were prepared by solution casting methods using MA-POSS nanoparticles in different ratios (Table 2). As a result of the DSC test performed at a heating rate of 20 °C/min, the T_g value for neat PVC was determined as 89 °C. The addition of 10 wt% of MA-POSS decreased T_g by approximately 26 °C compared to pure PVC. Increasing MA-POSS addition caused decreases in T_g values. The study emphasized that MA-POSS nanoparticle is a successful plasticizer for PVC [55].

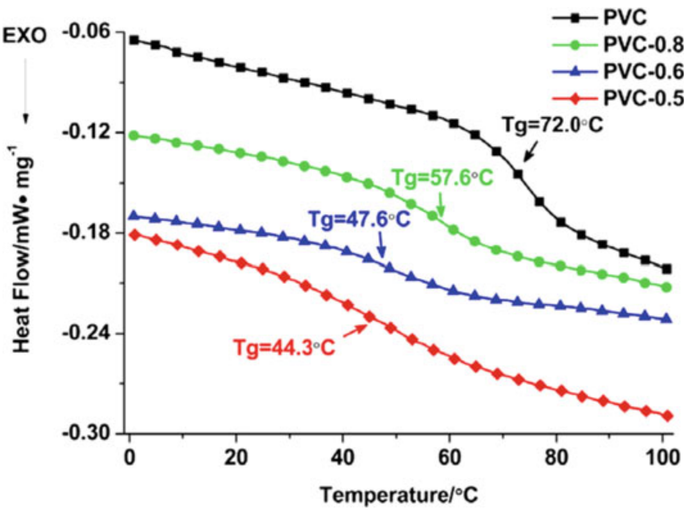


Fig. 15 Glass transition behavior of PVC and PVC/PEG-POSS nanocomposites [58]

Unlike previously investigated research studies, Tomaszewska et al. investigated the effect of polyhedral silsesquioxane containing methacryl and octyl groups (MeOctPOSS) at lower contents (e.g., 1–10 wt%) in PVC matrix. It was found that 1 and 2.5 wt% of MeOctPOSS ratios did not significantly alter the T_g values of nanocomposites (Fig. 16). However, when MeOctPOSS functional nanoparticles were introduced to PVC at 5 and 10 wt%, the T_g values of PVC nanocomposites significantly decreased. The interaction of PVC and POSS nanoparticles with octyl groups is suggested to be the cause of T_g reductions [54].

3.2 *Thermal Stability Analysis of POSS Reinforced PVC Nanocomposites*

Many industrial applications rely on the thermal stability of polymeric materials that are impacted by temperature changes. Thermogravimetric analysis (TGA) is one of the most widely used thermal analysis techniques in polymeric material characterization. PVC/POSS nanocomposites with different POSS ratios were prepared using various methods in several studies (Table 3). TGA measurements were performed to investigate the thermal stability of POSS reinforced PVC nanocomposites. The specification and testing parameters during the TGA analysis were also mentioned in Table 3. The inorganic structure (Si–O) of POSS nanoparticles reinforced the PVC nanocomposites thermally and made them more stable against heat transitions. Some of the research studies proved the positive impact of POSS inorganic core on the thermal stability of PVC nanocomposites.

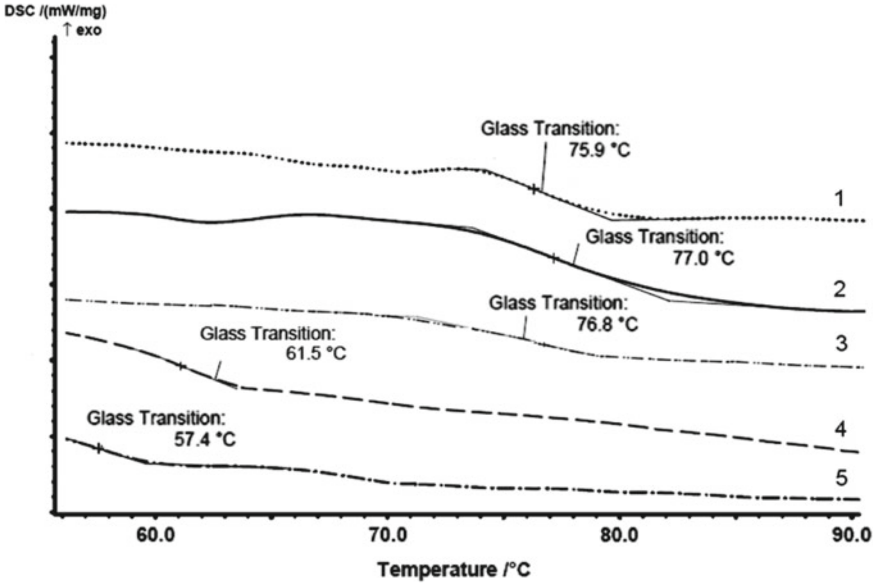


Fig. 16 DSC thermograms: 1-neat PVC, 2-PVC/1POSS, 3-PVC/2.5POSS, 4-PVC/5POSS, 5-PVC/10POSS [54]

Table 3 PVC-POSS studies and the TGA methods used in these studies

Nanocomposites	Nanoparticle ratio (%)	TGA Method	References
PVC/PEG-POSS	0 20 40 50	• 25 °C–680 °C–10 °C/min • Under a nitrogen atmosphere	Yang et al. [58]
PVC/MA-POSS	0 10 20 30 40	• 30 °C–800 °C–20 °C/min • Under a nitrogen atmosphere	Wang et al. [55]
P-PVC/VyPOSS P-PVC/GlyPOSS P-PVC/IBuPOSSOH P-PVC/PhPOSSOH	0.62	• 25 °C–800 °C–10 °C/min • Under a nitrogen atmosphere	Palin et al. [51]
PVC/POSS (chlorobenzyl methyl isobutyl POSS)	1 5	• 20 °C–600 °C–40 °C/min • Under a nitrogen atmosphere	Silva et al. [52]

In a previously discussed work, Yang et al. also investigated the thermal stability of PVC upon the addition of PEG-POSS into PVC. Thermogravimetric analysis (TGA) results showed that PEG-POSS showed a single degradation, while PVC showed a two-step degradation, as seen in Fig. 17. In PEG-POSS added PVC nanocomposites, the degradation step increased to three as the nano additive ratio increased. Step 3 was most clearly observed in the 50% PEG-POSS added nanocomposite (PVC-0.5). When the T_{max1} values of neat PVC and PVC-0.5 nanocomposite are examined, the PEG-POSS additive delays the HCl emission rate (Table 4).

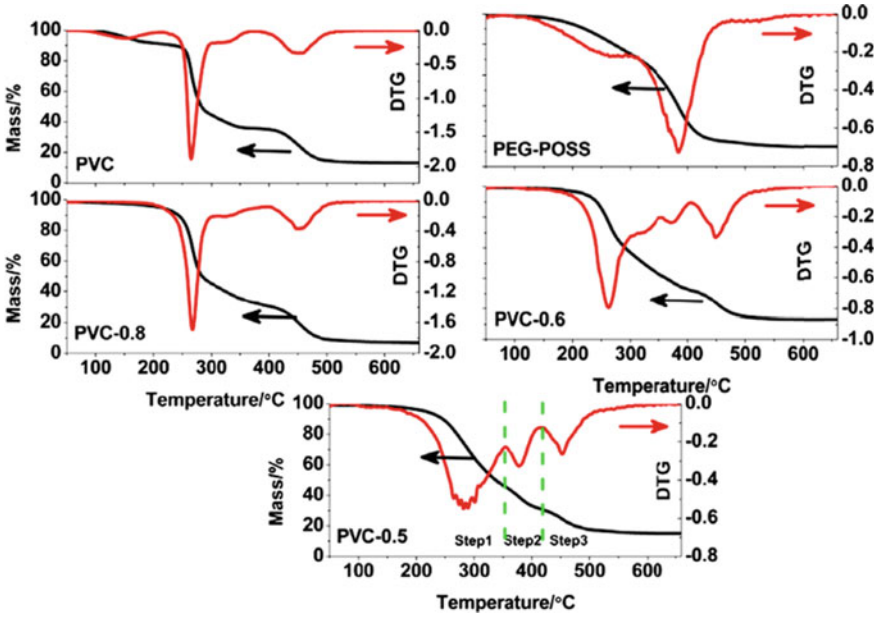


Fig. 17 TG traces of PVC, PEG-POSS and PVC/PEG-POSS nanocomposites [58]

Table 4 Thermogravimetric parameters of PVC and PVC/PEG-POSS nanocomposites[a] [58]

Sample	Step 1		Step 2		Step 3	
	T_{d1} (°C)	T_{max1} (°C)	T_{d2} (°C)	T_{max2} (°C)	T_{d3} (°C)	T_{max3} (°C)
PEG-POSS	–	–	196.5	384.9	–	–
PVC	252.5	265.3	–	–	412.4	443.5
PVC-0.8	252.6	267.2	–	–	427.5	445.2
PVC-0.6	249.3	264.3	–	372.2	428.4	449.3
PVC-0.5	253.2	285.7	–	378.1	432.7	452.5

[a] T_{d1}, T_{d2}: decomposition temperature at 5 wt% loss; T_{d3}: initial loss temperature of PVC in second decomposition process; T_{max}: maximum loss rate temperature of degradation product emission

Neat PEG-POSS exhibited single degradation, and the T_{max} value was 384.9°C. As the PEG-POSS ratio increased in the nanocomposite, T_{max} values increased but were lower than in neat PEG-POSS. Step 3 is due to the dehydrochlorination of PVC, T_{max3} values increased as the PEG-POSS ratio increased. It was emphasized that this was due to the non-pyrolysis residue of PEG-POSS [58].

In another study, Wang et al. investigated the impact of methacryl-functionalized polyhedral oligomeric siloxane (MA-POSS) nanoparticles on the thermal stability of PVC. TGA analyses were performed to assess the thermal stability of POSS reinforced PVC nanocomposites. The TGA curves of several PVC/MA-POSS blends, recorded from 25 to 800 °C at a heating rate of 20 °C/min, are shown in Fig. 18. Compared to pure PVC, pure MA-POSS had more excellent thermal stability. The first thermal decomposition temperature and char yield enhanced as MA-POSS content increased. The final step in the TGA curves corresponds to the pyrolysis of conjugated double bonds (for example, polyenes formed in the first step of PVC decomposition). Due to the retarding effect of MA-POSS nanoparticles on potential residual ash, the decomposition temperature and char yield rise with increasing MA-POSS concentration. Due to weak hydrogen bonds in the PVC/MA-POSS blends, TGA tests showed that adding MA-POSS nanoparticles could decrease the T_g of PVC and increase both its thermal degradation temperature and char yield while maintaining complete miscibility with PVC. To prevent DEHP from getting into touch with tissues or body fluids, MA-POSS has the potential to be an effective substitute for conventional plasticizers like DEHP. It might also be used as a blood bag [55].

Palin et al. used POSS nano additives with different cage structures and different R pendant groups. These POSSs were added to 0.62 wt% in plasticized PVC, and composites were prepared. The nano additives used, and their properties are shown in

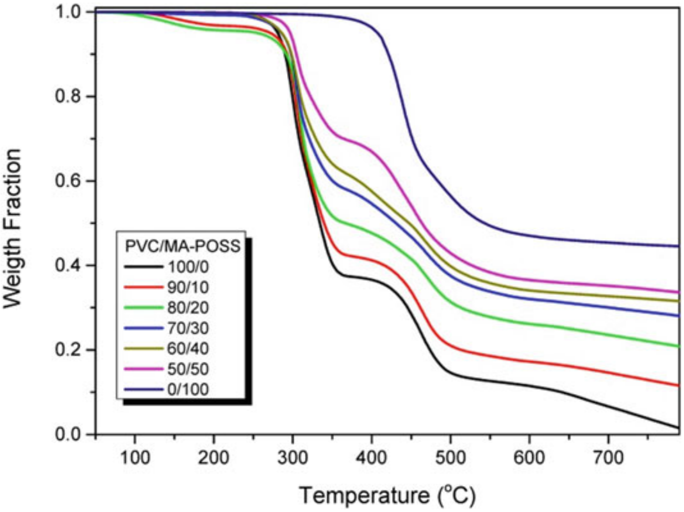


Fig. 18 TGA analyses of PVC/MA-POSS blends of various compositions [55]

Table 5. When the results were examined, all POSS additives improved the thermal properties of PVC. As can be seen in Fig. 19, the end groups rather than the cage structure play a more effective role in thermal stability. The best improvement was obtained in PVC-GlyPOSS nanocomposite, with an increase of about 11 °C in step 1 degradation [51].

Silva et al. prepared PVC-POSS nanocomposites with chlorobenzylethylisobutyl POSS in different ratios (1−5 wt%) to improve the thermal properties of plasticized PVC. TGA was used to characterize the thermal degradation of the plasticized PVC compound and the nanocomposites with the two POSS contents in an inert atmosphere. The results are displayed in Fig. 20. Similar to the plasticized PVC compound, PVC/POSS nanocomposites exhibited two-stage degradation. The first stage was attributed to the volatilization of hydrogen chloride molecules, followed by the formation of conjugated polyene sequences. The second stage is associated with the thermal cracking of the carbonaceous conjugated polyene sequences. The temperatures of the rapid degradation of each stage are represented by the two peaks in the first-derivative thermograms, representing the maximum weight loss rate of degradation. With the increase in POSS content, the thermogram did not show any

Table 5 Properties of POSS nano-additives used

Nanoadditive	Coding	Cage structure	R pendant groups
Vinyl-POSS	VyPOSS	Close	Vinyl
Glycidyl propyl ether-POSS	GlyPOSS	Close	Glycidyl propyl ether
Trisilanol heptaisobutyl-POSS	IBuPOSSOH	Open	Trisilanol heptaisobutyl
Trisilanol heptaphenyl POSS	PhPOSSOH	Open	Trisilanol heptaphenyl

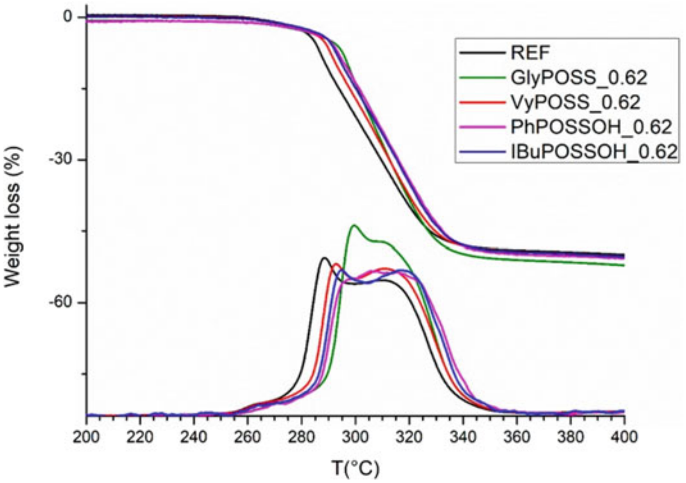


Fig. 19 TGA/DTG analyses of reference P-PVC (REF, black) and POSS formulated P-PVC [51]

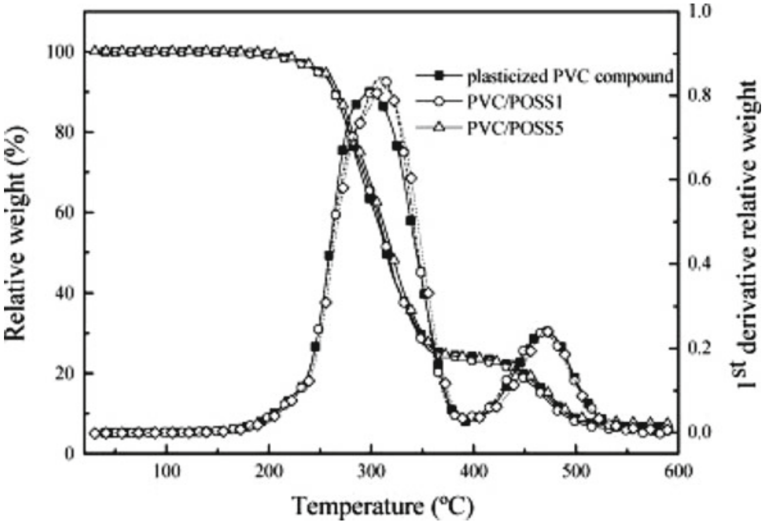


Fig. 20 TGA thermograms and first derivatives for plasticised PVC compound and PVC/POSS1 and PVC/POSS5 nanocomposites in inert atmosphere [52]

apparent alterations. This indicates that there are no significant interactions between PVC and chlorobenzyl ethyl isobutyl POSS [52].

4 Rheological Properties of POSS Reinforced PVC Nanocomposites

The rheological properties of polymers play a crucial role in the process and application of polymeric materials. POSS is typically used to modify the polymers; however, this process will also affect the melt viscosity and rheological behavior of polymers. This is because POSS can disperse at microlevel structure in the polymers.

4.1 Plasticizing Behavior of POSS Reinforced PVC Nanocomposites

Torque rheometers are used to determine the plasticization behavior of polymers. Torque rheometers measure the viscosity-dependent torque produced by the resistance to shear forces during the plasticization process of materials. By performing the tests at a certain temperature, data such as plastic time and equilibrium torque are obtained at the end of the test. In the plasticization process of PVC, the general approach is that the resin is first divided into parts, further reduced by high temperature and mechanical forces. Regardless of the POSS type, the plastic time of PVC decreased with the increase of the POSS nanoparticles ratio [49, 51, 61, 62]. This situation is associated with the lower volatility, low viscosity, and organic/inorganic hybrid structure of the POSS nanoparticle [48].

Gao et al. prepared PVC/MAP-POSS nanocomposites by synthesizing the polyhedral oligomeric silsesquioxanes, which contain methylacryloylpropyl groups (MAP-POSS). Nanoparticles were added into PVC at 0, 2, 3, 5, 7, 9 wt%. The effect of the percentage content of MAP-POSS in nanocomposites was examined. Figure 21 shows the MAP-POSS ratio versus balance torque and plastic time curves. It was observed that the balance torque values of the PVC blends increased with the increase of MAP-POSS composition in PVC. On the other hand, plastic time has decreased. Since the methylacryloylpropyl group on the POSS end groups is compatible with PVC. Besides, MAP-POSS acted as a plasticizer for PVC [62].

In another study, Du et al. used MAP-POSS as nanoparticles for PVC, similar to the previous study. Chlorinated polyethylene (CPE) was additionally preferred as an impact modifier. The blend composition (PVC/CPE) was determined as 90/10, and nano-additive were added at different amounts of 0, 3, 5, 7, and 10 g. Rheological analysis showed that balance torque and plastic time values decreased as nanoparticle composition increased in the PVC-CPE blend. The plastic time value decreased by 81 s in the composite containing 10 g MAP-POSS compared to the pure PVC-CPE blend. It is suggested that MAP–POSS has plasticizing effect and lubrication in the melt. Thus, the nanocomposites' balance torque and plastic time decreased with increasing MAP–POSS content. MAP–POSS can also be a processing aid for PVC/CPE blend [48].

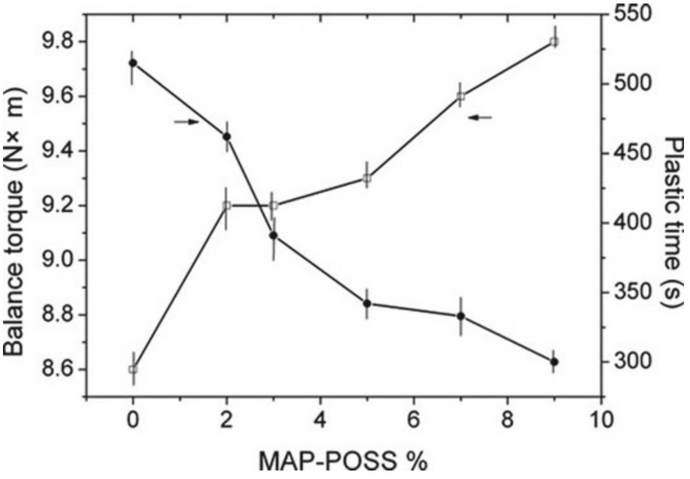


Fig. 21 Relationship of the balance torque, plastic time and the MAP-POSS content [62]

In another study, Yang et al. prepared the PVC/ACS/MAP-POSS nanocomposites. ACS has been added to the blend as a modified resin, which is compatible with PVC due to its sound processing and mechanical properties. ACS was added to PVC at a rate of 15 wt%. Using a torque rheometer, the plasticizing behavior of PVC/ACS/MAP-POSS nanocomposites was studied at 185 °C. Reduced plasticization times were observed with increasing MAP-POSS composition in the PVC/ACS. There was a slight increase in the balance torque values because MAP-POSS somewhat restricted the chain mobility of the blend and the possibility of weak hydrogen bonds between PVC/ACS [50].

In another study, a polyhedral oligomeric silsesquioxane that contains three chloropropyl groups (CP-POSS) was synthesized by hydrolytic reaction, and PVC/CP-POSS nanocomposites were prepared at 0, 3, 5, 7, 9, 11 wt% CP-POSS concentrations. As seen in Fig. 22, as CP-POSS increased in PVC, the plastic time of the nanocomposites decreased, and the balance torque values increased. The CP-POSS mixture has a low melting point, and the CP-POSS molecule, which is equivalent to nanometer particles, will fill the free volume between PVC molecule chains. So, the plastic time decreases with the increasing content of CP-POSS. But the chlorine atom of 3-chloropropyl on POSS can form a weak hydrogen bond with the PVC molecule. The hydrogen bonds hinder the movement of PVC chains. The friction force between PVC chains and CP-POSS increases, so the balancing torque increases with the content of CP-POSS [60].

Du et al. investigated the effect of polyhedral oligomeric silsesquioxanes containing octyl groups (O-POSS) on the properties of PVC. As the O-POSS content increased, the balancing torque and plastic time values decreased. The fact that the solubility parameters of PVC and O-POSS are relatively far from each other results in

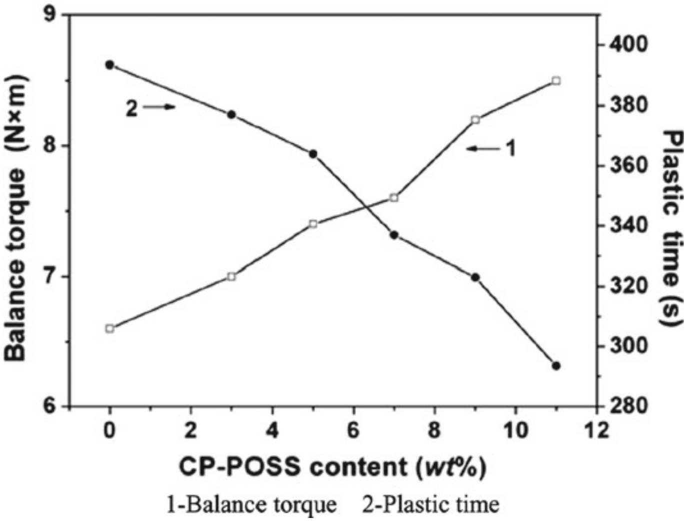


Fig. 22 Relationship between the balance torque, plastic time and the CP-POSS content [60]

poor compatibility between them. It has also been stated that the friction between the chains is reduced. Therefore O-POSS provides a plasticizer and lubricant effect [47].

As a result, balance torque values decreased as the O-POSS ratio increased [47] and increased as the CP-POSS ratio increased [48]. Balance torque was associated with weak hydrogen bonds due to compatibility between polymer and nanoparticle and crosslinking structure formed by the effect of temperature by Gao et al. [60]. These hydrogen bonds and crosslinked structures limited the movement of PVC molecules. O-POSS exhibits incompatible with PVC; however, CP-POSS and MAP-POSS showed good compatibility. With the increase of MAP-POSS ratio, balance torque values of mashed PVC and PVC-ACS nanocomposite increased [50, 60], while balance torque values of PVC/CPE nanocomposite decreased [48]. According to the studies, the plasticizing effect of POSS nanoparticles has been clarified regardless of whether they are compatible with the PVC. It has been observed that POSS nanoparticles with different end groups provide a plasticizer and lubricant effect for PVC. In addition, it was found that MAP–POSS can also be used as a processing aid for PVC/CPE blend [48].

4.2 *Dynamic Rheological Behavior of POSS Reinforced PVC Nanocomposites*

Oscillation rheometers are used for dynamic rheological measurements. In these rheometers, frequency, temperature, and strain sweeps can be made, and different modules can be studied. In frequency sweep experiments, the storage modulus (G′), loss modulus (G″), and complex viscosity (η*) of the melts are measured. The storage modulus (G′) of material gives information about its elastic behavior. The loss modulus (G″) is related to the energy dissipation. The change in storage modulus may be due to the difference in hardness and interaction between polymer chains [48, 60]. Some of the research studies are summarized in Table 6.

Du et al. prepared PVC-based nanocomposites with polyhedral oligomeric silsesquioxanes containing octyl groups (O-POSS). The properties of six different

Table 6 PVC-POSS studies and the rheological test methods used in these studies

	Test method	References
PVC/O-POSS	Frequency sweep experiments: 25 mm in diameter at 185 °C, the frequency ranges from 0.1 to 100 Hz, strain is 1.25%	Du et al. [47]
PVC/CPE/ MAP-POSS	Frequency sweep experiments: 25 mm in diameter at 185 °C, the frequency ranges from 0.1 to 100 Hz, strain at 1.25%	Du et al. [48]
PVC/ACS/ MAP-POSS	Frequency sweep experiments: 25 mm in diameter at 185 °C, the frequency ranges from 0.1 to 100 Hz, strain at 1.25%	Yang et al. [50]

PVC nanocomposites at 0, 1, 1.5, 2, 2.5, 3 wt% were investigated, and the prepared nanocomposites were abbreviated as P1, P2, P3, P4, P5, and P6, respectively. To determine the storage and loss modulus of nanocomposites, frequency scanning was performed between 0.1 and 100 Hz. The strain value was selected as 1.25%. As a result of the evaluations, it was concluded that the modulus increases with the amount of O-POSS up to 2% in both G′ and G″ values. It was observed that O-POSS restricted the chain mobility of PVC. Besides, the O-POSS addition increased the modulus values. It has been observed that these increments in rheological properties occurred faster in the low-frequency range. The authors stated that agglomeration of O-POSS beyond 2% resulted in weak mechanical properties such as modulus. The same phenomenon was observed for complex viscosity values. Stress relaxation tests were also performed at 185 °C at a 10% strain value. At higher content of O-POSS, the shear stress decreased; however, the time to reach the balance stress increased (Fig. 23). Below this ratio, these results are the opposite. By increasing melt elasticity, shear stresses increased, and more time was needed to reach equilibrium stress [47].

Du et al. investigated the rheological properties of MAP-POSS (different amounts of 0, 3, 5, 7, and 10 g) incorporated PVC-CPE blends, including 10 g of CPE. Figures 24 and 25 show the logarithmic plots of G' versus and G" versus frequency (Hz) of PVC/CPE/MAP–POSS nanocomposites at 185 °C, respectively. The PVC/CPE blend exhibited lower storage and loss modulus in the presence of MAP-POSS. The authors observed that the addition of MAP-POSS in low amounts showed a plasticizing and lubricating effect on PVC-CPE molecular chains. On the other hand, both storage and loss modulus increased as the MAP-POSS ratio increased in PVC-CPE blends. It was reported that hydrogen bonding occurred between the oxygen atom of the carbonyl group on MAP-POSS with -HCCl- on PVC and CPE molecules. G' and G" of the blend increased with the incorporation of MAP-POSS due to the

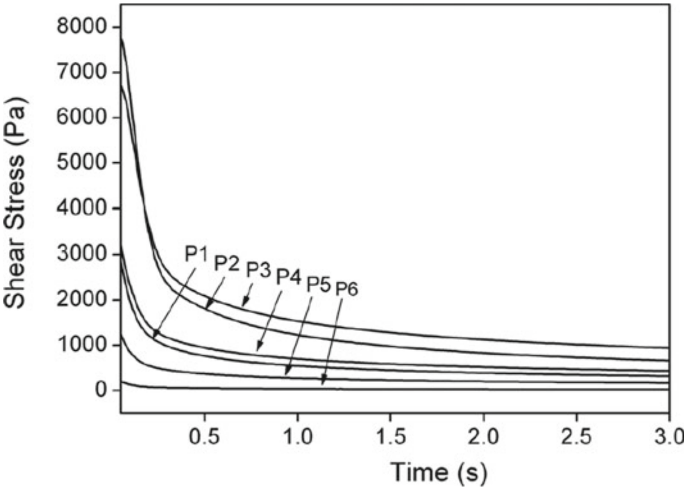


Fig. 23 Stress relaxation of PVC/O-POSS nanocomposites [47]

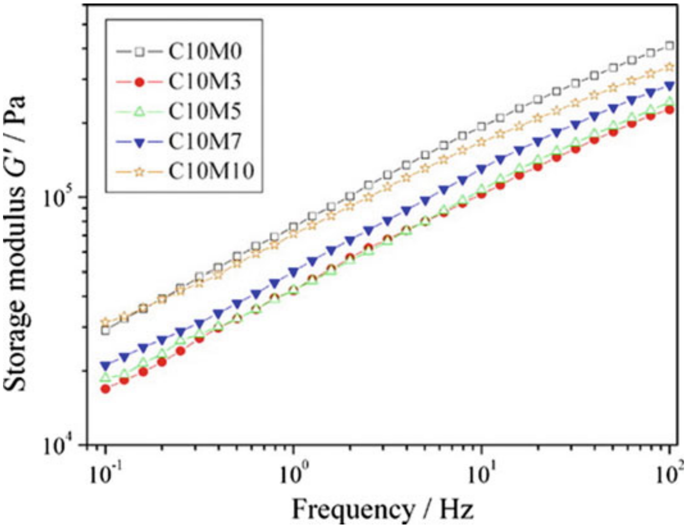


Fig. 24 Relationship between G′ and frequency of PVC/CPE/MAP-POSS melts [48]

restriction of free rotation and movement of molecular chains. When the complex viscosities were compared, decrements were observed with increasing frequency, while increments were observed with increasing MAP-POSS content. However, the complex viscosities were found lower than the neat PVC-CPE blend [48].

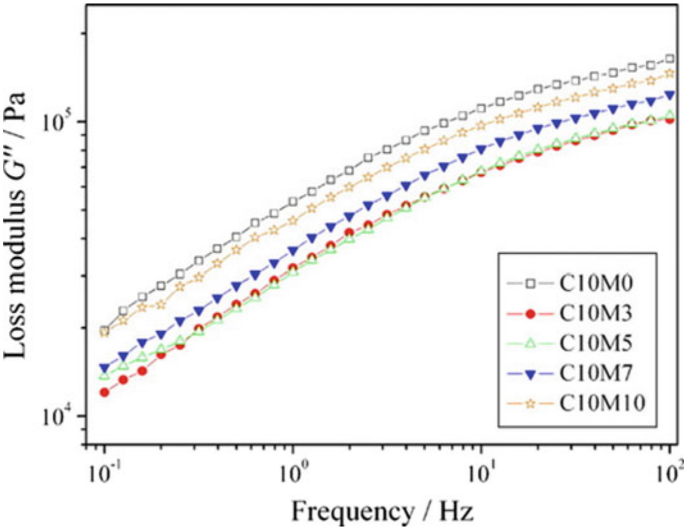


Fig. 25 Relationship between G″ and frequency of PVC/CPE/MAP-POSS melts [48]

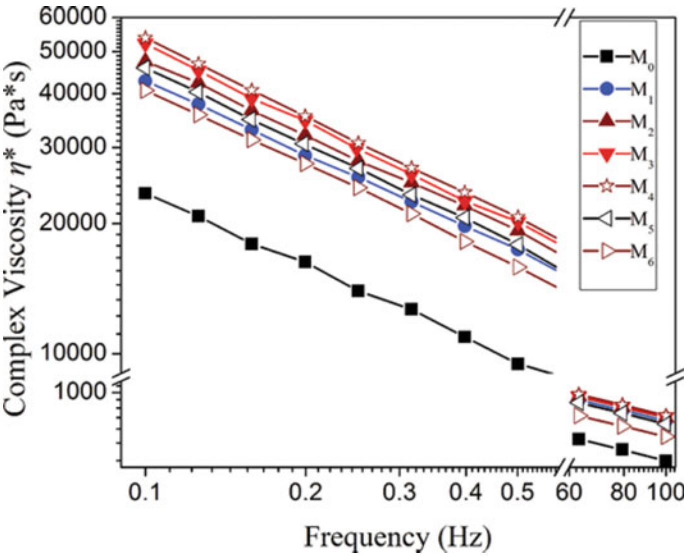


Fig. 26 Relationship between η* and ω for PVC/ACS/MAP-POSS [50]

Yang et al. prepared PVC/ACS nanocomposites consisting different content of MAP-POSS. Frequency sweep measurements were carried out at 185 °C. The storage and loss modulus and complex viscosity values of all MAP-POSS incorporated PVC/ACS nanocomposites were higher than the PVC/ACS. The maximum storage modulus value was obtained in 4 phr MAP-POSS added nanocomposites. On the other hand, rheological properties decreased as the POSS content increased. Complex viscosity values also showed a similar behavior with the modulus values (Fig. 26). While the complex viscosity values increased up to the addition of 4 phr MAP-POSS, the complex viscosity values decreased at higher MAP-POSS contents. This was attributed to the lubricating effect of MAP-POSS for PVC/ACS blends [50].

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Metal Particle Filled PVC Composites and Nanocomposites

Selcan Karakuş and Cemal Özeroğlu

Abstract In recent years, there has been an increasing interest in the research subjects of fabrication, characterization, and modification of metal particles filled PVC composites and nanocomposites used in many applications such as wastewater treatment, energy, fire resistant, polymer electrolytes, and power cable insulation systems. Herein, a comprehensive review of PVC composites/nanocomposites, which have different metal additives, including iron oxide (Fe_2O_3), silver (Ag), copper (II) oxide (CuO), zinc oxide (ZnO), zirconium (ZrO_2), alumina (Al_2O_3), titanium oxide (TiO_2), lithium perchlorate ($LiClO_4$), bismuth(III) oxide (Bi_2O_3), and magnesium carbonate ($MgCO_3$), was presented in this review. In addition, recent developments in investigations of PVC composite/nanocomposites have led to a renewed interest in their chemical resistance, electrical performance, thermomechanical, surface, and physicochemical properties. Finally, the approaches used to PVC composite/nanocomposites with these properties were also highlighted and criticized in detail.

Keywords PVC composite · Nanocomposite · Metal fillers

1 The Fabrication of Metal Particle Filled PVC Composites/Nanocomposites

Poly(vinyl chlorite) (PVC) is the most used polymer after polyethylene and polypropylene and has a wide range of uses in the fields of construction, electrical devices, automobiles, and packaging systems. With this intense interest, the investigations in the subjects of PVC and its composites/nanocomposites have been accounted

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for about 70% of all the studied plastics. The global challenges on energy, biomedical, and environmental problems and difficulties have led to the growing improvement and development of nanostructures by replacing conventional materials or integrating with nanoadditives in PVC based composites. In addition, the investigation of the mechanical property of metal based PVC composites is a continuing issue within the recent scientific strategies. A huge rise in the application of plastic based composite/nanocomposites have become one of the significant issues during the past twenty decades, and various green strategies on high performance metal particle filled PVC composites/nanocomposites have been presented to manufacture the increasing amounts of advanced plastic materials. The major benefits of the nanotechnological productions are the installation of effective, selective, low-cost manufacturing facilities, and to use of minimum energy in the fabrications of advanced smart nanomaterials. Metal particle filled PVC nanomaterials of large specific surface areas, particle nanosizes, and reactive sites are major useful features for large-scale water treatments, biomedical, and electronic applications. In the last few decades, the production of PVC composites/nanocomposites among various high-performance polymer composites/nanocomposites are one of the primary investigative issues due to their excellent properties and different types of fabrication techniques.

This review presentes at addressing the fabrication of metal particle filled PVC materials caused by PVC polymer matrix and metal/metal oxide fillers in presence of plasticizer and other additives such as fillers, pigment dyes, UV absorbers, heat stabilizers depending on the context of nanotechnological applications. With this purpose, the superior characteristics possessed by metal nanofillers make them an significant potential additive for the reinforced PVC polymer matrix. As known, metal nanofillers have added as zero-valent metals, single enzyme nanoparticles(NPs), metal oxides, natural polymers (biopolymers), thermoplastic polymer, and thermoset polymers/coplymers could be added in different types of polymer matrixes. The most commonly used thermoplastic polymer based materials for composite or nanocomposite fabrication include acrylonitrile–butadiene–styrene (ABS) copolymer, acrylic polymers, poly(lactic acid)(PLA), polycarbonates(PC), thermoplastic polyamide(poly(ε-caprolactam) or nylon 6), polyethersulfone (PES or PESU), polybenzimidazole (PBI), polyoxymethylene (POM), polyetherimide (PEI), polyethylene (PE), poly(ether ether ketone)(PEEK), poly(phenylene sulfide)(PPS), polypropylene (PP), poly(p-phenylene oxide) (PPO), polysulfone (PSf), poly(vinyl chloride)(PVC), poly(vinylidene fluoride)(PVDF), and polytetrafluoroethylene (PTFE). In Fig. 1, the schematic diagram of classification and application of PVC composites are given.

The development and fabrication of metal loaded PVC systems have drawn much attention among scientific researchers. In recent years, there has been an increasing interest in the fabrication of metal particle filled PVC composites/nanocomposites because of their excellent application features such as low density, ease of processing, low-cost, thermal, mechanical, biological, and insulating properties. Recent trends in metal particle filled PVC composites/nanocomposites have led to a proliferation of studies on various applications such as thermal insulation systems, protective coating systems, sound insulation materials, new antimicrobial PVC based composite agents,

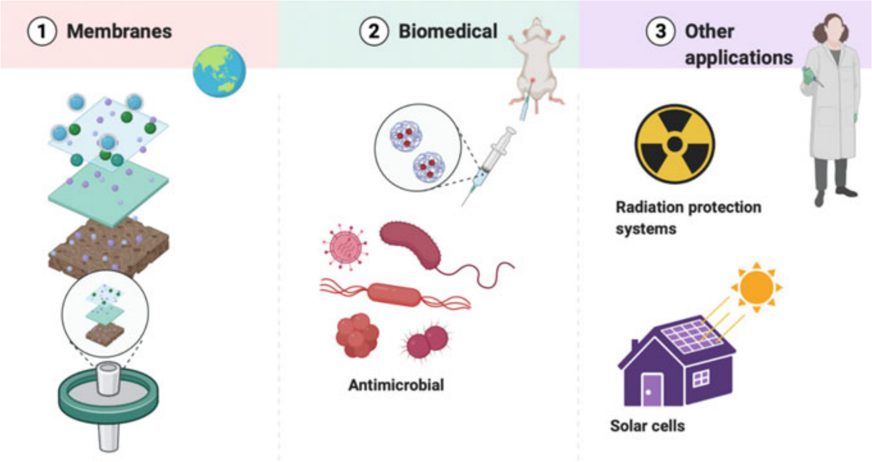

Fig. 1 The schematic diagram of classification and application of PVC composites. **Alt-text**: Different schematic diagrams of classification and application of PVC composites are presented. The shapes of three schematic diagrams of applications of PVC composites are shown. Different types of applications such as membranes, antimicrobial agents and other applications such as radiation protection systems and solar cell systems, respectively are shown

food packaging, piping materials, thermoplastic matrix composite materials, sensors, etc. In particular, it has been proven that the surface properties of metal particle filled PVC composites/nanocomposites such as uniform distribution and dimension have an important role in thermal, chemical, and biological applications. Morever, there have been a number of studies involving nanofillers that have reported the size and shape of the nanofillers widely effect the surface and chemical properties of the structure due to the interaction with matrix and additives. This review covers the recent advances and applications of the metal based PVC composites/nanocomposites, with a focus on the fabrication and design strategy of these composites/nanocomposites and their combination with chemical and biological properties for the advanced nanosystem. In literature, composites and nanocomposites are preferred due their unique surface properties in the range from micro- to nano-size, biological activity, good photostability, thermal stability, and effective adsorption capacity for large-scale water treatment. Inspired by the excellent advantages and challenges of metal based PVC composites/nanocomposites, various materials have been developed with excellent antimicrobial activity against a wide range of pathogenic microorganisms such as yeasts, gram-positive bacteria, and gram-negative bacteria, viruses, and fungi in biomedical applications. Also, the use of metal/metal oxide based nanofillers in a PVC polymer matrix enhances the thermal, optical, chemical, mechanical, and dielectric properties. In Fig. 2, the schematic diagram of properties of PVC composites are given.

Among metal/metal oxide based nanofillers, metal nanoparticles have been commonly used in the fabrication of metal particle filled PVC composites/

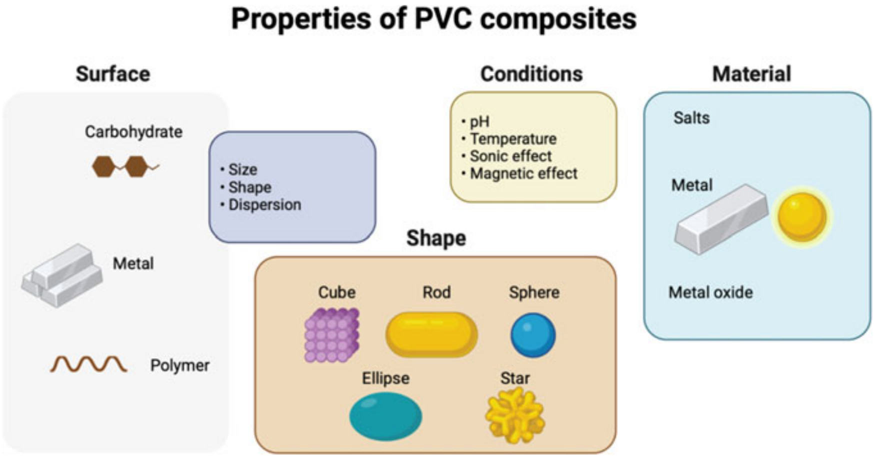

Fig. 2 The schematic diagram of properties of PVC composites. **Alt-text**: The schematic diagram of properties of PVC composites are presented. The shapes of four schematic diagrams of properties of PVC composites are shown. Different types of properties such as surface (carbonhydrate, metal additives, and polymer with different morphologies such as size, shape and dispersion), conditions (pH, temperature, sonic and magnetic effects), materials (salts, metal and metal oxide particles), and shapes (cube, rod, sphere, ellipse and star), respectively are shown

nanocomposites. As some nanofillers as metal and metal oxide exhibit high surface to volume ratio, high affinity, high surface reactivity, morphology, small size, and excellent interaction with the PVC matrix due to intermolecular forces and hydrogen bonding. Recently investigators have examined the effects of the amount of loading of nano-fillers on the nano-composites to obtain the superior properties and results showed that the optimum rate value of nanofillers is smaller than 10 wt% in the structure [1]. Common examples of thermoplastic polymer based systems used in composites or nanocomposites for the fabrication of novel advanced materials involve PVC that exhibit high strength, high chemical and mechanical stability, low temperature resistance, lightweight and easy to use. Among many properties of metal nanofillers based PVC materials, five of the most notable are (a) electrical conductivity, (b) mechanical strength, (c) flexibility, (d) thermal stability, and (e) surface functionality. With these advantages, an extensive effort has been devoted to design and incorporate metal /metal oxide nanoparticles into the PVC matrix in recent years. Various kinds of inorganic nanoparticles such as iron oxide (Fe_2O_3), silver (Ag), copper (II) oxide (CuO), zinc oxide (ZnO), zirconium (ZrO_2), alumina (Al_2O_3), titanium oxide (TiO_2), silicon dioxide (silica, SiO_2), lithium perchlorate ($LiClO_4$), bismuth(III) oxide (Bi_2O_3), calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) have been used as a additive to fabricate novel composite and nanocomposite materials, which were improved with metal particle incorporation.

2 Iron/Iron Oxide Filled PVC Composites/Nanocomposites

As a general trend, encapsulation of inorganic nanofillers in a thin polymer matrix layer for use in different applications is necessary to reduce in vivo toxicity and increase anti-corrosion protection. With this purpose, various polymer-based encapsulation methods have been investigated for the development of smart metal /metal oxide fillers based nanoformulations. Iron/iron oxide nanofillers with unique superparamagnetic performance are widely used in various applications such as biomedical, preclinical, clinical, cosmetic, wastewater treatment, textile, paint, food safety, sensors, etc. In literature, iron/iron oxide based PVC composites/nanocomposites have been prepared different methods such as spin-coating method, stretching, chemical co-precipitation method, coating, sintering, electrospinning method, phase inversion method, phase separation, track-etching, and sol–gel method in literature.

Exposure to ultraviolet radiation has a major role on the photooxidative degradation of polymer based materials. It is related to molecular weight, exposure time, compositions of materials, breaking of the chain of the polymer matrix, and generating of free radicals. Like many polymer based materials, thermoplastic PVC are influenced by exposure to UV irradiation with a rapid color change and gradual embrittlement. The metal filler loaded PVC polymer matrix is an increasingly important area in various industrial applications. Especially, metal/metal oxide nanoparticles could be incorporated into the PVC polymer matrix to effect the UV blocking properties of materials. In the previous reports of development of UV-protective materilas based on metal fillers loaded nanocomposites, the fabrication and characterization of metal nanoparticles in the PVC polymer matrix have been thought of as a key factor in applications due to the ultraviolet protection performance. The addition of metal fillers in PVC polymer matrix significantly changes the morphology, structure of the metal fillers/PVC based composites, and mobility of free radicals. As known, different stabilizing agents such as UV absorber metals/metal oxides, excited state molecules, light screeners, and free radical scavengers have been used. With this purpose, Yang et al. described the photodegradation effect of FePcCl16 based on PVC [2]. The novel perchlorinated iron (II) phthalocyanine (FePcCl16) based PVC composite film was prepared using a simple spin-coating method to show their photodegradation activities. According to the experimental results, it was shown that the PVC–FePcCl16 composite film had a high photodegradation activity and good photostability in the photoreaction due to the intermolecular energy transference.

Water pollution is s a major global environment issue and it threates health and aquatic ecosystems. With increasing consumption and product opportunities, industrial and scientific studies have gained great momentum in the last decades. The world, which consumes a large amount of products, is faced with the problem of increasing quality and safety problems of water. Especially wastewater containing different pollutants such a many pathogenic organisms, dissolved effluent organic matter, industrial effluents, dyes, pigments, toxic contaminants, proteins, heavy metals, drugs, polysaccharides, dissolved solids, and organophosphorus pesticide is an important source of water pollution. With this reason, advanced technologies have become significant solution and strategy of health problems in smart wastewater treatments. Many different polymers such as polyacrylonitrile (PAN), poly(vinyl alcohol) (PVA), cellulose acetate (CA) polymer, PES, PSf, and PVDF have been focused on the development of polymer based membrane seperation systems in literature. Since the 1980s, PVC composite based membranes have been investigated and reported for their high performance purification, efficiency, and selectivity in environmental separation applications. Recently, high performance inorganic fillers based PVC membrane separation approaches are designed with different separation mechanisms for water and wastewater treatment processes in the advanced environmental technology. In the case of inorganic filler based PVC composite membranes, Liu et al. reported a novel magnetic Fe_3O_4/oxidized multi-walled carbon nanotubes (o-MWCNTs)/PVC composite membrane using non-solvent induced phase separation method and chemical co-precipitation method [3]. In this study, they showed that the directional migration of Fe_3O_4/o-MWCNTs NPs was observed under magnetic field due to their controllable nanotubular structures and electrostatic interaction between additives and PVC matrix.

Since PVC matrix has a highly hydrophobic structure, fouling problem occurs in PVC-based membranes. For this reason, inorganic fillers are used to improve the performance of the PVC composite membranes. Besides severely increasing the performances of the metal fillers loaded PVC membranes, the production of Fe_3O_4 based PVC composite is based on different strategies such as sonication, microwave, wet chemical, mechanical, physical, electrochemical, etc. With this purpose, Chiscan et al. developed novel electrospun Fe_3O_4 based PVC composite nanofibers with small diameters ranging from 100 to 600 nm using a versatile electrospinning method in the microwave assisted absorption applications [4]. Taha et al. fabricated novel $La_{0.95}Bi_{0.05}FeO_3$ based PVC nanocomposites using a sol–gel method and they compared their excellent thermal, optical, and dielectric properties [5]. In this report, they combined the PVC matrix with $La_{0.95}Bi_{0.05}FeO_3$ nanoparticles additives. The characterization results indicated that the nanostructure had an orthorhombic structure and uniform surface morphology with some agglomerations. In addition, they showed that the nanostructure had thermal stability and decreased the film transparency due to the complexation between nanoparticles (crystallite size, 39.30 nm) and PVC matrix. Additionally, there have been four types of membrane separation categories: (a) reverse osmosis, (b) nanofiltration, (c) microfiltration, and (d) ultrafiltration. To improve separation and mechanical performances of the metal based PVC membrane, Demirel et al. demonstrated a novel Fe_2O_3 nanocomposite based PVC membrane with unique properties such as rejection, pure water flux, and antifouling for advanced ultrafiltration separation systems [6]. In this report, the Fe_2O_3 nanocomposite based PVC membrane was prepared using a phase inversion method. According to the experimental results, they showed that the addition of Fe_2O_3 nanocomposite with varying amounts (0–2.0% wt.) improved the performance of the Fe_2O_3 nanocomposite based PVC composite membranes with high capabilities, high sodium alginate (SA) rejection rate, and good antifouling properties in the wastewater treatment applications. In this regard, previous research has indicated that various iron/iron oxide nanostructures have a positive impact on the quality improvement and performance due to the uniform disperison of particles in the optimum experimental conditions.

3 Ag Filled PVC Composites/Nanocomposites

One key focus in nanotechnology is the investigation of Ag nanoparticles for drug delivery systems, imaging agents, biosensors, therapeutic nanoagents, chemotherapeutic systems, and nanomaterial-based antimicrobial coatings. Several studies investigating Ag nanostructures PVC composites/nanocomposites based have been carried out on the development of antibacterial, antifungal, antialgal, and antifouling agents. In 2018, Behboudi et al. developed novel antifouling and antibacterial Ag nanoparticles based PVC hollow fiber ultrafiltration membranes using a wet spinning method [7]. According to the antibacterial test results of prepared Ag nanoparticles based PVC membranes, it was clear that there had been no bacterial growth of *Escherichia coli* (*E. coli*) using the zone inhibition method. With this motivatition, the experimental results revealed that antimicrobial activity of Ag nanoparticles based PVC membranes increased with the homogeneous distribution of Ag nanoparticles in the PVC polymer matrix.

This review presented possibility and opportunity to advance the understanding of the stability and dispersion of metal fillers in the PVC polymer matrix to improve a strong repulsion between fillers aqueous medium using different surfactants or other surface modifiers. For this purpose, Zampino et al. prepared novel Ag - zeolite with varying amounts (2–20%, w/w) based PVC composites and the experimental results showed that the prepared composites had a significant antimicrobial activities against *E. coli* and *Staphylococcus epidermidis* (*S. epidermidis)* [8]. Braga et al. (2018) reported the preparatation of antimicrobial Ag nanoparticles based PVC films. This film was prepared using a single solvent based film casting method. The antimicrobial results showed that Ag nanoparticles based PVC films had high antibacterial and antifungal activities against *Bacillus subtilis*, *Aspergillus niger*, and *Fusarium solani* [9]. Similar approach for metal based PVC film was developed by Sun et al. (2021), who reported synthesis of Ag nanoparticles(Ag-NPs) with PVC polymer matrix using a simple, efficient, and low-energy two-step autocatalytic deposition method [10].

4 Cu/CuO Filled PVC Composites/Nanocomposites

Previous studies have reported that CuO fillers have antimicrobial property, in vitro and in vivo biodegradability, biocompatibility, thermal stability, chemical stability, electron affinity, and a bandgap energy ranging from 1.2 to 2.8 eV. Over the past 20 years, PVC matrix has played a target function in the fabrication of the PVC based wires and cables insulation systems in electrical and electronic devices. Many studies showed that the use of metal based nanofillers for the insulating PVC based composites/nanocomposites to eliminate their limitations of heavyweight, corrodibility, and high manufacturing cost. Furthermore, metal based nanofillers have enhanced the electromagnetic interference shielding efficiency of insulating polymers. Attributing to the excellent electromagnetic interference shielding performance, Rani et al. developed a novel flexible shielding material including montmorillonite nanoclay and CuO nanoparticles based PVC nanocomposites film using a solution casting method. In this report, it was found that the electromagnetic interference shielding efficiancy of the proposed nanofillers based PVC film were be − 30 dB (0.3 wt% of CuO NPs) and − 35 dB (4.7 wt% of MMT) for nanocomposites [11]. In another study, Abouhaswa et al. prepared CuO based PVC nanocomposites in the presence of different CuO nanoparticles ratios (0.25 -15.0 wt%) using a sol–gel method with an average particle size of 27.33 nm. They found well distribution of CuO nanoparticles on the PVC matrix, high optical and dielectric properties in the presence of 15.0 wt% of CuO nanoparticles [12]. With regard to the antibacterial performance for CuO coatings, Rodríguez-Llamazares et al. prepared novel CuO/Cu_2O based PVC composites in a twin-screw extruder using a melt-blending method and suggested that the proposed Cu_2O based PVC composites had an effective antimicrobial activity against *E. coli* in the presence of 1% of metal fillers [13]. For example, a novel Cu–MoS_2 hybrids based PVC composite reported by Zhou et al. demonstrated improved thermal stability. In this study, the Cu–MoS_2 hybrids based PVC composite was prepared by a facile wet chemical method and it had a high thermal stability and inhibited influenced the release of pyrolysis products with 0.5 wt% Cu–MoS_2 hybrids [14]. In summary, Cu/CuO fillers are favorable nanostructures for various applications because (1) the high conductivity of the PVC support composites, (2) chemical bonding at surfaces between PVC matrix and Cu/CuO fillers, and (3) colloidal and thermal stability.

5 ZnO Filled PVC Composites/Nanocomposites

Drawing on an extensive range of previous reports, the scientists and researchers set out the different preparation methods for the development of ZnO nanoparticles (ZnO-NPs) filled PVC composites/nanocomposites. Previous studies have confirmed the ZnO-NPs have been decorated with different shapes such as hexagonal wurtzite, cubic zinc blend, and cubic rocksalt under different experiemental conditions such as solvent mixtures, microwave, ultrasonic, UV and visible light. The n-type semiconductor ZnO fillers have excellent properties such as low-cost, nontoxic in vitro and in vivo, high mobility, high chemical stability, high antibacterial activity, high antifungal activity, good biocompatibility, permeability, ultraviolet light absorption performance with a high free-exciton binding energy of 60 meV and a wide band gap of 3.37 eV at 25 °C. For instance, El-Lateef et al. reported in 2020 that different metal oxide fillers such as ZnO, TiO_2, and ZnO-TiO_2 based PVC nanocomposite systems were prepared and they could be promising corrosion protection materials in acidic solutions medium [15]. According to corrosion results, they observed that the ZnO, TiO_2, and ZnO-TiO_2 based PVC composite materials had high protection capacities in ranges from 96.2% to 97.1% against corrosion of carbon steel at 10 days after exposure.

An alternative method for preparing nanoscales homogenous ZnO based PVC films is by using Linda et al. designed a novel thin film composed of cellulose/PVC/ZnO with a smaller size for enhanced photo degradation of dyes (congo red and crystal violet dyes) under UV light irradiation in a very short UV irradiation time [16]. Donnadio et al. developed novel antibacterial and antifungal nanoagents including PVC - ZnO nanoparticles with different shapes such as rods, rod flowers, and petal flowers using a hydrothermal process. According to the experimental results, it was observed that the rod flower shaped PVC - ZnO nanoparticles had more effective the antimicrobial activity against *Staphylococcus aureus* (*S. aureus)* and *Candida albicans* (*C. albicans*) due to the covalently bonded ZnO nanoparticle uniform dispersion on the mercaptopropyltrimethoxysilane modified surface of PVC [17]. In 2014, Machovsky et al. developed a novel antibacterial ZnO fillers based PVC composites with containing 0.5–5 wt.% of ZnO particles by a microwave method. This study contributed to the fabrication and antibacterial activity of novel ZnO fillers based PVC composites with microparticulate character against different pathogens such as *E.coli* and *S. aureus* [18]. Research on applying antibacterial ZnO nanoparticles based PVC bed sheet to advanced coating materials have been reported by Kurniawanl et al. ZnO nanoparticles based PVC composites were prepared using a multiple-layer coating technique and examined against *S. aureus*, *S. epidermidis*, *E. coli*, and *P. aeruginosa* [19]. In another study, polyamide and chitosan modified ZnO nanoparticles based PVC nanocomposite used as a novel nanoplatform have been achieved on article substrates by Hajibeygi et al. developed using a solution casting method [20]. According to the experimental results, it was clear that the correlation between polyamide - chitosan modified ZnO nanoparticles and PVC matrix was interesting because it improves significant effects on the thermal stability (195 °C–243 °C, 5% mass), low heat release rate (131 W/g for PVC matrix and 104 W/g for nanocomposite), and mechanical property (35.4 to 53.4 MPa) of polyamide - chitosan modified ZnO nanoparticles PVC nanocomposite. In order to improve the surface, thermal and chemical properties of PVC matrix, ZnO filler additives were used during the fabrication process.

6 ZrO_2 Filled PVC Composites/Nanocomposites

A number of researchers have reported that ZrO_2 fillers have a wide band gap in ranging from 5.0 to 7.0 eV, high active biocompatibility, and different shapes such as nanofluid, nanodot, and nanocrystal. In 2018, modified ZrO_2 fillers have been explored to prepare bovine serum albumin (BSA) modified ZrO_2 nanoparticles based PVC nanoformulations via an ultrasonic route (the frequency: 25 kHz) [21]. This study was published by Mallakpour et al., it was focused on the advanced thermal, optical, mechanical and chemical properties of the spherical BSA - ZrO_2 nanoparticles based PVC nanocomposites. The prepared nanocomposites had a particle size of $\sim$ 25 nm due to the acoustic cavitation effect. The BSA as a protein was used as a modifier agent to improve the affinity towards ZrO_2 nanoparticles, dispersion in PVC matrix and to reduce aggregation of ZrO_2 nanoparticles. The energy gaps values were found to be 3.6 eV for ZrO_2, 3.6 eV for BSA - ZrO_2 nanoparticles, 4.4 eV for BSA - ZrO_2 nanoparticles based PVC nanocomposites, respectively. In summary, they found that the BSA - ZrO_2 nanoparticles based PVC nanocomposites had high thermal stability (800 °C), good mechanical, and wettability properties (contact angles (°) values: 71 for PVC and 61 for PVC nanocomposites) compared to the polymer PVC matix. In addition, PVC can be used in the polymer blend matrix with different polymers such as polystyrene (PS), poly(vinyl formal) (PVF), carboxylated poly(vinyl chloride) (CPVC), glycerol, PC, PAN, PVDF, etc. Blending PVC polymer with different polymers can support to obtain low cost materials with differences in coagulation bath condition, temperature, solvent ((N-methyl-2-pyrrolidone, dimethylacetamide (DMAc), tetrahydrofuran (THF), and N,N-dimethylformamide (DMF)), solvents ratio, viscosity, membrane thickness, concentration, solubility, evaporation time, and thermodynamic property (interaction between polymer and metal additives). In addition, a number of researchers have reported that different salts such as sodium chloride (NaCl), potassium chloride (KCl), ammonium chloride (NH_4Cl), calcium chloride (($CaCl_2$), and magnesium chloride ($MgCl_2$) have been used in the fabrication of sensitive PVC-membrane ion selective electrodes. In the past few years, chemically modified PVC membranes are subject to an attractive issue to obtain the high performance materials with controlled morphology, pore size, and pore density of nano-fillers. One of the most significant current strategies and discussions in blend polymer matrix is the modification of the polymer matrix surface. For this reason, recent studies have focused on chemically modified the surface of the PVC matrix to improve conductivity, fouling resistance, and hydrophilicity properties. The fabrication and characterization of lithium bis(oxalato)borate (LiBOB) - ZrO_2 nanofillers based PVC/ PVDF polymer blend composite polymer electrolytes was reported by Aravindan et al. [22]. The ZrO_2 nanofillers based PVC composite was prepared using a solution casting method by varying amount of the filler (2.5 wt%-10 wt%). In this study, they also emphasized on the the formation of a amorphous structure in the presence of fillers by increasing the ionic conductivity using ZrO_2 fillers in the crystalline structure of the composite polymer electrolytes.

7 Al_2O_3 Filled PVC Composites/Nanocomposites

Mimicking nature in engineering applications and improving properties of Al_2O_3 fillers based materials have been considered as an advanced strategy in the investigation and evaluations of high performance materials. Recently, some engineers and scientists have examined the effects of Al_2O_3 fillers on polymer/polymer blend matrix due to their unique properties such as low-cost, optical performances, high electrical resistivity, and high thermal conductivity. Al_2O_3 nanoparticles based PVC composites show a high light weight, workability, and mechanical performance. They also improve electrical insulation property for high-voltage mateials in industry applications and anti-knocking ability for the improvement of the biodiesel property. Moreover, Al_2O_3 nanoparticles based PVC composites exhibit excellent optical properties. For example, Taha et al. fabricated Al_2O_3 nanoparticles based PVC nanocomposite films with varying amount of the Al_2O_3 fillers (2 wt% - 6 wt%) using a solution casting method. According to the characterization results, it was observed that the prepared Al_2O_3 based PVC nanocomposite films well distributed in PVC polmer matrix and had an average particle size of 10 nm. In this study, optical observations showed that the proposed Al_2O_3 nanoparticles based PVC nanocomposite films had an excellent optical performance with high refractive index values (> 1.65) and could be a promising multifunctional nanomaterial for optical and photovoltaic devices in solar cells systems [23]. In literature, metal/metal oxide particles based PVC membranes have been reported with large specific surface areas, small particle sizes, and reactive sites for the adsorption of pollutants in advanced water treatments. The rapid increase in the use of metal nanofillers in applications, Ahmad et al. developed a novel TiO_2/Al_2O_3 based PVC membranes using a sol–gel method for wastewater treatments. According to the photocatalytic experiment results it was obsrved that the prepared TiO_2/Al_2O_3 based PVC membranes had an excellent photocatalytic performance with 95% of Congo red dye degradation [24]. However, the prepared TiO_2/ Al_2O_3 composite membranes showed more high adsorption capacity than Al_2O_3 membrane due to the porous structure, pore size distribution, and adsorption sites of the TiO_2 particles among other PVC templates.

8 TiO_2 Filled PVC Composites/Nanocomposites

More recent attention has focused on the provision of the hydrophilicity and antimicrobial activity of TiO_2 based filtration membranes due to their perfect optical property, good antifouling property, low cost, high chemical stability, low cost, and nontoxicity. There are various previous reports about the investigation of the TiO_2 particles based polymer composite films as an antimicrobial agent against pathogenic microorganisms. With this purpose, Haghighat et al. prepared a novel Ag/TiO_2 nanoparticles based PVC ultrafiltration membrane and observed that the addition of 1.0 wt% Ag/TiO_2 nanoparticles improved hydrophilicity with the lowest water contact angle value (56°) [25]. Furthermore, the prepared Ag/TiO_2 nanoparticles loaded PVC ultrafiltration membrane exhibited good antibacterial activity against Gram-negative bacterias such as *Pseudomonas aeruginosa* (*P. aeruginosa*) and *E. coli*, and *S. aureus* and Gram-positive bacterias. In another study, Behboudi et al. prepared novel antifouling and sponge shaped TiO_2 particles (2.0 wt%) based PVC ultrafiltration membranes using via a non-solvent induced phase separation method with an uniform asymmetric structure [26]. The contact angles of the PVC membran with various amounts of TiO_2 particles (0.0- 2.0 wt%) were examined by a contact angle goniometer and contact angle measurement results showed that hydrophilicity of PVC membranes enhanced with increasing amount of TiO_2 particles. It was concluded that the addition of 2.0 wt.% TiO_2 (contact angle:8.2°) increased the hydrophilicity of metal fillers based PVC ultrafiltration membranes by blending TiO_2 particles in the polymer PVC membrane matrix.

9 Other Metal Fillers Based PVC Composites/ Nanocomposites

Not limited to these mention metal fillers, other metals, such as Li, Bi and Mg, were also studied for the development of metal fillers based PVC composites/ nanocomposites. The current literature on studies with different metal additives ($LiClO_4$, Bi_2O_3, $MgCO_3$, etc.) loaded PVC composites pay particular attention. In 2018, Ahmad et. al prepared and characterized of novel $LiClO_4$ based PVC composite electrolyte [27]. In this study, they examined the conductivity of PVC- $LiClO_4$ based composite polymer electrolyte in the presence of different fillers such as ZnO, TiO_2, and Al_2O_3. According to the experimental results, it was observed that the prepared PVC- $LiClO_4$ based composite polymer electrolyte with 20% of ZnO particles had the highest ionic conductivity achieved was to be 3.7×10^{-7} S cm^{-1}. Moreover, the value of the glass transition temperature of the the $LiClO_4$ based PVC composite was decreased with the addition of high amount of fillers due to the increasing of formation of amorphous structure.

Over the past decade most research in Bi_2O_3 particles has emphasized the use of low dose X-ray equipments. As known, Bi_2O_3 particles based materials have attracted attention for the development of advanced mammography devices and X-ray equipments. In 2021, Nuñez-Briones et al. developed a novel Bi_2O_3 particles based PVC composites for the low energy X-ray radiation shielding in the applications of radiation protection materials [28]. The Bi_2O_3 particles was prepared using a dual method with the mechanical milling method and molten salt method. According to the experimental results, the prepared Bi_2O_3 particles based PVC composites exhibited low transmission value for the addition of 50%wt of Bi_2O_3 particles based PVC composites at X-ray tube voltages ranges of 20 kV – 30 kV. With the continuous impreovement of metal fillers based PVC composites, graphite/MgO fillers based PVC composites was fabricated using a vulcanizing process and were demonstrated by Li et al. in 2019 and it was reported as a novel type of thermally stable composite. The thermal stability of the graphite/MgO fillers based PVC composites showed a higher glass transition temperature value (88.60 °C) and decomposition temperature value (305.59 °C) as compared to PVC [29]. In another study, the fabrication, surface, structural (the crystal size: 35–40 nm) dielectric (frequency: up to 50 kHz), and optical properties (the optical band gap: 5.14–4.54 eV and the direct transition: 4.50–3.75 eV) of PVC-PbO nanocomposites with varying amounts of PbO (0.2–25% wt.) reported by Elsad et al. [30].

10 Challenges and Future Research

The objective of this chapter is to review the novel metal fillers based PVC composites developed for various applications. In this review, the morphology, structural, antifungal, antibacterial activities, optical, mechanical, and electrical of metal fillers based PVC composites as well as the functions affecting their superior advantages were compared. Till now, various preparatition routes of metal fillers based PVC composites have been used for advanced properties such as controlling small size, uniform particle distrubition, surface functionality, biocompatibility, and increasing photocatalytic activity, antimicrobial activity against pathogens, degradation of dyes.

Surprisingly, the improved experimental results can be observed using synergistic combination methods to obtain smart metal fillers based PVC composites /nanocomposites. However, these rapid changes are having a serious effect on the uncontrolled accumulation of nanomaterials. Along with this growth in PVC membrane, however, there is increasing concern over to an accelerating amount of micro and nanoplastics with their smaller sizes. To date there has been little agreement on the systematic methods to determining the toxicology of nanomaterials. The experimental data are rather controversial, and there is no general agreement about the role of the accumulation of nanoparticles in target area unintentional hazardous effects. In this regard, previous studies have consistently shown that these results are not adequate to understand the nanotoxicity of metal fillers based PVC composites. As a result, this advanced and high performance metal fillers based PVC composites /nanocomposites could be used in varous applications, but more research is needed on the in vitro and in vivo toxicity assessment of nanofillers.

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Nanocomposite of PVC with CNT

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Abstract Poly(vinyl chloride) (PVC) with various advantages such as good chemically stability, biocompatibility and relatively low price could be one of the widely used polymers in industries. However, low electrical and thermal conductivity and poor mechanical strength have been the main problems of PVC limiting its practical applications sofar. Over the past decade, to enhance electrical and thermal conductivity and mechanical strength of PVC, a lot of research has been carried out using various nanofillers. Carbon nanotubes (CNTs) with high modulus (1 TPa), high strength (stronger than steel), high thermal stability (2800 °C in vacuum), excellent electrical conductivity (higher than copper), and high thermal conductivity (higher than diamond) are excellent candidates for PVC-based nanocomposites preparation as nanofillers. Recently, PVC/CNTs nanocomposites have received considerable attention as an interesting and important research area, worldwide. But, further research on optimization of the PVC/CNTs nanocomposites properties is necessary to find their future applications for practical uses. Current progresses in development of PVC/CNTs nanocomposites are being reviewed, in this chapter.

Keywords Poly(vinyl chloride) · Carbon nanotubes · Composite · Nanocomposite · Nanofiller

1 Introduction

For many years, combination of two or more materials to create new materials with improved properties has been a common procedure. Composites as a combination of two or more materials provide characteristics that not achievable by either material alone. Compared to the traditional materials, composites are lighter, stronger and less expensive. Therefore, today, composites have become increasingly necessary in a wide variety of structural applications [1, 2]. Composites are fabricated by matrix

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materials and fillers, in which the former surrounds the latter. The fillers impart their special characteristics to the matrices. With rapid development of composites, polymers with good processibility have replaced many of the conventional matrices of composites [2].

Polymers with distinct characteristics including simplicity of manufacture, light weight, and ductility are commonly employed in various applications. Low electrical conductivity, poor mechanical strength and low thermal stability are the main problem of polymers that limit their practical applications. Therefore, improving electrical, mechanical and thermal properties of polymers using fillers including fibers, platelets, or particles has recently received much attention. Even with minimal level of fillers, improvements in characteristics of polymers could often be obtained [1, 2].

In recent decades, polymer nanocomposites (PNCs), made up of nanofillers embedded in polymer matrices, have received much attention by researchers and industries. The PNCs properties depend on their interfacial characteristics beside properties of their individual elements. Large interface area between the nanofiller and the polymer matrix is a key issue for PNCs. According to the theoretical assumptions, the objective of PNCs is to create large interface between nanofillers and polymer macromolecules. In comparison to traditional polymer composites containing microfillers, the larger interface between nanofillers and polymer macromolecules results in remarkable properties in PNCs [3]. These properties can also be related to the properties of nanofillers (size, shape, and surface area), and polymers (molecular weight, chemistry, and architecture), and fabrication procedure (concentration of nanofillers, nanofillers/polymer interaction, and nanofillers dispersion in polymers). In addition, the nanofillers can impart their functionality to the polymer matrices including thermal, electrical and mechanical properties. Importantly, PNCs retain the polymers' desirable features, such as processability and low mass density [4]. For example, incorporation of nanofillers to rubber matrix of car tires can boost mechanical strength, wear resistance, and traction with preserving low cost and weight [5]. PNCs have features that make them suitable for a variety of applications, including land and air transportation vehicles (automotive and aerospace sectors), as well as sports equipment. PNCs also have good barrier, permeability, and selectivity properties, making them good candidates for gas separation and water and wastewater treatment as well as food packaging [6–12]. For example, blending fumed silica as nanofiller with poly(4-methyl-2-pentyne) (PMP) results in significant increase in both n-butane/methane selectivity and n-butane permeability, two properties that are frequently in competition [13]. On the other hands, incorporation of nanofillers into polymer matrices can contribute functional features, particularly optical and electrical capabilities. For example, addition of silver nanowires, carbon nanomaterials, or other conductive nanofillers into insulating polymer matrices can increase their electrical conductivity [14–17].

Polyvinyl chloride (PVC) as a widely-used polymer is inevitable for our modern daily life. Various applications of PVC include packaging, bottles, electrical cables insulation, plastic cards, pipes, clothing, inflatable products and etc. The PVC properties can be tuned by using fillers for different applications, such as clay, glass, calcium carbonate bamboo, pine flour, and wood fibers. Carbon Black (CB) can be used effectively as PVC filler [18]. As reported in literature, elongation at break of the CB-PVC composite decreases with increasing CB amount, but tensile strength of the CB-PVC composite increases with increasing CB amount until 15 wt%, then decreases. Nanostructured materials (nanofillers) are frequently used as PVC reinforcing agents [19]. Han Wang et al. reported fabrication of the PVC nanocomposites containing multilayer graphene (MLG) with improved glass transition temperature and tensile modulus [20]. Sajini et al. reported fabrication of PVC nanocomposites filled with graphene with high thermal stability and mechanical strength [21].

Carbon nanotubes (CNTs) with unique characteristics including high thermal stability (2800 °C in vacuum), high modulus (about 1 TPa), high strength (100 times stronger than steel), excellent electrical conductivity (1000 times higher than copper), high thermal conductivity (2 times than diamond), high aspect ratio and high flexibility are excellent candidates for PVC-based nanocomposites preparation as nanofillers. However, van der Waal interactions between CNTs prevent their widespread usage as PVC nanofillers, because CNTs with inert surface tend to aggregate in the polymer matrix. Uniform CNTs dispersion in the polymer matrices can improve PNCs characteristics, significantly. Hence, to avoid CNTs agglomeration and improve their dispersion within organic solvents and polymer matrices, CNTs functionalization with specific functional groups is of great importance. CNTs functionalization can modify CNTs physical and chemical properties, resulting in fabrication of CNTs-based PNCs with improved properties and performance for various applications [22–26].

Current progresses in preparation and characterization of PVC/CNTs PNCs are being reviewed, in this chapter.

2 CNT-Based PNCs Preparation

Uniform CNTs dispersion in polymer matrices is a critical issue in PNCs preparation. The polymer/CNTs properties can be improved by several factors including CNTs distribution and orientation in the polymeric matrices, surface adhesion between the both components (CNTs and polymers) and manufacturing processes. Solution mixing, melt mixing, and in-situ polymerization are some techniques which can be used to make CNT-based PNCs [27–29].

2.1 Solution Mixing

The simplest and most widely used technique for CNT/PNCs preparation is called solution mixing or solvent molding. This method involves CNTs dispersion in PVC solution by energetic agitation, controlled solvent evaporation and casting CNTs/PVC nanocomposite films on substrates surface. Upon solvent evaporating, PVC chains may reassemble and wrap CNTs as nanofillers. Agitation can be performed by shear mixing, refluxing, magnetic stirring, and sonication as the most commonly used methods [30]. It is well known that simple magnetic stirring is ineffective in completely dispersing intact CNTs in solvents, and the use of high-speed shear mixing or ultrasonication is more effective in formation of the CNTs dispersion. Dispersion, emulsification, comminution, and activation of nanomaterials in solvents are all common uses of sonication. As reported in literature, sonication as a high-speed agitator or mixer is useful in dispersing aggregated and entangled CNTs in solvents for PVC-based PNCs preparation [31]. Although sonication can be used to break CNTs aggregation in solutions, sonication of raw CNTs is not usually enough due to re-aggregation of CNTs after stopping sonication. Surface modification of CNTs that is accomplished by adding functional groups to the CNTs surface is another method to create desired and permanent CNTs dispersion. In some cases, the functional groups of CNTs and the polymer matrices may be incompatible. Although solution mixing method has a number of advantages, for the extensive use of this method, the effective removal of solvents used during the procedure remains as a significant problem. In other words, high solvents cost and their disposal have negative effects on scaling-up of this method [32, 33].

2.2 Melt Mixing

Melt mixing is one of the most efficient and environmental-friendly methods of PNCs production. This method involves heating a mixture of polymer and nanofiller (CNTs) to generate a viscous liquid. In other words, this method consists of CNTs dispersing in molten polymer matrix by mechanical shearing action [34–40]. In this method, a shear mixer improves the CNTs dispersion in the molten polymeric matrix using extrusion or injection. High temperature shear mixer can also be used to automatically disperse CNTs into polymer matrix [41]. Compared to the solution mixing method, one of the challenges of the melt mixing method is the lower CNTs dispersion in the polymer matrix due to the higher viscosity of the dispersion media (molten polymeric matrix) [42]. Melt mixing is performed in the presence of an inert gas including argon, nitrogen, or neon. Melt mixing is an environmental-friendly method due to the absence of organic solvents and is compatible with current industrial processes including injection and extrusion molding. Therefore, the melt mixing method has become more popular, due to its potential in industrial applications for mass production and also its cost-effectiveness. Poor dispersion of nanofillers in the polymer matrices, specifically in higher nanofiller loadings is also the main disadvantage of this method which can be afforded by the CNTs functionalization. Crushing and shortening of nanofillers (CNTs) is another disadvantage of this method due to strong shear forces applied for the nanofillers dispersing that can affect negatively PNCs properties [34–40].

2.3 In Situ-Polymerization

In situ-polymerization has been used extensively in the last decades for PNCs preparation with excellent dispersion and distribution of nanofillers in polymeric matrices. This method involves nanofillers mixing in a monomer (or monomers) or a monomer (or monomers) solution, and then polymerization in the presence of the dispersed nanofillers. Both thermoplastic and thermosetting polymers can be processed using this method. As reported in literature [43–46], in the resulting PNCs fabricated by this method, covalent linkages between the nanofillers and the polymer matrices occur. To avoid the nanofillers aggregation during the polymerization, grafting offers an excellent possibility for direct covalent linking of the polymer matrices and nanofillers. Polymers can either be grafted to or from the nanofillers surface. However, using this procedure noncovalent nanocomposites can also be obtained. In comparison to the melt mixing method, high level of nanofillers dispersion can be achieved, because this method allows for direct integration of well-dispersed nanofillers in bulk polymeric matrix. One of the advantages of this approach is grafting of the polymer molecules onto the CNTs walls, resulting in improved dispersion of CNTs in polymer matrices [43–46].

3 Carbon Nanotubes

Carbon nanotubes (CNTs) as a member of carbon nanomaterials family, discovered by Ijiima [47], in 1991, have been widely considered during the last decade as the century material [48–50]. Because of their unique one-dimensional tubular structure and outstanding mechanical, thermal and electrical properties, CNTs have attracted enormous scientific attention and their various applications specially in PNCs preparation have been continuously under further investigation. Other extraordinary chemical and physical properties of CNTs include high specific surface area, high aspect ratio (length to diameter ratio), high mechanical stiffness, ease of functionalization, high flexibility, low mass density, frictionless surface and effective π–π interactions with aromatic compounds. CNTs consist of one, two or several carbon sheets with thickness of one-atom of carbon as graphene sheets which are rolled in hollow cylindrical structure with diameter of less than 100 nm and length of more than several micrometers [51, 52]. There are three CNTs types: single walled (SWCNTs), double walled (DWCNTs) (two layers of rolled graphene sheets) and multi walled (MWCNTs) (multiple layers of rolled graphene sheets) as shown in Fig. 1. CNTs diameters typically range 0.4–3 nm for the SWCNTs, 1–3 nm for the DWCNTs and 2–100 nm for the MWCNTs, with length ranging from 1 to 50 μm [53–55]. Strong covalent bonds hold the carbon atoms in graphene sheet structure and Van der Waals forces (π-stacking) hold graphene sheets together in DWCNTs and MWCNTs structures. Therefore, CNTs have the highest strength-to-weight ratio among the other nanomaterials [56]. CNTs mass density is very low and their aspect ratio is over than

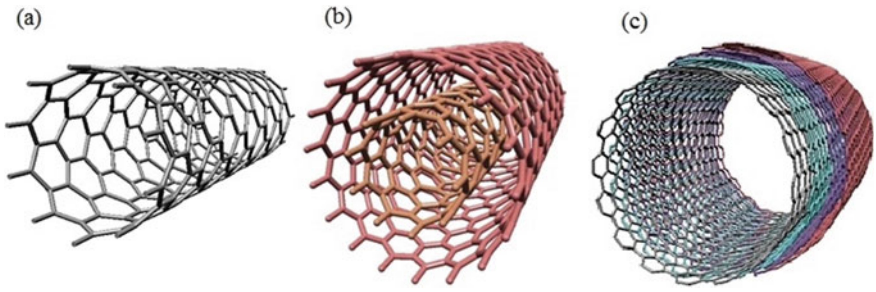

Fig. 1 A schematic of **a** SWCNT, **b** DWCNT and **c** MWCNT

1000. According to the experimental results, tensile modulus and tensile strength of CNTs are remarkably high. As different factors such as CNTs length and diameter can affect their electrical properties, CNTs can be conductive or semi-conductive. CNTs provide freely movement of electrons thorough their long-hallow cylindrical structure. Hence, CNTs can be more conductive than copper [57, 58].

At present, the main methods of CNTs synthesis are arc discharge [59], electric laser ablation [60], and chemical vapor decomposition (CVD) [61, 62]. The last method due to its relatively low growth temperature, and high purity and yield is the most promising method for possible scale-up [63]. CNTs purification is an essential issue that to be addressed because as-prepared CNTs at low growth temperature usually contain metallic or carbonaceous impurities. Chemical oxidation as a common method has been developed for increasing CNTs purity [64]. Open end or closed end CNTs can be obtained depending on the synthetic procedure. In general, synthesis of CNTs is a striking challenge, because walls number, dimensions (diameter and length) and alignment (chiral, armchair or zig-zag) of CNTs should be controlled [65].

There are several methods for CNTs functionalization including non-covalent and covalent functionalization and oxidation (defect functionalization) [53, 66]. Covalent modification is an effective method but deteriorates the intrinsic properties of CNTs. For the first time, Smalley and co-workers [67] were successfully cut and functionalized SWCNTs with carboxylic groups, under ultrasonic waves using strong acid [25, 26, 68].

4 PVC-Based PNCs

Polyvinyl chloride (PVC) is one of the most commonly used polymeric materials because of its superior chemical, mechanical, and thermal properties, and also its relatively low cost compared to other polymers. PVC is soluble in a wide range of solvents, including tetrahydrofuran (THF) [69], N,N dimethyl acetamide (DMAc) [70], dimethylformamide (DMF) [71], and N-Methylpyrrolidone (NMP) [72]. PVC can be generated via three methods, commercially. PVC generated by suspensions polymerization, emulsion polymerization, and bulk or mass polymerization is named as SPVC, EPVC, and MPVC, respectively. Surfactants are used to disseminate vinyl chloride monomer in water during emulsion polymerization [25, 73–75]. PVC was first commercially produced via emulsion polymerization in the early 1930s in Germany. PVC's heat processing and stability were enhanced for the first time in 1932, with discovering plasticizers and stabilizers [76].

PVC is an important commercial polymer that can be used in variety of industrial fields [77]. In particular, PVC is one of the most common polymers used in production of PNCs due to its properties including widely developed processing, relatively low cost, high environmental resistance, and ability to be modified [78–80]. The limitation of PVC is mainly related to its relatively high glass transition temperature (T_g), which results from the strong polar interactions between the PVC molecules due to the presence of chlorine atoms [81, 82]. T_g of a polymer is widely dependent on its molecular structure and molecular weight [83]. However, specific plasticizers, which are inserted into the polymeric macromolecular structure, can usually reduce the T_g value of PVC [84]. Although several studies have been conducted on the effects of nanofillers on the PVC nanocomposites properties, only a few of them have addressed the effect of nanofillers on thermal properties of this polymer in its glassy state [85, 86]. Incorporation of very small amount of CNTs with outstanding properties into PVC matrix can improve thermal, mechanical, and electrical properties of PVC for various engineering applications. Also, CNTs with excellent transport properties can improve separation properties of PVC membranes [73, 74, 87]. General properties of PVC are presented in Table 1.

Table 1 General properties of PVC

Properties	Value
Density	1380 kg/m^3
Elongation at break	20–40%
Glass transition temperature	87 °C
Tensile strength	50–80 MPa
Young's modulus	2900–3300 MPa
Melting point	212 °C
Heat transfer coefficient	0.16 W/m.K
Specific heat	0.9 kJ/kg.K

5 Effect of CNTs on the PVC-Based PNCs

5.1 *Mechanical Properties*

Mechanical properties of CNTs are outstanding. CNTs with Young's modulus of 270–950 GPa and tensile strength of 11–63 GPa are the stiffest and strongest materials yet discovered. These excellent mechanical properties are due to the covalent sp^2 bonds between carbon atoms in the CNTs structure. In the axial direction, CNTs are very strong. CNTs are at least 30 times stronger than Kevlar (used in bulletproof vests) and 117 times stronger than steel. CNTs with high aspect ratio (length to diameter ratio), excellent spring-like flexibility, and extraordinary mechanical properties can be used as polymer reinforcement agent, effectively. Preparation of the CNTs-based PNCs with improved mechanical properties is now a challenge, because homogenous dispersion of CNTs in polymeric matrices is difficult due to the agglomeration tendency of CNTs. Therefore, one of the most concerns in the CNTs-based PNCs field is how to enhance the CNTs dispersibility in polymer matrices. The CNTs functionalization has significant effect on reaching the CNTs-based PNCs with optimum mechanical properties. By enhancing the interaction between CNTs and polymers, controlling the CNTs amount and adjusting the CNTs orientation in the polymeric matrix, mechanical properties of the CNTs-based PNCs can be improved. On the other hands, poor CNTs dispersion in polymer matrix results in poor stress transfer [2].

There are three approaches to improve the CNTs dispersity in polymer matrices including mechanical mixing, sonication and covalent or non-covalent functionalization of CNTs. Sonication is a common method to achieve good dispersion of CNTs in polymer matrix. Although covalent functionalization of CNTs introduces structural defects to the CNTs surface, the stress transfer from the polymer matrix to CNTs can be greatly improved by this functionalization. Covalent functionalization of CNTs can be achieved by oxidation or in-situ polymerization that in this method monomers react with oxygen-congaing functional groups on CNTs to introduce polymer chains on CNTs wall. In general, in situ-polymerization technique is scalable for large-scale production of the CNTs-based PNCs [2].

Aljaafari et al. [88] reported fabrication of two groups of PVC-based PNCs loaded with different CNTs contents. Their results demonstrated that CNTs have lower electrical and mechanical percolation threshold than other nanofillers like carbon nano powder (CNP). It was found that with incorporation of 1 wt.% CNTs in PVC matrix, elastic modulus increases 2.3 times greater than with incorporation of 2 wt.% CNP. The T_g value was slightly changed with addition of either nanofillers. It was found that the interfacial effect cannot be ignored when the interaction between polymer and CNTs is strong.

Mechanical properties of the CNT/PVC PNCs containing 0.5 wt.% CNTs were investigated by Yazdani et al. [89]. It was found that failure strain of the fabricated PNCs is affected by CNTs, significantly. In the presence of CNTs, failure strain reduces, up to 60%, regardless of the dispersion quality of CNTs. The PVC-based PNCs were also synthesized by Blake et al. [90]. It was found that strength, Young's modulus and toughness of the fabricated PNCs are improved as the functions of nanofiller content. Shi et al. [91] grafted poly n-butyl methacrylate (PBMA) onto CNTs to improve the CNTs dispersion in PVC matrix. It was found that the grafted PBMA-CNTs are better dispersed in PVC matrix and the load transfer efficiency from the polymer matrix to the CNTs is improved. Also, it was found that even at lower CNTs content, Young's modulus, storage modulus, tensile strength, yield stress, toughness, and ultimate strain of the fabricated PNCs are significantly improved. The load transfer from PVC to the CNTs is also improved due to the strong miscibility between PVC and PBMA. Pan et al. [92] fabricated the PVC/CNTs PNCs, using the modified CNTs covalently and non-covalently with N-epoxypropyl PPTA (PPTA-ECH). It was found that compared with the neat PVC, mechanical properties of the fabricated PNCs are significantly improved. The physicochemical features of PVC/CNTs functionalized with riboflavin (RIB) were investigated by Abdolmaleki et al. [93]. It was found that the PNC containing 12 wt.% RIB-CNTs exhibits better mechanical and thermal behavior compared to the other CNTs contents. Katarzyna et al. [94] investigated the improved dispersion of CNTs in the PVC matrix using methyl oleate and oleic acid. The results showed that the obtained samples demonstrate lower agglomeration rate of the modified CNTs with their higher stability in the PVC matrix.

5.2 Thermal Properties

For a single CNT, longitudinal thermal conductivity is about 2800–6000 W/m.K, at room temperature. Thermal conductivity of CNTs with aspect ratio in the order of 10^3, is higher than those of graphite and carbon fibers and is comparable to diamond. Theoretical studies predicted ultrahigh thermal conductivity values for CNTs (3000 W/m K for MWCNTs and 6000 W/m K for SWCNTs), while, smaller thermal conductivity values have been obtained by experimental measurements (3218 W/m K for SWNTs and 15–1500 W/m K for MWNTs) [95, 96]. The CNTs structure such as morphology, size and dispersion ability have significant effects on the CNTs thermal conductivity. CNTs along their length have high thermal conductivity, but across their width have poor thermal conductivity. Therefore, it is required that CNTs to be aligned through thickness of a PNC layer to conduct heat from one face to other face of the PNC layer. Carbon-based conductors such as CNTs can be replaced with copper wire with a weight reduction of up to 90%. PVC is thermally weak and decomposed at 140 °C, thus incorporating CNTs as a reinforcing material into PVC matrix can improve its thermal stability. It was shown that the thermal and electrical transfer mechanism of CNTs-based PNCs is better than composites filled with metallic particles [13]. A combination of insulating polymer matrix with low content of conductive CNTs is expected to develop thermally and electrically conductive composites [5, 14]. It was shown that thermal conductivity of a polymer matrix containing a segregated structure of conductive filler is higher than that of a polymeric matrix containing a random distribution of filler. Mamunya et al. [97] investigated the concentration dependence of CNTs/PVC PNCs thermal conductivity. Due to the high CNTs anisotropy and presence of segregated CNTs structure within the PVC matrix, an ultra-low value of electrical percolation threshold (0.05 vol.%) was obtained. It was found that, at higher CNTs contents, an improved thermal conductivity can be obtained.

5.3 Electrical Properties

As reported in literature, CNTs have high electrical conductivity (10^2–10^6 S/cm for SWCNTs and 10^3–10^5 S/cm for MWCNTs) [96, 98]. CNTs conduct electricity by vibration of covalent bonds holding carbon atoms together. Since each carbon atom in the CNTs structure has four electrons and only three electrons are used to form the covalent bonds, there is one remaining electron in outer sell that is highly mobile and available for electrical conduction. Therefore, this intrinsic high conductivity of CNTs makes them as logical choices for tuning the polymers electrical conductive properties. Estabrak et al. investigated electrical properties of PVC/CNTs PNCs. The PNCs were prepared by THF as solvent, followed by the film casting. It was found that with increasing the amount of CNTs, electrical conductivity of the fabricated PNCs increases [99]. As reported in literature, PNCs containing small amounts of CNTs have better electrical and thermal properties than PNCs filled with metallic particles [99]. Broaza et al. found that with uniform dispersion of CNTs in the PVC matrix, electrical conductivity of the PVC/CNTs PNCs increases [100]. Mamunya et al. investigated electrical behavior of the PVC/CNT PNCs by the percolation theory. It was found that electrical conductivity of the PVC/CNT PNCs depends on the CNTs content enabling to reveal the ultra-low percolation threshold value which is 0.05 vol.% [97].

5.4 Permeation Behavior

Polymer nanocomposite membranes (PNMs) with improved properties and performance than polymeric membranes have attracted enormous interest for various separation applications, in recent years. This improvement could be obtained by incorporation of inorganic nanomaterials including metal organic framework (MOF), carbon nanomaterials (for example carbon nanotubes (CNTs)), carbon molecular sieve (CMS), silica, zeolite, and titanium oxide (TiO_2) as nanofillers into polymer matrices. These membranes combine advantages of both polymeric and inorganic membranes and compensate their disadvantages [101–110]. CNTs with unique structure and extraordinary chemical and physical properties have attracted considerable attention as a new type of nanofillers for novel PNMs fabrication. CNTs can be

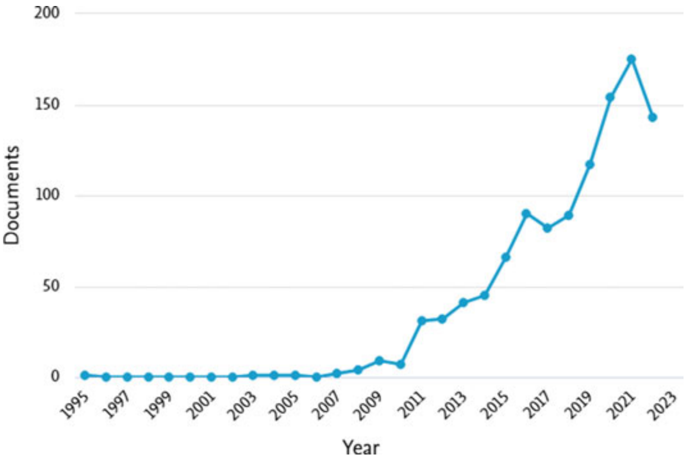

Fig. 2 Publications number in the field of "CNTs", "PVC" and "membranes", over time (Reprinted from Scopus)

incorporated with polymeric membranes by embedding into the polymer matrix or modification of the membrane surface. The potential advantages of CNTs incorporation in polymer matrices are improved membrane performance (rejection and permeability), increased membrane mechanical strength, reducing fouling tendency, and controlling pore size and etc. [102, 111–115].

Figure 2 shows the increasing number of publications on the topic of CNTs/PVC PNMs in the recent years.

CNTs with outstanding properties including high mechanical strength and chemical and thermal stability, ease of functionalization, large surface area, high aspect ratio, and fast water transport rate (3–4 orders of magnitude faster than the rate predicted by the Hagen–Poiseuille equation) that is due to the molecular ordering phenomena and atomic-scale CNTs walls smoothness could be used for development of high performance PNMs in water purification and desalination applications [116–118]. The enhanced antifouling properties of the PNMs containing CNTs have been related to the hydrophilic functional groups [119–121].

Haghighat and Vatanpour reported fabrication of PVC nanofiltration nanocomposite membranes containing polypyrrole-functionalized CNTs (PPy-MWCNTs). It was found that flux recovery ratio and antifouling capabilities of the prepared nanocomposite membranes increase during BSA filtration. In the presence of 0.25 wt.% PPy-MWCNTs, pure water flux (PWF) increased from roughly 59.7 LMH for the neat membrane to 75.2 LMH for the optimized nanocomposite membrane. Furthermore, the fabricated membranes showed effective rejection of BSA and Reactive Blue 50 dye (higher than 95%). It was found that hydrophilicity of the fabricated nanocomposite membranes increases by increasing the PPy-MWCNTs content, due to the presence of amine groups on the membrane surface which facilitates hydrogen bonds formation with water molecules. The results showed that adding the optimum amount of PPy-MWCNTs to the casting solution can enhance the mean pore radius and porosity of the fabricated membrane. In comparison to the neat PVC membrane, all of the modified nanocomposite membranes exhibited better antifouling properties [122]. Rajabi et al. reported fabrication of PVC/MWCNTs nanocomposite membranes for gas separation application. The membranes were prepared using both raw and functionalized MWCNTs. The functionalized CNTs showed better gas separation performance (higher CO_2/CH_4 selectivity). The CNTs incorporation into the PVC matrix improved mechanical properties (tensile module) of the fabricated membranes, significantly [123]. Zhao et al. reported fabrication of PVC/SWCNTs ultrafiltration nanocomposite membranes with enhanced antibacterial properties. It was found that surface roughness of the nanocomposite membranes enhances after being blended with SWCNTs. The surface hydrophilicity of the fabricated nanocomposite membranes was also improved. As a result, the membranes permeation flux increased. However, the inclusion of SWCNTs significantly resulted in diminished membrane elongation and mechanical properties [124]. Vatanpour & Haghighat fabricated PVC nanofiltration nanocomposite membranes incorporated with MWCNTs/triethylenetetramine (TETA) as nanofiller. It was found that formation of hydrogen bonds between the functional groups of MWCNTs and water molecules increases hydrophilicity and permeability of the fabricated membranes. Compared with the neat membrane, fouling rate of the nanocomposite membranes was significantly reduced. BSA, Lanasol Blue 3R dye and their combination rejection of the nanocomposite membranes was also enhanced compared to the neat membranes [125]. Hosseini et al. reported fabrication of PVC/MWCNTs nanocomposite cation exchange membranes. The effect of MWCNTs content as additive on electrochemical properties of the prepared membranes was investigated. The membrane water content was originally raised by increasing the MWCNTs content up to 4 wt.%, but subsequently began to decline with increasing the additive content. Ion exchange capability was reduced when the loading ratio of MWCNTs in the casting solution increased. For monovalent ionic solutions, increasing the MWCNTs content up to 4 wt.% decreased the membrane permselectivity and transport number, and then increased with increasing the MWCNTs content. The membrane permselectivity and transport number were enhanced for bivalent ionic solutions by increasing the MWCNTs content up to 8%, but subsequently significantly decreased with increasing the additive content. The increased MWCNTs content improved the monovalent ionic flux. The ionic flux for bivalent ions was also improved first by increasing the MWCNTs content up to 2 wt.%, then decreased by increasing the MWCNTs content from 2 to 8 wt.%. With increasing the MWCNTs content, the bivalent ionic flux showed an increasing trend. The increased MWCNTs content reduced the membrane electrical resistance [126]. Masoumi et al. reported fabrication of PVC nanocomposite membranes containing pristine and modified MWCNTs. To achieve well-dispersion of MWCNTs within the membranes, MWCNTs was carboxylated. It was found that at the presence of pristine and modified MWCNTs, the number of pores on the membranes surface increases and the pore size distribution curves shift towards smaller pores. With increasing the pristine and modified

MWCNTs content up to 0.3 wt. %, tensile strength, PWF, hydrophilicity, and abrasion resistance of the membranes increased and then decreased due to the MWCNTs agglomeration. It was found that, at the same content of the pristine and modified MWCNTs, the modified MWCNTs show more significant effect on the membrane performance in humic acid (HA) removal. For the PVC membrane containing 0.3 wt. % modified MWCNT, HA rejection reached 96.88%. On the other hands, with increasing the modified MWCNTs content, antifouling properties of the fabricate membranes improved [127]. In other work, Masoumi et al. used functionalized MWCNTs (F-MWCNTs) to modify polyvinylidene fluoride (PVDF)/PVC blend ultrafiltration nanocomposite membranes fabricated via solution blending method. Influence of the F-MWCNTs content (0–1%) on performance and properties of the F-MWCNTs/PVDF/PVC nanocomposite membranes was studied. It was found that with increasing the F-MWCNTs content, hydrophilicity of the membranes was improved. Also, performance and antifouling properties of the prepared membranes were improved in the presence of F-MWCNTs. Maximum permeate flux and dextran rejection were achieved by incorporation of 0.3–0.5 wt.% of the F-MWCNTs [128]. Garudachari et al. reported fabrication of PVC nanocomposite membranes containing 0.01, 0.25, and 0.5 wt.% CNTs by immersion precipitation method. A reduced surface roughness and an improved macrovoid structure with increasing the CNTs content were observed [129].

6 Conclusion

PVC with superior chemical, mechanical, and thermal properties, and also its relatively low cost compared to other polymers can be one of the most commonly used polymeric materials in industries. However, low electrical and thermal conductivity and poor mechanical strength have been the main drawbacks of PVC limiting its practical applications so far. Over the past decade, a lot of research has been carried out using various nanofillers to enhance electrical and thermal conductivity and mechanical strength of PVC. CNTs with superior mechanical, thermal and electrical properties are excellent candidates for PVC-based PNCs preparation as nanofillers. Solution mixing, melt mixing, and in-situ polymerization are some techniques which can be used to make PVC/CNT PNCs, effectively. The PVC/CNTs PNCs properties can be improved by several factors including CNTs dispersion in the PVC matrix, surface adhesion between CNTs and PVC and manufacturing processes. As a drawback, uniform dispersion of CNTs in polymer matrices is a critical issue in PNCs preparation. There are three approaches to improve the CNTs dispersity in polymer matrices including mechanical mixing, sonication and covalent or non-covalent functionalization of CNTs. Finally, although, PVC/CNTs PNCs have received considerable attention as an interesting and important research area, worldwide, further research is needed to be performed regarding CNTs/PVC PNCs to optimize their properties and commercialize their practical applications in very near future.

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Mechanical Properties of PVC Composites and Nanocomposites

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Abstract This chapter is a review on the mechanical properties of PVC-based composite and nanocomposite materials. These materials are suitable for many applications such as automotive industries, construction, packaging, and aerospace due to their good mechanical properties. However, these properties are influenced by many parameters mainly fiber size, processing conditions and interfacial adhesion between fiber and matrix. Several studies are reported in this paper about mechanical properties of composite and nanocomposite materials based on PVC matrix. Prediction of mechanical properties of polymer-based composites/nanocomposites using mathematical and numerical model is also reported in the last section of this chapter.

1 Introduction

Composite and nanocomposite materials are as old as the world. Several millennia ago, craftsmen in ancient Egypt were already increasing the mechanical properties of bricks by adding short straw to fresh clay [1].

The development of composite materials is a science that is constantly growing, especially due to the needs of society, not only for high technical applications such as aeronautics, but also for conventional applications in the automotive, transport or even House. In this sense the choice of adequate reinforcement of polymeric materials is one of the main targets for their development [2].

The thermoplastics most commonly used in the manufacture of composites and nanocomposites are polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC) [3].

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Although PE is the dominant polymer, it is also expected that there will be a drastic increase in composites and nanocomposites based on PVC. The demand for materials based on PVC is expected to increase by approximately 200% from 2003 to 2010 compared to 130% for PP composites, and 40% for PE composites [4].

PVC-based composites are widely used in the field of building materials, as they offer acceptable mechanical properties, good chemical and fire resistance, low water absorption and long service life (UV resistance). Additionally, PVC matrix composites can be cut, sawn, nailed, screwed, and processed by conventional woodworking equipment [5].

In 1975, a Swedish company named Sonesson Plast AB (Malmö, Sweden), developed a PVC/wood composite product under the trademark "Sonwood". It is probably the first commercial PVC/WF product. Wood was used as a high-quality substitute. In 1993, the Andersen Company (Bayport, MN) patented the technique of manufacturing PVC/WF composites for doors and windows using extrusion and injection molding [6].

Teed Corporation (Valley Forge, Pennsylvania) began selling PVC/Wood window profiles in 1998 and their product line has received National Rating Service (NES) assembly approval. in October 2001 [7]. Currently, most PVC/WF composites are used for window/door profiles, fencing and exterior cladding. Marine applications are under development [8, 9].

Nanocomposites are also widely used. Indeed, we can obtain the significant improvements of properties, mainly the mechanical properties, using the nanofillers [10–13]. The nano-fillers increase the interphase surface of constituents and superficial area/volume ratio leading to enhancement of overall performances. According to literature [14], in comparison to traditional micro-fillers, very low loading of nanoclay is sufficient to achieve the excellent development of properties without substantially increasing the density and cost or reducing the light transmission properties of base polymer.

Nanosilica has been used to enhance the mechanical properties of PVC [15], graphite was used as a flame retardant [16] and graphene oxide (GO) improved mechanical properties in PVC nanocomposite films [17].

On top of that, hybrid composites are also used and can lead to high mechanical properties. Indeed, the combination of PVC/Glass fiber/Graphene composites enhanced the mechanical strength of the manufactured composites because the carbon nanotube can improve the interfacial adhesion. According to Shanmugasundar et al. [18], the increase in the graphene content improved the dispersion of filler and increased nanocomposites strength due to the good dispersion. That combination enhanced the mechanical strength of the composites. The carbon improved the adhesion between polymer and fiber then the matrix phase is strengthened, and an increase in the axial compressive strength and stiffness was observed.

Nanocomposites have flooded the global market due to their excellent mechanical properties, light weight, good modulus and improved dimensional stability, better scratch resistance, and better impact resistance. These qualities have enabled this type of nanocomposite to replace certain components, of a metallic nature for example, in

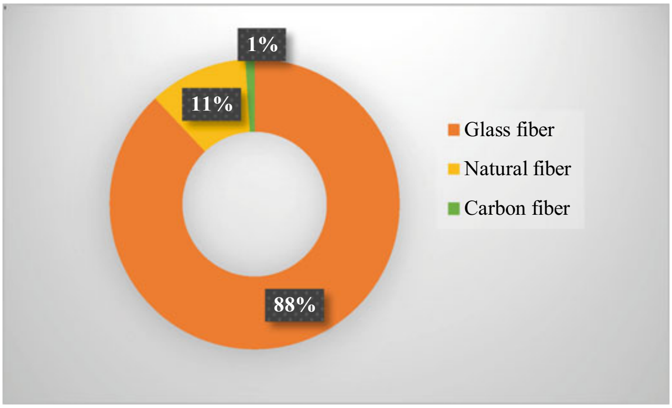

Fig. 1 Kind of reinforcement of the most produced composites

the automotive sector and also in other sectors. Recent estimates show that nanomaterials accounted for 73% of the nanotechnology market in 2015. This share reached 82% in 2019 [19].

According to the global composites market, At the reinforcement level, glass fibers are the most produced followed by natural fiber as Fig. 1 indicates [20].

2 Mechanical Properties of Composites

Generally, polymers are easily processed and have high productivity at low cost but for some applications, some mechanical properties, such as the strength and toughness of polymers can be limited. To improve those properties, fillers and fibers are so added. However, mechanical properties of composites depend on various parameters like additives, interfacial adhesion between fiber and matrix, the content, the size, and the dispersion of fiber…etc.

To obtain PVC with satisfactory manufacturing and high-performance diverse additives are incorporated mainly plasticizers. Laurent et al. [21] investigate the effects of plasticizers on the properties of PVC composites. According to obtained results, at low contents of plasticizer, the Young's modulus increased due to the anti-plasticization phenomenon, in contrast at higher plasticizer contents, the Young modulus decreased with increasing the plasticizer content. It is also reported the adding of rigid fiber increased the modulus of the composites because of the higher modulus of the fibers.

Indeed, composite's high performance requires high fiber content, an increase in tensile properties can be achieved with an increase in fiber content [22].

In terms of particle size, many studies were investigated. According to Saini et al. [23], improvement in properties PVC composites was significant in the presence of filler, having a small particle size. Based on the approach presented in [24], the

$CaCO_3$ particle size is generally comparable in size with particles of PVC and hence are capable of generating interparticle friction with PVC articles, increasing shear, and promoting gelation. $CaCO_3$ could also act as a fusion promoter. One possible explanation for the observed trend could be that the finer particles having a larger surface area would have a larger contact surface with the PVC particles, creating a higher shear heating and increasing the fusion speed. $CaCO_3$ is usually surface treated with stearic acid, producing a layer of calcium stearate on the filler surface. This results in improved processing and dispersion leading to high mechanical properties.

Another work is described in [25]. They investigated the effect of diameter size and loading content on the mechanical properties of date palm trees reinforced polyvinyl chloride composite. They reported it can be related to the fiber geometry as it may affect the stress transfer of the load applied to the composites which occurs by shear at both interface along the fiber length and at the ends of the fibers. fiber size has an influence on the flexural strength of the PVC composites. According to the results, the no sieved composites have the highest flexural strength, the flexural strength of which increased from $\leq$ 125–125-500 μm and then decreased. The $\leq$ 125 μm fiber available in the no sieved composite may be able to fill the voids around the larger fiber size, making the composites more compact. Hamour et al. [26] investigated the effects of fiber particle sizes of alfa fiber on the mechanical properties of composites based on PVC. The presence of small particle sizes exhibited a beneficial effect on the mechanical properties by improving the quality of adhesion between polymer and fiber.

It is natural to think that the performance of composite materials depends on the properties of the basic constituents included in their composition. However, these would not exist if the fibers and the matrix could not associate. The interface is the seat of this association and constitutes a real strategic region capable of ensuring in particular the transfer of loads from the matrix to the reinforcements. The characteristics of the interface depend on the quality of the fiber/matrix link, which calls for the notion of adhesion. The bonds created at the interface between fibers and polymers determine the physico-mechanical properties of composite materials. The improved quality of the fiber-matrix adhesion is usually achieved by the external (physical) activations, the compatibilizers, which have reacted or deposited on the fiber or in some cases in the polymer [27].

Aouat et al. [28] incorporated the wheat husk as the reinforcing filler in the PVC matrix and to improve interfacial adhesion, the surface of fiber is chemically treated with acetic anhydride (AA). According to the results, incorporation of fiber has significantly increased the modulus with increasing fiber loading nevertheless there is a weak bonding between the filler and the matrix that obstructs the stress propagation and leads to the decrease in the tensile strength. however, the chemical treatment gives better interfacial adhesion between the fiber and the matrix occurs, imparting improvement in the mechanical properties of the composites.

The reinforcement capacity is reduced when the adhesion between the fibers and the matrix is low. The treatment of fibers and some additives used in the composite ensure the modification of the tension at the interface and the improvement of the properties of these materials. As reported by Aouat et al. [29], an improvement in tensile strength was observed for treated PVC/olive husk flour composites with benzoylation and PVC-g-MA compared to untreated ones, which may be due to better dispersion of the filler, and better adhesion between PVC and olive husk flour.

Hammiche et al. [30] has also investigate the effects of PVC-g-MA as a compatibilizer on the Mechanical properties of PVC/alfa. when the composite is modified with coupling agents the improvement of tensile strength is more extensive and progressive. The coupling agent improves the mechanical capacity of the material by means of a chemical mechanism. This mechanism is based on the establishment of ester bonds between the –OH groups of the alfa fiber and the maleic anhydride functionalization of PVC-g-MA, thereby giving rise to a chemical anchoring of the polymer matrix on the surface of the fibers.

The results obtained by Hammiche et al. in [31] suggest that the tensile strength of the composites (see Table 1) decreased with the increase of fiber content due to the weak interfacial adhesion and a low compatibility between the alfa fiber and PVC leading to the increase in the micro-voids between the fiber and the matrix, which weaken the fiber–matrix interfacial adhesion. However, he tensile strength of the composites after adding 3% PVC-g-MA was appreciably higher than those of the composites untreated because of increased interfacial adherence. The synergy between fibers and the matrix reinforces material and increases energy necessary to break it.

Boukerrou et al. [32] argue that upon mechanical studying of PVC/OHF composites shows better behavior in the treated composite materials. This improvement is the result of higher interfacial adhesion fiber/matrix. The incorporation of fiber reinforcement allows the increase of rigidity in materials and the treatment allows for the obtainment of even higher mechanical properties (Young's modulus).

Several publications have appeared in recent years documenting the effect of processing method of PVC composites properties as well. Conditions that vary with processing method result in different final plastic product properties and identify a suitable adequate process according to application aimed.

As reported by Koubaa et al. [33], tensile modulus of rupture and flexure modulus of rupture of composites manufactured with injection molding were higher than those prepared with injection molding. It is suggested that the differences in mechanical

Table1 Tensile strength of PVC/alfa composites with and without treatment

	PVC/10%alfa fiber		PVC/20%alfa fiber		PVC/30%alfa fiber	
	Without treatment	With treatment	Without treatment	With treatment	Without treatment	With treatment
Tensile strengh (MPa)	12.64	15.34	11.45	12.5	9.24	11.6

behavior with the processing method could be explained in part by the fiber orientation in the composite structure. The extrusion process is generally accompanied by fiber breakage when slender fibers are used. It is possible that the compounding and injection-molding processes resulted in less fiber breakage than the extrusion process.

Much research on this parameter has been done. Hammiche et al. [34] developed PVC/alfa composites using three techniques: calendering, Brabender, and injection molding. The comparison study revealed that the mechanical properties of PVC and its composites were different. Regarding PVC, the tensile strength and young modulus were higher in the two-roll milled compared to Brabender and injection molding because calendering was the best technique used for the PVC process. When the most interesting performances of composites were obtained for those processed by injection molding. Indeed, composites obtained by injection molding presented the highest tensile strength and Young modulus. As known, the young modulus is increased because it strongly depends on the good dispersion of fibers in the matrix and the agglomeration of fiber leads to an insufficient composite homogeneity and acts as crack initiation sites under loading. The phenomenon and extent of fiber agglomeration are subjected to the forces, on the other hand, that attract the fibers or try to separate them. The hydrogen bonds, which are responsible for fiber interaction, are strong enough.

Başboğa et al. [35] also studied the effects of processing methods on the mechanical properties of PVC/wood flour composites. Higher Tensile and flexural strength were obtained with the Injection-molded process compared to the compression-molded one.

Based on the approach presented in [36], PVC reinforced with wood and glass fiber is manufactured by compression molding or by twin-screw extrusion process. The comparison of mechanical properties of the composites suggested that the compression process was more effective than the twin-screw extrusion process as the high mechanical properties of the PVC composites was obtained by using the compression molding technique as a result of lower shearing stress and low breakage of glass fiber and higher specific density.

From the research that has been carried out it is possible to conclude that PVC is uniquely responsive to functional additives which permits the generation of rigid and flexible products, useful in designed engineering application. When fibers only act as filler, that contribute less to mechanical strength improvement.

3 Mechanical Properties of PVC Nanocomposites

Polymer-layered silicate nanocomposites have experienced an important development over the past 20 years, and it was the focus of academic and industrial attention because the final materials often exhibit a desired enhancement of mechanical relative to the original polymer matrix, even at very low clay contents. According to Kiersnowski et al. [37], the processing conditions for low-filled polymeric nanocomposites are similar to these of pristine resin and typical problems of micro-composites' processing do not occur. On account to nanometric dimensions of clay particles, which are close to the molecular dimensions, large interphase area is reached at low filler content.

Though PVC is one of the major thermoplastic polymers, PVC/clay nanocomposites are still in the introductory phase [38].

As already reported in introduction section, very low loading of nanoclay is sufficient to achieve the excellent development of properties. Siddique et al. [39] fabricated nanocomposites based on polyvinyl chloride (PVC) matrix with different compositions of polypyrrole and barium hexaferrite by solution casting method with 0.5 mm film thickness. By adding 2.5 wt% barium hexaferrite, maximum elongation and strength are reached owing to the complete dispersion and strong interaction of fillers with the PVC matrix. However, after adding 5 wt% barium hexaferrite, there was a decrease due to minor agglomeration of fillers in the matrix. In addition, the modulus, decreased with increasing the polypyrrole content as even small stress was applied the chains in the PVC matrix were free to move because Polypyrrole did not cause the chain restriction. While the modulus increased by increasing the hexaferrite concentration in nanocomposites because the presence of hexaferrite leads the chain restriction and more force was required to allow the chains in the PVC matrix to move freely due to which modulus increased.

The effect of titanium oxide nanoparticles content on mechanical properties of PVC composites were also considered by Nagat et al. [40]. To achieve a good dispersion and improve the compatibility between nanoparticles and PVC, the titanium oxide surface is treated with vinyl silane and amino silane. Vinyl silane showed better improvements in mechanical properties compared to the amino silane, especially in cases of high weight fractions of nanoparticles. This is because of the improvement in the PVC-titanium oxide interfacial region arise from the similarity of polarity and surface tension values of vinyl silane with that of PVC matrix and nanoparticles. According to Leszczynska et al. [41], when nanoparticles are properly modified and dispersed in the polymer matrix, effective interactions arise between organic and inorganic phases of composite material that can cause synergistic effects.

Organic nanofiller is widely used in nanocomposite materials as well. Nanocellulose may well imparts its high stiffness and strength to improve the mechanical properties of nanocomposites. The main reason to use nanocellulose as reinforcement in polymer matrix is because one can potentially exploit the high stiffness of the cellulose crystal for reinforcement [42]. Based on the approach presented in [43], PVC was reinforced with nanocellulose at different weight percentages (2, 4, 6, 8 and 10%) to prepare nanocomposites by solution casting method. The tensile strength of the nanocomposites decreased with increasing nanocellulose loading and the highest value was obtained for 2 wt% nanocellulose reinforced PVC nanocomposites.

The use of nanocellulose as reinforcing in PVC matrix is also investigated by Hammiche et al. [44, 45]. Cellulose nanowhiskers (CNW) were prepared from alfa fiber (Stipa tenacissima) by an alkali treatment at room temperature in association with a bleaching treatment followed by a sulfuric acid hydrolysis [44]. They compared properties of nanocomposites based on cellulose nanowhiskers which were dispersed with two different methods. They tried the dispersion of CNW in clay (Cloisite 30B) (1) and in polyethylene glycol (PEG) (2). It has been found that the dispersion method and the organization of the reinforcements play a key role in the nanocomposite's properties. The results showed higher organization with the Cloisite 30B/CNW system. This system also showed higher enhancements. The dispersion in clay was advantageous for improved Young's modulus of nanocomposites. However, the presence of PEG leads to the decrease in this property due to the effect plasticization of PEG [45].

Prabu et al. [46] prepared Hybrid nanocomposites containing a fixed amount of Carbon Black and varying amount of halloysite nanotubes by melt-mixing method using a two-roll open mill. Tensile strength, Elongation at break and modulus of hybrid nanocomposites increases by 12.87%, 13.91% and 23.22%, respectively, with the using 4phr of Carbon Black in PVC matrix. According to authors, synergistic effect of hybrid fillers, enhanced interfacial interactions and formation of intercalated structures are responsible for the superior mechanical properties of the hybrid nanocomposites.

In the study conducted by Abbas et al. [47], polymer composites of PVC were loaded up with micro and nano PbO/CuO particles. At the same content, composites containing nanofillers show higher mechanical properties than composites based on bulk fillers. This is attributed to the homogeneous dispersion of nanoparticles in the PVC matrix. Thereby, at the same particle content, the nanoparticle filler is more efficient than the bulk filler in strengthening the polymer matrix which additionally improves the mechanical properties, in other words, smaller particles give better reinforcement.

The influences of processing conditions on the mechanical properties of carbon nanotube-filled polyvinyl chloride composites are examined by Yazdani et al. [48] using four different dispersion methods (i.e. probe sonication, bath sonication, mechanical stirring and batch mixing). The mechanical properties of a composite could be used as an indicator for the quality of filler dispersion in the composite. Findings indicated a direct relationship between the dispersion quality and mechanical properties of the composite specimens. Well dispersed specimens, using probe sonication, exhibited larger tensile strength and failure strain.

Sterky et al. [49] compared the effect of processing techniques on the mechanical properties of PVC reinforced with 5 phr montmorillonite by using two-roll mill or in a micro-compounder. It is noted that the processing technique used affects the degree of dispersion/exfoliation of the clay and the occurring mechanical properties. The elongation at break and impact strength was better for the roll milled samples. However, modulus and tensile strength were significantly better for the micro-compounded samples despite the larger particle size. This can be attributed to a higher degree of orientation in these samples.

4 Mathematical and Numerical Modeling of PVC-Based Composites/Nanocomposites

Different parameters play an important role in the preparation of polymer- based composites/nanocomposites. These parameters such as, orientation, dispersion statue, buckling, volume fraction, aspect ratio, and type of nanofillers can affect considerably the polymer based- composites/nanocomposites mechanical proprieties. To test all different material combinations for all properties to understand their mechanical behavior is a very time consuming and computationally intensive task.

Prediction of mechanical properties of polymer-based composites/ nanocomposites is an important work for material design and optimization. The main objective in using mathematical and numerical models is to predict the structure as well as the physical and mechanical properties of polymer-based composites/nanocomposites from minimum input parameters. It is well established that mathematical and numerical tools offer a complete analysis of the mechanical behavior of polymer-based composites/nanocomposites and on dependence of mechanical properties on the shape of the inclusions and the interrelated effects of their orientation, volume fraction, aspect ratio, modulus, and interfacial properties with the matrix.

Since then, several scientific papers and many reviews were published, during the last decade, where the authors have presented theoretical models in order to predict the mechanical properties of polymer- based nanocomposites. On the one hand, it is well known that this class of materials presents a very complex mechanical behavior containing large deformations, plastic and viscoelastic properties that exceed the theory of linear elasticity. On the other hand, factors controlling the nanocomposite play an important role in determining the effective properties of polymer-based composites/nanocomposites.

For this purpose, micromechanical models namely: Guth model [50, 51], Mori–Tanaka model [52, 53], Halpin–Tsai model [54, 55], Tandon-Weng [56] and Halpin-kardos model [57] have been proposed to estimate the effect of the volume fraction of the reinforcement on the mechanical properties of polymer-based composites/ nanocomposites [58]. However, the fact that these analytical approaches are limited to simple cases, powerful numerical tools such as the finite element analysis have been proposed, since the early 1970s, to predict the mechanical properties of composite materials [59, 60]. Since many authors have developed several models based on the finite element method in order to analyze kinds of polymer-based composites/ nanocomposites and to study the factors controlling them [61, 62].

In their work, Pulngern et al. [63] investigated creep behavior of PVC-based composite using experimental and finite element simulation with ABAQUS software. The creep parameters were determined experimentally based on power law models. Good agreements are obtained between finite element simulation and experimental results. Later, Pulngern et al. [64] studied the mechanical properties in terms of flexural performances of reinforced PVC-based composites. Uniaxial tensile tests were carried out experimentally to identify the stress–strain relationships. Analytical models based on non-linear material theory were proposed and three-dimensional finite element analysis (FEA) was applied to predict stress–strain relationships. The authors obtained good agreement of analytical, numerical, and experimental results.

Recently, Eakintumas et al. [65] investigated the load bearing behavior of wood polyvinyl chloride composite (WPVC) composite log-wall panels using steel flat bars (SFBs). The load–displacement relationships were determined experimentally. The authors validated a numerical finite element model in order to examine the loading behavior of the studied material. The numerical results show a good agreement with the experimental results.

5 Conclusions

The combination of a plastic matrix and reinforcing fibers gives rise to composites having the best properties of each component. This chapter describes the influence of many parameters on mechanical properties of PVC-based composite and nanocomposite materials. Less compatibility resulting in poor adhesion between fiber and matrix decreases the mechanical properties. Therefore, to improve mechanical behavior, the content and the size of fiber must be optimized, and processing techniques and surface treatment should be selected as well. The modelling is also used to predict high mechanical properties of composite and nanocomposite materials.

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Scattering (X-ray, Light, Neutron) Studies of PVC Composites and Nanocomposites

Sora Yasri and Viroj Wiwanitkit

Abstract PVC (polyvinyl chloride) is the world's third most widely used thermoplastic polymer. Currently, growing polymer product usage produces huge volumes of waste, causing public concern about the environment and people's livelihoods. PVC formulation necessitates a specialized technique. Basic material science technology can be used to create PVC composites and nanocomposites. The essential foundation is the use of various compositing techniques to combine PVC with other components. Several types of PVC composites and nanocomposites are currently available. The characteristics of different composites are usually different. Scattering is one of the qualities that is altered. The scattering property of PVC composites and nanocomposites can be defined by X-ray, light, or neutron scattering. The authors focus on this chapter in particular. The authors will concentrate on PVC composites and nanocomposites scattering investigations. The theory of scattering is discussed, as well as instances of scattering (X-ray, light, neutron) examinations of PVC composites and nanocomposites.

Keywords Scattering · PVC · Composites · Nanocomposites

1 Introduction

Polyvinyl chloride (PVC) is the third most commonly used thermoplastic polymer in the world, after polyethylene (PE) and polypropylene (PP) [1]. After extensive research and experimentation, German chemist Eugen Baumann developed PVC in 1872. Inside a flask of vinyl chloride that had been stored on a shelf shaded from sunlight for four weeks, the polymer appeared as a white solid. Polyvinyl chloride in its purest form is a white, brittle substance. In alcohol, it is insoluble,

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while tetrahydrofuran is slightly soluble [1, 2]. PVC is one of the most frequently used synthetic polymers [1, 2], with numerous uses in pipes, ducts, and electrical insulation. The rigid type of PVC is used for electrical insulation, whereas the flexible form is chosen for other uses. PVC begins to dissolve at 140 °C, despite its great hardness and outstanding mechanical qualities; nevertheless, its thermal properties can be increased by adding heat stabilizers [1, 2].

Polymerization of the vinyl chloride monomer produces polyvinyl chloride (VCM). Suspension polymerization accounts for around 80% of production. Polymerization of emulsions accounts for around 12% of total polymerization, while bulk polymerization accounts for 8% [1, 2]. Suspension polymerization produces particles with average sizes of 100–180 m, whereas emulsion polymerization produces particles with small diameters. VCM and water, as well as a polymerization initiator and other chemicals, are added to the reactor [1, 2]. Because of its high fire resistance.

Suspension, emulsion, bulk, and solution polymerization are the four major techniques used to make PVC resins. The majority of PVC suspension resins are dust-free and granular, with different degrees of particle porosity [1–5]. PVC emulsion resins are fine powders with a limited amount of free monomer. PVC resins in bulk are identical to PVC resins in suspension, but the particles are more porous. PVC resins in solution are smaller in particle size than PVC resins in suspension, with high porosity particles containing almost no free monomer [3–5]. The PVC polymers are robust and linear. The monomers are organized primarily head-to-tail, with chlorides on alternating carbon centers. PVC has a mostly atactic stereochemistry, meaning that the relative stereochemistry of the chloride centers is unpredictable [1, 2]. A certain degree of syndiotacticity in the chain results in a few percent crystallinity, which has an impact on the material's properties. Chlorine makes up more than half of the mass of PVC [1, 2]. The inclusion of chloride groups in the polymer gives it features that are substantially different from those of the structurally comparable polyethylene [1].

PVC resin is used to make pipes for municipal and industrial uses, accounting for over half of all PVC resin produced each year. PVC is a common building material that is both robust and light. Plasticizers are used to make it softer and more flexible. PVC is also extensively used as the insulation of electrical cables such as teck, however it must be plasticized for this function [1, 2]. Lead has traditionally been used to stabilize flexible PVC coated wire and cable for electrical applications, however this is being phased out in favor of calcium-zinc-based solutions. PVC is an important plastic resin for construction, pipe and tubing, siding, and other uses. Currently, the increased consumption of polymer products generates significant amounts of waste, causing public worry about the environment and people's lives. Exposures to vinyl chloride monomer during the early years of production resulted in an important sentinel health event: the recognition of an excess of a rare liver cancer, hepatic angiosarcoma, at facilities throughout the world. Several other syndromes, including acro-osteolysis, also have been associated with PVC [3–5]. Since 1974, the RVCM concentration of PVC resin has been significantly reduced, lowering the cancer risk for workers in PVC fabrication factories and consumers of PVC products. To yet, no "no-effect" level for vinyl chloride monomer (VCM)-induced carcinogenesis has been discovered, hence the significance of human exposure to low levels of residual VCM remains unknown [3–6].

2 PVC Composites and Nanocomposites

Although many advantages of PVC are recognized, the important concern is on its adverse health effect. Due to concerns about PVC's health effects, developing new environmentally acceptable PVC formulations with improved operating qualities is a pressing need. The specific process for PVC formulation is necessary. The PVC composites and nanocomposites can be produced based on basic material science technology. The basic fundament is the combining of the PVC with other components based on various compositing techniques. The PVC will act as matrix and other material will be use as reinforcements (Fig. 1). However, the process is usually difficult. To compensate for the fact that PVC matrix and reinforcements have poor compatibility and homogeneity in their natural state, a variety of coupling agents and surface modifiers are used. The compositing process might be macro, micro or nano—levels. The property of the resulted composite usually based on the reinforcement material. In-situ polymerization, melt blending, and polymer dissolution mixing are three alternative ways to make polymer nanocomposites [7]. When it comes to improving the properties of polymer nanocomposites, the type, size, and surface morphology of the nanoparticles are crucial. Nanoparticles can be made using a variety of methods, including sol–gel, chemical precipitation, and electrode deposition [7]. At present, several kinds of PVC composites and nanocomposites are available. Good examples are chitin and chitosan based PVC composites and nanocomposites, carbon fibre and carbon black reinforced PVC composites and nanocomposites, clay reinforced PVC composites and nanocomposites, mica and glass fibre filled PVC composites, metal oxide reinforced PVC composites and nanocomposites, silica reinforced PVC composites and nanocomposites and metal carbonate reinforced PVC composites and nanocomposites.

The different composites usually have different properties. One of several properties that are changed is scattering. PVC composites and nanocomposites scattering property can be defined by the property of X-ray, light or neutron scattering. Basically, the change of scattering can result in several phenomena. The change of color is best example. Studies have been conducted to see if the color of identically shaded resin composites was indeed similar. Color variances amongst materials with the same shade designation were discovered. The scattering is an important factor related to the color change. In this specific chapter, the authors will focus on scattering studies of PVC composites and nanocomposites.

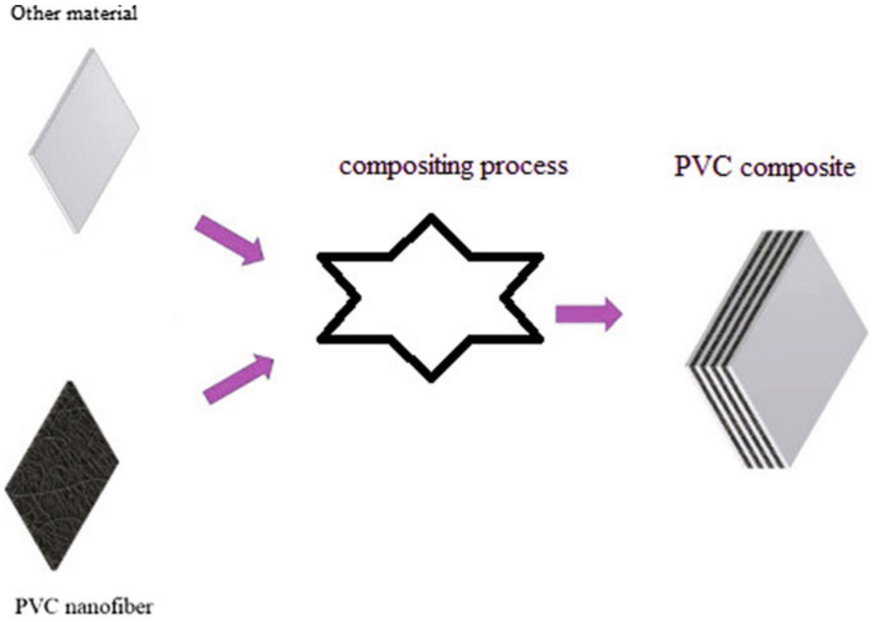

Fig. 1 Concept for creating PVC composites and nanocomposites

3 Scattering Principle

Scattering is a physics term that refers to a variety of physical processes in which moving particles or radiation of some kind, such as light or sound, are forced to deviate from a straight path due to localized non-uniformities (including particles and radiation) in the medium through which they pass. This also includes departure of reflected radiation from the angle anticipated by the law of reflection in traditional usage. Diffuse reflections are often referred to as scattering reflections, while specular (mirror-like) reflections are referred to as unscattered reflections. The phrase was originally limited to light scattering [8]. It is now recognized that every beam can exhibit scattering properties. Electromagnetic waves are one of the most well-known and frequently seen types of dispersing radiation. The scattering of light and radio waves is very significant. Several elements of electromagnetic dispersion are unique enough to have standard names [8].

When only one localized scattering site scatters radiation, this is known as single scattering. Because scattering sites are often close together, radiation can scatter many times, resulting in multiple scattering. Despite the fact that the combined results of a large number of scattering events tend to average out, the main difference between single and multiple scattering effects is that single scattering can usually be treated as a random phenomenon, whereas multiple scattering can be modeled as a more deterministic process. Multiple scattering is frequently modeled using diffusion theory.

Because the location of a single scattering center in relation to the course of the radiation is rarely known, the outcome, which is highly dependent on the exact entering trajectory, appears random to an observer. An electron fired at an atomic nucleus is an example of this type of scattering. Because the atom's specific position relative to the electron's journey is unknown and unmeasurable in this circumstance, the electron's exact track after the collision cannot be anticipated [9, 10]. Probability distributions are frequently used to characterize single scattering. Since then, the use of light scattering techniques in a wide range of scientific fields has exploded, particularly in the field of analytical chemistry [9, 10]. From molar mass distributions to macromolecular interactions responsible for aggregation processes, to structure and function determinations, a number of applications in analytical chemistry have resulted in a better knowledge of various macromolecular processes. Such analytical approaches are now virtually universally used to gain a better knowledge of nanoparticle structure and function [9, 10]. A more extensive investigation employing light scattering became necessary as the need to calculate the molar mass of more complicated and bigger molecules grew. The scattering of light incident on bigger molecules would display a fluctuation in intensity with scattering angle. The molar mass and size/shape of the scattering particles have to be deduced from this fluctuation [9].

4 Determination of Scattering

The inelastic scattering of light by chemical bonds, known as Raman scattering, can reveal molecular specificity. It may be utilized in imaging mode as well as pure spectroscopy mode [10]. The number and variety of imaging techniques created for examination in numerous industries, including pharmaceuticals, food, and especially biomedicine, has exploded in the last decade. Users no longer accept single-dimensional information and instead want multidimensional evaluation of samples. Raman imaging is a highly attractive analytical technique because of its high specificity and the fact that it requires little or no sample preparation [11]. This provides impetus for continued advancements in its supporting technology and application [11].

While various Raman spectroscopy and imaging applications in the biomedical field have been established thus far. To determine scattering is a challenge. Regarding light scattering, which is the most basic known form of scattering, ocular scattering is an optical phenomenon that degrades the retinal image in the human eye. However, when it comes to defining and measuring ocular scattering, there is still a lack of consistency [7]. Raman imaging combines two powerful analytical techniques: Raman spectroscopy and microscopy [7]. The information of inelastically scattered monochromatic (laser) light is employed in Raman spectroscopy to analyze the chemical composition of materials. By default, this technique is non-destructive and even non-contact [7]. Raman microscopy (-Raman) is a technique that combines ordinary light microscopy with Raman spectroscopy to identify a specific chemical. Both approaches are powerful on their own, but when used together, they enable chemical examination of the smallest objects (less than 0.5 m) and thereby link spectral and spatial information. Raman microscopes are significantly easier to collapse than infrared microscopes because they use light that is compatible with ordinary glass optics. As a result, Raman microscopes are frequently built on the foundation of a high-quality optical microscope [7]. Several Raman imaging systems based on the parallel detection of Raman spectra, which may reach high spatial and temporal resolution suited for imaging, have recently been developed [7]. Raman microscopy can map the distribution of specific target small molecules with minimal perturbation from the tag when used in conjunction with tiny Raman tags in the cellular silent area [12]. Several devices and techniques have been detailed in the last decade, however the majority of them have yet to be confirmed or proven to be reliable. In visual science, the creation of a standard approach for measuring and describing ocular scattering is still a work in progress [7]. However, as earlier mentioned, scattering is the properties of electromagnetic waves, not only light. The measurement of scattering of scattering of other electromagnetic wave is also useful in analytical chemistry. The specific approaches for determination of scattering of different electromagnetic waves are available. The specific details of determination for different electromagnetic wave will be further discussed.

A. Light

In nanotechnology and biological sciences, ultrasensitive detection and characterization of single nanoparticles is critical. The simplest and most straightforward way for particle detection is to measure the elastically scattered light from individual particles and nanoparticles. Particles scatter light, which is a fundamental principle that we all experience when it comes to color. The classical light-scattering theory for polymer solutions is extended to copolymer solutions that are polydisperse in chain composition and molecular weight. The particles in the surface determine whether the surface is glossy or matte. The size, charge, and molecular weight of materials can be determined by measuring the angle of light scatter, the frequency of light scattering, and the intensity of such scatter. Many technologies are built on this foundation.

Light scattering is part of a group of surface texture measurement techniques known as area-integrating methods. Light scattering methods probe an area of the surface and return parameters that are indicative of the texture of the area as a whole, rather than depending on coordinate measurements of surface points [12]. Light scattering techniques provide noninvasive, fast, and frequently real-time investigation of a wide range of materials in a variety of situations [12].

The oscillations of macromolecules (MM) are measured by dynamic light scattering (DLS) or Brownian motion. Dynamic light scattering, also called as photon correlation spectroscopy or quasi-elastic light scattering, is a technique for measuring the Brownian motion of macromolecules in solution caused by solvent molecules bombardment and relating this motion to particle size. Small MM move quickly, while huge MM move slowly. The relaxation of these MM's movements, as well as their diameters and hydrodynamic diffusion coefficients, can be measured using DLS [13, 14]. The process by which minuscule particles scatter light, creating optical phenomena such as the blue color of the sky and halos, is known as light scattering by particles.

Theoretical and computational methods for describing light scattering are based on Maxwell's equations, but because exact solutions to Maxwell's equations are only known for a few particle geometries, light scattering by particles is a branch of computational electromagnetics that deals with electromagnetic radiation scattering and absorption by particles [13, 14]. The DLS is a very important technique in nanoscience at present. It is useful for determining the molecular property of the nanomaterial. It is critical to properly characterize nanoparticles in order to generate well-defined nanoformulations with applicable potential. Particle size and surface charge of nanoparticles must be determined in order to properly characterize nanoparticles [13, 14].

The solutions are commonly determined in terms of infinite series for geometries for which analytical solutions are known. The original Maxwell's equations are discretized and solved in the case of increasingly complicated geometries and inhomogeneous particles. Radiative transfer techniques are used to deal with the multiple-scattering effects of light scattering by particles. Combining DLS with other techniques are present commonly used approach for determination of particle' properties. DLS and zeta potential measurements have become common methods for determining particle size and surface charge because they are simple, easy, and repeatable. Laser diffraction and dynamic light scattering are two techniques used to analyze light scattering particles. What they see and detect, as well as how they make their separate measures, are fundamentally different. Regarding laser diffraction (laser light scattering or Fraunhofer diffraction), it is a method of illuminating individual particles in a wet or dry environment using a beam of light, usually from a laser. When light interacts with particle edges, it scatters and generates a pattern of light waves behind the particle. Both methods are confined to calculating the size of individual features, despite their differences in particle characterisation procedures.

B. X-ray

An X-ray, often known as X-radiation, is a type of penetrating high-energy electromagnetic radiation. The wavelength of most X-rays ranges from 10 picometers to 10 nanometers, corresponding to frequencies of 30 petahertz to 30 exahertz (301015–301018 Hz) and energies of 145eV to 124 keV. X-ray wavelengths are shorter than UV wavelengths and often longer than gamma ray wavelengths.

Photoabsorption, Compton scattering, and Rayleigh scattering are the three basic ways that X-rays interact with materials [15]. Because the X-ray photon energy is far higher than chemical binding energies, the intensity of these interactions is determined by the energy of the X-rays and the material's elemental composition, rather than chemical qualities. In the soft X-ray realm and for lower hard X-ray energies, photoabsorption or photoelectric absorption is the dominating interaction mechanism. Compton scattering dominates at higher energy

[15]. X-rays have been the most generally available, typically fastest, and usually most cost-effective medical imaging modality since Wilhelm Conrad Röntgen's discovery in 1895 [15].

In analytical chemistry, X-ray technology is also useful for determination properties of particles. As a tool for investigating the protein conformational ensemble, X-ray crystallography is undergoing a resurgence. However, because to the inherent limits of Bragg analysis, which only shows the mean structure, a spike in interest in diffuse scattering, which is produced by structure fluctuations, has emerged.

X-ray crystallography is an experimental science that determines the atomic and molecular structure of a crystal by causing a beam of incident X-rays to diffract in many different directions according to the crystalline structure. All macromolecular crystallography experiments include diffuse scattering. Recent research sheds light on the origins of diffuse scattering in protein crystallography and offers insight into how to employ diffuse scattering to describe protein movements in atomic detail [16–18]. For characterizing crystalline materials, X-ray diffraction is a potent nondestructive technique. Structures, phases, preferred crystal orientations (texture), and other structural data such as average grain size, crystallinity, strain, and crystal defects are all included [16]. The constructive interference of a monochromatic beam of X-rays dispersed at certain angles from each pair of lattice planes in a sample produces X-ray diffraction peaks. The distribution of atoms within the lattice determines the peak intensities. As a result, the fingerprint of periodic atomic configurations in a specific material is the X-ray diffraction pattern [16]. Hybrid approaches that are used to obtain insight into complex difficulties linked to biomolecular mechanisms rely heavily on X-ray technology [19].

X-ray microscopies are a hybrid of electron and light microscopy that can image very big and complicated structures. X-rays, which have dominated the imaging of crystallizable materials, could also be quite useful in imaging very large non-crystalline structures [20]. The links between the issue and X-ray crystallography are highlighted throughout the treatment [20]. Using hard-X-ray imaging microscopy, internal features in specimens with a spatial resolution of a few tens of nanometers can be viewed non-destructively [21]. Highly sensitive phase-contrast X-ray imaging microscopes could be made using the self-image phenomenon [21]. These technologies outperform classic X-ray imaging microscopes, such as the widely used Zernike X-ray phase-contrast microscopes, by providing a powerful means of quantitative visualization with great spatial resolution and sensitivity, even for thick specimens [21]. Soft x-ray microscopes are starting to deliver information that complements what optical and electron microscopy can provide [22]. Soft x-ray microscopy can produce images of hydrated cells up to 10 microns thick with a resolution of 30 nanometers, and efforts are underway to achieve better resolution [22]. Although living specimens can only be investigated in single exposures, fixed samples can be photographed at high resolution, and flash-frozen specimens can be analyzed without considerable chemical change or radiation damage [22].

New nonlinear X-ray spectroscopic techniques to investigate coherent electronic motion could be enabled by ultraintense X-ray free-electron laser pulses of attosecond length [17]. Stimulated electronic X-ray Raman scattering is the most basic nonlinear X-ray spectroscopic principle. We offer a summary of recent experimental discoveries that are paving the path to the realization of nonlinear X-ray spectroscopy [17].

C. Electron

Electron scattering is the deflection of an electron's path as it passes through a substance (typically a metal, semiconductor, or insulator). Electrostatic forces acting between negatively charged electrons and atoms within the solid generate deflections, or collisions (see quantum electrodynamics). Circular dichroism spectroscopy is an important tool for studying molecular structure and magnetic materials. However, spatial resolution is restricted by light wavelength, and sensitivity adequate for single-molecule spectroscopy is difficult to achieve [23]. Electron crystallography is a potent method for determining the structural properties of substances that form thin microcrystals. Similar to X-ray crystallography, electron-beam crystallography is a useful analytical technique for determining properties of molecules [24]. In addition to the traditional 'direct' methods employed by all crystallographers nowadays, the notion of electron crystallography benefits from the utility of electron micrographs for providing phase information [25]. Various sorts of specimens, ranging from small organics to proteins, as well as some inorganic materials, have been subjected to numerous uses [24]. While electron crystallography isn't the best approach for finding precise bonding characteristics, it's frequently used when only microcrystalline specimens are available [24]. The results for tiny organics, polymethylene compounds, different polymers, and even intracellular membrane proteins accord well with independent X-ray crystal structure determinations, which were not required to address the crystallographic phase problem from electron scattering data [25]. Because multiple-beam dynamical scattering can cause measured diffraction intensities to diverge greatly from their kinematical values, it's important to show that ab initio conditions can be established [26].

D. Neutron

Neutrons are useful as tests of bulk characteristics because they are electrically neutral and penetrate deeper into materials than electrically charged particles of comparable kinetic energy [27]. Because thermal/cold neutrons are a noninvasive probe that do not deposit energy into the researched sample, neutron scattering is the technique of choice for condensed matter investigations in general [27]. In neutron scattering experiments, neutrons interact with atomic nuclei and magnetic fields from unpaired electrons, creating significant interference and energy transfer effects [27]. Neutrons interact largely with the nucleus itself, unlike an X-ray photon of comparable wavelength that interacts with the electron cloud surrounding the nucleus. The cross sections of neutron scattering and absorption differ greatly from isotope to isotope [27]. Neutron scattering provides a lot of advantages when it comes to studying the structure of tiny molecules. Because cold (slow) neutrons are non-destructive and primarily interact with the atomic nucleus, neutron beams can penetrate deeper into samples, allowing for greater flexibility in sample design [28]. Because it deals with molecules in huge, complex, dynamic structures and can quickly distinguish between distinct chemical species, neutron scattering is well suited to assist in both of these areas. This is due to neutrons' high penetrating strength and sensitivity to the differences between molecules [29].

For determining of scattering, the basic requirement is the tool for analysis. The first step is to prepare the specimen for analysis. The different tools are available for analysis based on the principles of scattering as already described. The tool will have two important parts. The first part is the source of electromagnetic wave to beam to the molecules within the specimen. The second part is the detector for scattered back reflection from molecules. The detector will act as sensor and there will be a specific system for data interpretation (Fig. 2).

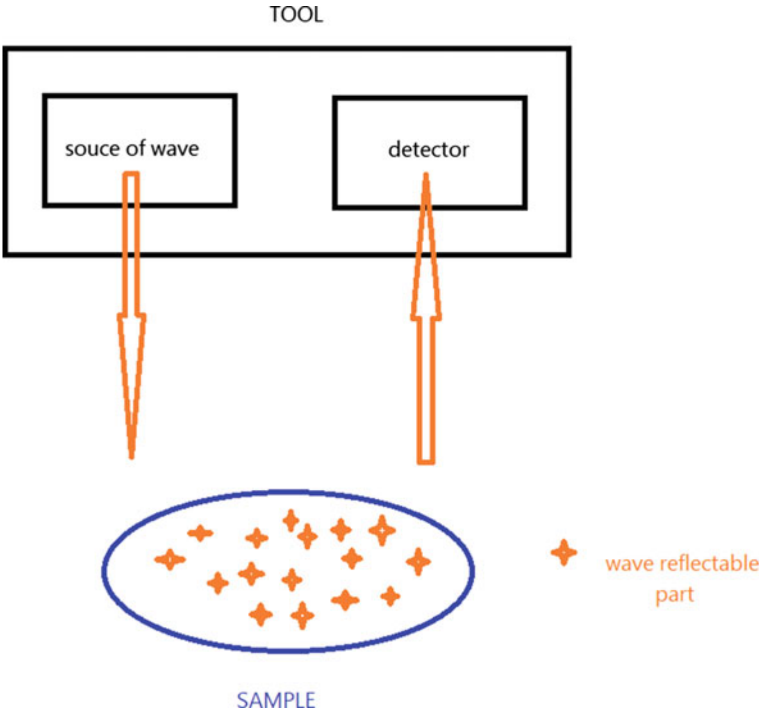

Fig. 2 Concept and tool for determination of scattering

5 Important Reports on Scattering Studies of PVC Composites and Nanocomposites

There are some reports on scattering studies of PVC composites. The studies include researching on properties of the newly developed PVC composites and nanocomposites. Applications are in several fields including physical science and biomedical science. Important reports will be summarized and presented.

A. Light scattering studies of PVC composites and nanocomposites

Important reports on light scattering studies of PVC composites are listed in Table 1 [30, 31].

B. X-ray scattering studies of PVC composites and nanocomposites

Important reports on X-ray scattering studies of PVC composites are listed in Table 2 [30, 32–40].

C. Electron scattering studies of PVC composites and nanocomposites

Important reports on electron scattering studies of PVC composites are listed in Table 3 [41–45].

D. Neutron scattering studies of PVC composites and nanocomposites

Important reports on neutron scattering studies of PVC composites are listed in Table 4 [46, 47].

Table 1 Important reports on light scattering studies of PVC composites and nanocomposites

Authors	Details
Li et al. [30]	Li et al. set out to create a regression model that might be used to create PVC formulations with specific mechanical and multimodal medical imaging capabilities [30]. The mechanical properties of three variables were varied and measured in this study: (1) the ratio of softener to PVC polymer, (2) the mass fraction of mineral oil, and (3) the mass fraction of glass beads. The relationship between the mechanical and medical imaging properties of PVC and the values of the three composition components of PVC was described using a regression model [30]. The model was validated by comparing the properties of a PVC sample to those of other samples [30]
Lecoeur et al. [31]	For the analysis of plasticizers (ATBC, DEHA, DEHT, and TOTM) in PVC tubing used as medical devices, Lecoeur et al. compared the quantitative performances of SFC-light scattering detection (ELSD) to HPLC-ELSD [31]. The composition of plasticized-PVC medical equipment was determined using both approaches. SFC and HPLC hyphenated with ELSD produced similar results, according to the findings [31]

Table 2 Important reports on X-ray scattering studies of PVC composites and nanocomposites

Authors	Details
Li et al. [30]	Li and colleagues set out to develop a regression model that might be utilized to develop PVC formulations with specialized mechanical and multimodal medical imaging capabilities [30]. This study altered and measured the mechanical properties of three variables: (1) the ratio of softener to PVC polymer, (2) the mass fraction of mineral oil, and (3) the mass fraction of glass beads. A regression model was used to describe the link between the mechanical and medical imaging properties of PVC and the values of the three composition components of PVC [30]. By comparing the properties of a PVC sample to those of other samples, the model was validated [30]
Bao et al. [32]	Bao et al. Bao et al. looked at the adsorption behavior of 3-OHP on PVC microplastics in aqueous solutions, as well as the adsorption mechanism. Scanning electron microscopy (SEM), X-ray diffraction, and Fourier transform infrared (FT-IR) spectroscopy were used to analyze the PVC microplastics [32]. Bao et al. discovered the mechanism of interaction between PVC microplastics and organic compounds, which contributes to a better understanding of PVC microplastics' environmental behavior in aqueous solutions [32]
Gupta et al. [33]	Gupta et al. studied on a composite with CuS particles and PVC as a matrix [33]. Gupta et al. demonstrated a simple, affordable, and repeatable process for fabricating Cu(II) ion-selective electrodes [33]. X-ray diffraction, Fourier-transform infrared spectroscopy, ultraviolet–visible spectroscopy, scanning electron microscopy (SEM), and energy-dispersive X-Ray spectroscopy were used to characterize CuS particles produced by chemical precipitation [33]
Tworek et al. [34]	Tworek et al. studied on properties of PVC membranes containing cadmium pigments, irradiated with UV radiation [34]. Thermogravimetric analysis was used to analyze the changes in the PVC membrane [34]. X-ray diffraction was used to determine the crystallinity of the pigments and membrane [34]
Gao et al. [35]	Synthesis of a Solid Superacid and Its Application in Flame-Retardant PVC Material was reported by Gao et al. [35]. In this study, TiO2/PO4 3-solid superacid was produced by precipitation immersion and studied using X-ray diffraction and an energy-dispersive spectrometer; it was then used as a flame retardant in fPVC composites
Shen et al. [36]	Enhancing mechanical properties of PVC-based wood-plastic composites with pretreated corn stalk was investigated by Shen et al. [36]. Shen et al. discovered that the C sample, which was stripped of both lignin and hemicellulose, has the highest degree of crystallinity as determined by X-ray diffraction analysis and fibrous morphology with the highest aspect ratio as determined by scanning electron microscopy images [36]

(continued)

Table 2 (continued)

Authors	Details
Nadagouda et al. [37]	Novel thermally stable PVC composites for sulfate removal were described by Nadagouda et al. [37]. Scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray mapping, X-ray diffraction, thermogravimetric analysis, and inductively coupled plasma mass spectrometry analysis were used to evaluate the PVC composites [37]. When compared to the pure PVC described in the literature, Nadagouda et al. discovered that several of the composites \were thermally more stable [37]
Mallakpour and Hajjari [38]	Ultrasound-assisted surface treatment of ZrO 2 with BSA and incorporation into PVC to improve the characteristics of the resulting nanocomposites was reported by Mallakpour and Hajjari [38]. Fourier transform infrared spectroscopy, Transmission electron microscopy, Field emission scanning electron microscopy, X-ray diffraction, ultraviolet–visible spectroscopy, photoluminescence spectroscopy, thermogravimetric analysis, energy dispersive X-ray spectroscopy, wettability tests, and mechanical tests were used to characterize the products [38]
Mallakpour and Darvishzadeh [39]	The physicochemical properties of PVC reinforced with ZnO nanoparticles were investigated in this experiment. First, ZnO nanoparticles were irradiated with ultrasound to modify them with bovine serum albumin as an organo-modifier and biocompatible material [39]. Fourier transform infrared spectroscopy, X-ray diffraction, thermogravimetric analysis (TGA), transmission electron microscopy, and field emission scanning electron microscopy were used to analyze the nanoparticles [39]
Hamid et al	Hamid et al. investigated the physio-chemical appraisal of green synthesized lead oxide nanoparticles in lead oxide-PVC nanocomposite polymer membranes in this study [40]

6 Conclusion

PVC (polyvinyl chloride) is the third most commonly used thermoplastic polymer on the planet. Growing polymer product usage currently generates massive amounts of garbage, increasing public worry about the environment and people's livelihoods. A particular procedure is required for PVC formulation. PVC composites and nanocomposites can be made using basic material science methods. The use of various compositing techniques to blend PVC with other components is the key foundation. PVC composites and nanocomposites come in a variety of shapes and sizes. The properties of various composites are usually distinct. One of the features that is changed is scattering. X-ray, light, and neutron scattering can be used to characterize the scattering properties of PVC composites and nanocomposites. The instrument for analysis is the most important necessity for determining scattering. The specimen must first be prepared for analysis. The various techniques for analysis are based on the previously established scattering concepts. There will be two major components to the tool. The first component is the electromagnetic wave source that will be

Table 3 Important reports on electron scattering studies of PVC composites and nanocomposites

Authors	Details
Baibarac et al. [41]	A new approach for obtaining PVC spheres is disclosed in this paper [42], which involves an interaction between commercial PVC grains, hexyl ethyl cellulose, and lauroyl peroxide at a temperature of 60 °C. When the GO concentration in the PVC/GO composite mass grows from 0.5 to 5 wt. percent, scanning electron microscopy experiments showed that this approach allowed for the transformation of PVC grains with diameters ranging from 75 to 227 m into spheres with sizes ranging from 0.7 to 3.5 m [41]
Chuayjuljit et al. [42]	PVC film packed with microcrystalline cellulose made from cotton fabric waste was described by Chuayjuljit et al. [42]. X-ray diffractometer, scanning electron microscope, laser light scattering particle size analyzer, and thermogravimetric analyzer were used to characterize the structure, morphology, particle size, and thermal disintegration of the produced MCC, respectively [42]
Roh et al. [43]	A wormlike morphology poly(vinyl chloride)-g-poly(oxyethylene methacrylate) (PVC-g-POEM) graft copolymer was used as a soft matrix in this study to construct a mixed matrix membrane with mesoporous MgTiO3 perovskite using a solution-casting approach [43]. Transmission electron microscopy [43] revealed that the structure and morphology of the PVC-g-POEM graft copolymer were carefully controlled by manipulating polymer–solvent interactions [43]
Saberi et al. [44]	Using the dry-jet wet-spinning process, PVC/SiO2 nanocomposite hollow-fiber membranes with varied nano-SiO2 particle loadings were created in this study [44]. SEM was used to evaluate the effects of SiO2 nanoparticles on the morphology of the produced hollow-fiber membranes [44]. According to Saberi et al., integrating silica nanoparticles into the PVC matrix is a potential strategy for developing cost-effective hollow-fiber ultrafiltration membranes with antifouling properties and good transport [44]
Koh et al. [45]	Using a sol–gel technique aided by poly(vinyl chloride-graft-4-vinyl pyridine), PVC-g-P4VP graft copolymer and a ZnO nanorod template, porous TiO(2) nanotube arrays with three-dimensional interconnectivity were created [45]. Wide-angle x-ray scattering, energy-filtering transmission electron microscopy, and field-emission scanning electron microscopy were used for analyzing properties of the new nanoparticles [45]. In dye-sensitized solar cells, the ordered and interconnected nanotube design enhanced light scattering and increased polymer electrolyte penetration [45]

directed at the molecules within the specimen. The detector for scattered back reflection from molecules is the second part. There are several studies on using scattering analysis to assess the new PVC composites and nanocomposites. Physical science and biomedical science are two domains where applications might be found. There will be a summary and presentation of important reports. The scattering analysis is proven a useful tool for determining the proper of newly develop PVC composites and nanocomposites. Data from the analysis can guide further modification aiming improvement of newly designed PVC composites and nanocomposites.

Table 4 Important reports on neutron scattering studies of PVC composites and nanocomposites

Authors	details
Kalvoda et al. [46]	Structure and textural study of PVC foils by neutron diffraction was described by Kalvoda et al. [46]. Using wide-angle neutron diffraction, the crystalline order of molded and then bi-axially stretched foils made from atactic PVC resin is examined [46]. According to Kalvoda et al., the average size of coherently scattering regions is around 4–8 nm [46]
Ye et al. [47]	Small-angle neutron scattering was used to investigate the microstructure of plasticized PVC membranes in the dry state and throughout the process of soaking in heavy water in this work [47]. According to this study, the kind of plasticizer, the amount of plasticizer used, and the inclusion of a lipophilic salt all had a substantial impact on water uptake, however water uptake did not modify the microstructure due to the membranes' inherent inhomogeneities [47]
Zorn et al. [48]	Zorn et al. compared the effects of plasticization on the microscopic dynamics of a glass-forming polymer with and without the commercially available plasticizer dioctylphthalate [48]. Dielectric spectroscopy and inelastic neutron scattering using the neutron spin echo technique were used by Zorn et al. [48]

Conflict of Interest None.

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Thermal Characteristics, Stability, and Degradation of PVC Composites and Nanocomposites

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Abstract PVC composites are frequently and widely used in numerous engineering applications because they offer a cost-effective and versatile solution with improved mechanical, thermal, and barrier properties for various applications. Investigating the thermal characteristics, thermal stability, and thermal degradation of PVC-based composites is essential to ensure their optimal performance, safety, and durability in polymer material science. The current study briefly explains the thermal properties and degradation mechanism of PVC and then focuses are placed on the composites with PVC matrix. In particular, the thermal characteristics of different composite formulations and strategies based on different reinforcements were presented and compared within each strategy and in between. This overview will help to gain a profound understanding of the current state of PVC-based composites and nanocomposites in the context of thermal properties and thermal degradation to determine the best formulation, processing processes, and conditions of such composite materials.

1 Introduction

Polymer matrix composites are used to achieve combinations of properties that could not be attained with the individual polymeric materials. In other words, by the combination of materials that can be in the form of particles, fibers, or sheet laminates and

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as well as the possible synergetic effects arising from this contribution, polymer-matrix composites have properties that are unique and cannot be obtained from each material acting alone [1]. Amongst commercial polymeric materials, polyvinylchloride (PVC) has outstanding chemical resistance to a wide range of corrosive fluids and offers more strength and rigidity than most other thermoplastics [2]. In addition, it is easy to fabricate and it can last for a long time. Therefore, various approaches have been developed to enhance the characteristics of PVC.

Thermal stability is an important characteristic of PVC, specifically for its applications at elevated temperatures. The thermal stability of PVC can be altered by forming composites/nanocomposites. Thermal characteristics of the composite provide information to determine the behavior of the material under the action of heat and the safe operating temperature range. Also, geometrical, and structural changes such as expansion and contraction during heat cycling in the case of intimate contact with other materials may affect the application constraints of the composite material. In particular, it is extremely important to determine the relationship between key thermal properties of composites and nanocomposites fabricated from PVC and their details of the manufacturing process from an experimental or theoretical point of view. Therefore, thermal characterization of PVC and PVC-based composites is one of the basic analyses for providing detailed knowledge of the structure–property relationship that indicates the opportunity to find specific practical applications of such composites.

In this context, the current chapter focuses on a step-by-step ideology of the thermal stability and degradation of PVC and PVC-based composites and nanocomposites. The thermal degradation behavior of PVC has been evaluated under three main titles: (i) thermal degradation of PVC polymer (ii) thermal degradation of PVC-composites (iii) thermal degradation of PVC-nanocomposites.

2 Thermal Characteristics of PVC

In the field of polymer materials science, various parameters should be considered to fully characterize the thermal behaviors of polymer matrix composites such as thermal conductivity, thermal expansion, and heat capacity. Table 1 lists the typical ranges of such thermal properties several of which are intrinsic to the characteristics of the PVC sample. It is also important to consider that various additives need to be inserted into the PVC resin to make it applicable for specific purposes. The most commonly used additives are known as heat stabilizers, plasticizers, fillers, lubricants, processing aids, etc. Undoubtedly, the type and amount of the additives have an enormous impact on the thermal characteristics of PVC. For instance, the glass transition temperature (T_g) of processed PVC is known to be decreased when plasticizers are added [3].

According to the Table 1, typical values of thermal conductivity of PVC are between 0.146 and 0.209 W/m·K This is known as the capacity of a material to transport heat by conduction heat transfer mechanism or heat transfer except by

Table 1 A summary of thermal properties of PVC [13, 14]

Property	Value/or Range
Thermal conductivity (at 20 °C)	0.146–0.209 W/m·K
Thermal expansion coefficient	2.8×10^{-5}–5.6×10^{-5} K^{-1}
Melting temperature	150–160 °C
Crystalline melting point	285 °C
Thermal diffusivity (at 20 °C)	0.98×10^{-3}–1.19×10^{-3} cm^2/s
Heat capacity	0.97 J/K·g
Glass transition temperature	78–107 °C

radiation or convection mechanisms. There are three kinds of carriers in solids to transport energy: phonons, electrons, and photons [4]. PVC polymer is regarded as a heat insulator which means the electrons will not play an important role in thermal conduction. Phonons are quantized modes of vibration in a rigid crystal lattice, which is the fundamental mechanism of heat conduction in most polymers [5]. PVC is an amorphous state that has defects that contribute to numerous scattering, leading to low thermal conductivity. The thermal conductivity is determined by considering the orientation, geometry, properties of fillers, interphases, the morphology of the components of PVC composites or nanocomposites, and their interaction with the fillers and the matrix together with possessing technology and external conditions [6, 7].

The coefficient of thermal expansion of a homogeneous polymer is the change in the length of the material when the temperature is raised [8]. Polymeric materials with a high thermal expansion coefficient may lose their performance due to unacceptable resizing during the heat treatment processes. PVC has a thermal expansion coefficient range between 2.8×10^{-5} and 5.6×10^{-5} K^{-1} depending on its characteristics such as chain length. In the design, production, and processing of polymer-matrix composites, it is important to define both a minimum degree of cure and a minimum glass transition temperature (T_g) to be attained after the cure to provide the mechanical characteristics required for a specific structural application [9]. The restrictions of PVC usage in some applications are mostly related to the relatively high T_g of PVC which is due to the strong polar interactions between chlorine and carbon [10].

The heat capacity indicates heat storage capacity and the amount of energy required to create a unit temperature increase within the material. It is one of the most essential thermophysical characteristics of polymers, and frequently used to compute other thermodynamic properties including enthalpy, entropy, and Gibbs free energy. The value of heat capacity for pure PVC is known to be around 0.97 J/K·g [10].

Thermal diffusivity is another key thermal characteristic that governs heat transfer in a composite material. It is defined as the energy flux, across any section per unit enthalpy gradient under unsteady conditions which is the ratio of thermal conductivity, specific heat, and density [11]. It is crucial in the thermal design of heat insulators and heat dissipaters because it has a direct impact on the temperature distribution within them. The thermal diffusivity of PVC is in the range of 0.98×10^{-3}–1.19×10^{-3} cm^2/s which is lower than that of other commonly used polymeric materials [12].

The ability of a polymeric material to withstand the action of heat and maintain characteristics such as strength, toughness, or elasticity at a particular temperature is referred to thermal stability. Thermal methods including thermogravimetric analysis (TGA), accelerating rate calorimetry, differential photocalorimetry, and differential scanning calorimetry (DSC) can be performed to determine the thermal stability of polymers and composites, although the most commonly used technique is TGA. Moreover, some analytical instruments including spectroscopic, chromatographic, and rheological measurements can be performed to understand the structural characteristics of the polymer during thermal degradation. The chemical structure, degree of crystallinity, and molecular weight of a polymer all have an impact on its thermal stability.

2.1 *Thermal Degradation of PVC*

The thermal degradation behavior of PVC and PVC-based composites and nanocomposites, should be investigated in-depth. to fully understand their thermal stability. As explained before, TGA is one of the commonly preferred instrumental techniques for the visualization of the changes during heat treatment. To achieve a general idea about PVC degradation, TGA under several experimental conditions is performed as given in Fig. 1. The experiments were conducted at different heating rates (between 5 and 40 °C/min) and in different atmospheres (under nitrogen and air) to understand the pyrolytic and oxidative degradation of PVC. A a stepwise degradation occurred and the main degradation zone extended approximately from 235 to 535 °C at a heating rate of 10 °C/min under an inert atmosphere (Fig. 1a). Around 285 °C maximum dTG peak temperature indicated the higher rates of decomposition. When the heating rate was increased, the onset and terminal degradation temperatures shifted to higher temperatures, and the peaks became sharper (Fig. 1b). Also, the increase in heating rate hindered the thermal degradation products on the surface to diffuse, thereby the internal thermal degradation was postponed resulting in a thermal hysteresis (or thermal lag). The temperature variation throughout the sample section in the TGA furnace caused thermal hysteresis. Higher heating rates shortened the reaction time for samples that are not conductive to heat transfer since the reactions need a certain amount of time [15, 16]. To observe the effect of the atmosphere on the thermal degradation of PVC, analyses were performed on both inert and oxidative conditions comparatively and the resulted thermograms are given in Fig. 1c. The thermograms of PVC under air atmosphere beared a striking dissimilarity to the thermograms taken under nitrogen atmosphere, indicating that different mechanisms of decomposition occur in the presence of oxygen. For oxidative degradation of PVC, an additional weight-loss stage was noticeable showing the char formation and char combustion at higher temperatures, which is known as char combustion or secondary carbonization.

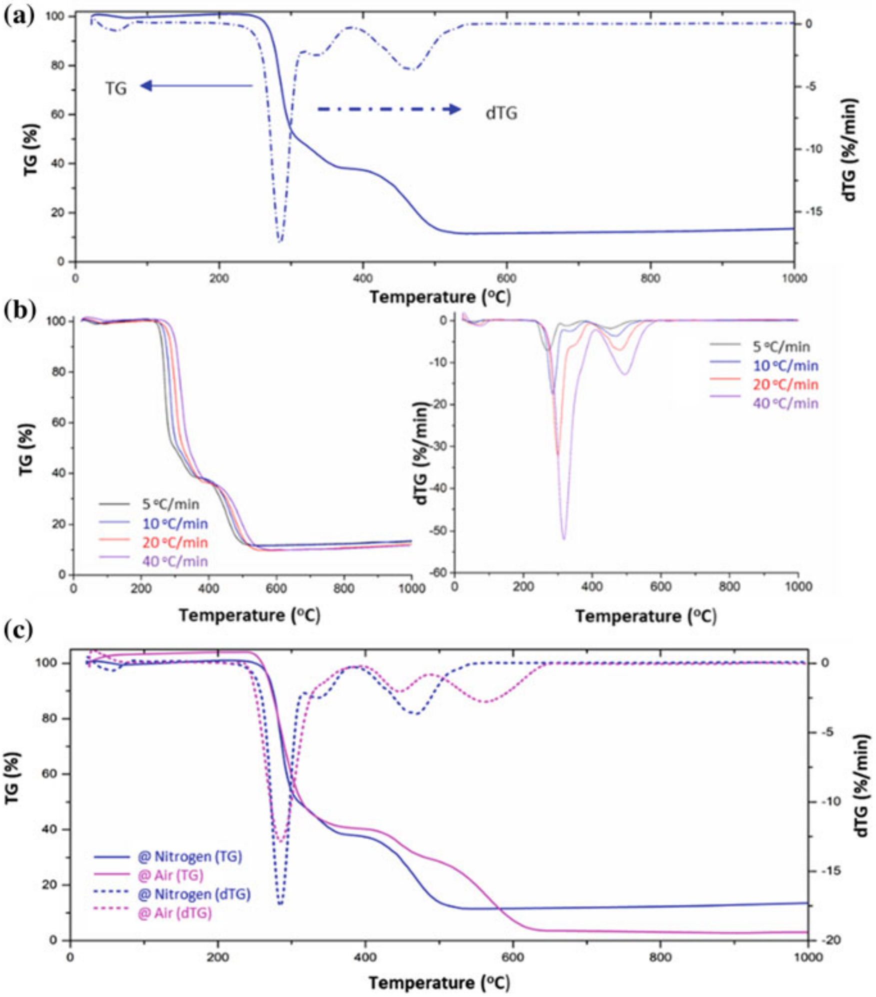

Fig. 1 TG and dTG curves or PVC degradation, **a** at 10 °C/min, **b** effect of heating rate, **c** effect of degradation atmosphere (Reprint with permission from [33, 35])

To provide a precise and full image of the mechanisms lying behind thermal degradation, some of the published literature clearly states the critical mechanistic features of PVC and its relation to decomposition. It is known that PVC pyrolysis begins with HCl elimination or dehydrochlorination, which is triggered by the scission of the Cl–C bond, resulting in chlorine radical at lower temperatures. The dehydrochlorination process also produces conjugated pi bonds and polyene radicals, as well as the formation of certain hydrocarbons, notably unsubstituted aromatic hydrocarbons. In the thermal decomposition of PVC, the evolution of HCl is crucial because degradation follows an autocatalytic dehydrochlorination route with the formation of conjugated pi bonds [17, 18]. In other words, the HCl generated during dehydrochlorination can catalyze degradation resulting in the formation of polyene sequence. The release of HCl gas makes allylic chlorine more active in the polymer backbone and unzipping initiates until the conjugation is stabilized by resonance itself. The products during this dehydrochlorination step are HCl, a small amount of benzene, alkyl aromatic hydrocarbons (toluene, xylene isomers, ethylbenzene, etc.), and condensed ring aromatic hydrocarbons (naphthalene, indene, indene, etc.) [19, 20]. The formation of volatile aromatic compounds increases as the temperature rises, and the breakdown is accompanied by cracking into low hydrocarbons with a linear or cyclic structure [18, 21]. Therefore, the formation of alkyl aromatics with some char formation occurs because of condensation and dehydrogenation with severe dealkylation, isomerization, chain scission, crosslinking, and aromatization after the dehydrochlorination step. Eventually, aromatic and polyaromatic compounds and a small amount of char are generated after the main thermal degradation zone of PVC in an inert atmosphere [22].

The thermal degradation behavior of PVC under an oxidative atmosphere differs from inert atmosphere treatment due to the different reactions taking place in the presence of oxygen. It's worth noting that, oxidative thermal degradation of PVC aided devolatilization, resulting in a decreased weight proportion of residual char. The solid residue left is substantially smaller than the residue left after degrading under an inert atmosphere, which is around 2%. According to Valko et al. [23] the catalytic impact of oxygen, particularly during the HCl elimination stage, might be responsible for this significant weight loss and the occurrence of the final char burning stage. Some oxidation reactions were anticipated to form volatile products such as CO_2, CO, H_2O, and oxygen-containing compounds in the air atmosphere. As a result, less char residue had remained after degradation in the air atmosphere than in that of an inert atmosphere. Another important observation on the differences between oxidative decomposition and pyrolytic decomposition was that thermal decomposition under an air atmosphere exhibited a wide mass loss temperature range. It is most likely that in the oxidative degradation of PVC, the heating rate was the decisive factor in the termination temperature since differences in termination temperature under an air atmosphere were higher than that of an inert atmosphere. It may indicate that the char oxidation stage required further time under the air atmosphere.

The peak deconvolution technique is also a beneficial approach at the initial stage of mechanistic studies to explain the degradation behavior of PVC. Figure 2 shows deconvoluted peaks for PVC degradation at a 10 °C/min heating rate under a nitrogen flow with a flow rate of 20 cm^3/min. When the Asym-2 sig function has been applied to the experimental dTG thermogram of PVC pyrolysis, the function succeeds to deconvolute the complex PVC degradation with reasonable suitable statistical indicators (reduced chi-square = 0.01301 and Adj. $R^2 = 0.9807$). It showed that three different deconvoluted peak model is favorable to describe thermal degradation of PVC which included several decomposition pathways. The description of each reaction route, obtained from deconvolution, could be used in the further kinetic analysis and interpretation of the kinetic triplet. As seen in the Fig. 2, the splitting of multiple peaks was associated with multi-stage reaction routes during the thermal degradation of PVC. This result was also compatible with the kinetic findings and comments of previous researchers [24–33].

Several researchers published further studies on the thermo-kinetics for the PVC pyrolysis and also investigated evolved gasses during PVC degradation with the combination of techniques such as TGA/FT-IR, TGA-MS, and Py/GC–MS. Evolved gas analysis from thermal analyzers by spectroscopic and coupled chromatography–spectroscopy techniques can be extremely significant from a safety and hazard standpoint because data from such measurements can be used to predict toxic or polluting gases from fires and thermal degradation [34]. Figure 3 shows the main evolved gasses determined by coupled FT-IR and MS spectroscopy with TGA. In the 3-dimensional FT-IR spectrum (Fig. 3a) the most prominent bands between 3100 and 2650 cm^{-1} may be attributed to the rotational spectrum of the asymmetrical stretch of HCl. The instantaneous FT-IR spectrum of PVC degradation (Fig. 3c) also proved

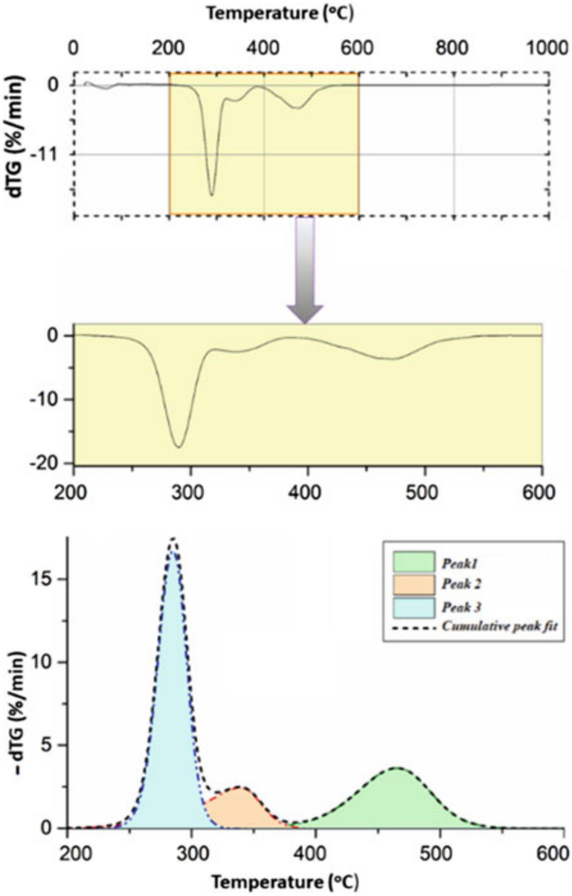

Fig. 2 Deconvoluted dTG curves for PVC degradation (Reprint with permission from [33, 35])

the release of HCl, which could be observed by an asymmetric H–Cl stretching vibration between 3100 and 2650 cm^{-1} and –C–Cl stretching vibrations between 800 and 600 cm^{-1}. Additionally, some skeletal vibrations of aromatic hydrocarbons were observed between 1500 and 1400 cm^{-1}. The simultaneous MS spectrum (Fig. 3b) also focused on the evolution of $-CH_3$, HCl, CO_2 and C_6H_6 with m/z values of 15, 36, 44, and 78, respectively. According to the findings, the dehydrochlorination step seemed to be a rapid reaction that starts at approximately 280 °C and reached its maximum at approximately 370 °C. The formation of HCl proceeded with a decreasing intensity until the completion of the heating process during thermal degradation. After dehydrochlorination, the formation of alkyl aromatics with a small amount of char was known to be occurred due to condensation and dehydrogenation reactions with deep dealkylation, isomerization, chain scission, crosslinking, and aromatization. The evolution of $-CH_3$, and CO_2 were also related to such kind of complex degradation mechanisms. Especially, CO_2 evolution in Fig. 3b is representative of step-wise degradation mechanisms which resulted in decarboxylation. Concerning the evolution of aromatics, the release of C_6H_6 was presented with an $m/z = 78$ curve during the PVC pyrolysis. Aromatization of smaller molecules, primarily by Diels–Alder type cyclization processes, may have resulted in the creation of benzene. The C_6H_6 formation nearly started at around the same temperature as the dehydrochlorination reactions but came to an end earlier by exhibiting a narrower peak with a maximum of 285 °C [35, 36].

A recent study by Zhou et al. also explained the complex degradation mechanism of PVC. The authors quantitatively determined the formation of several classes of compounds including chlorinated hydrocarbons, alkenes (alkadienes and cycloalkenes), aromatics (monocyclic aromatics, PAHs), and HCl at different temperatures. Figure 4 displays a plausible representation of occurring reactions during thermal degradation of PVC that involved the formation of alkenes, chlorinated hydrocarbons, monocyclic aromatics, and PAHs. According to the results, the relative content of the main four classes of chemicals varied depending on the final temperature as aromatics, alkenes, HCl, and chlorinated hydrocarbons. The relative amount of alkadienes increased as the final temperature increased while that of cyclic alkenes and monocyclic aromatics increased and then declined, and that of PAHs decreased and then increased. Alkenes, monocyclic aromatics, and PAHs had carbon numbers ranging from C_5 to C_{10}, C_6 to C_{11}, and C_9 to C_{17}, respectively at various temperatures [37].

3 Thermal Degradation of PVC Composites

It is generally accepted that some of the weaknesses of PVC, such as its poor impact strength and thermal stability, limit its use, utilization in industrial applications, and hence, becomes necessary to achieve detailed knowledge on its material characteristics [38]. Among most of the other thermoplastic matrices, PVC differs in composites since it allows extensive customization of physicochemical, mechanical, and

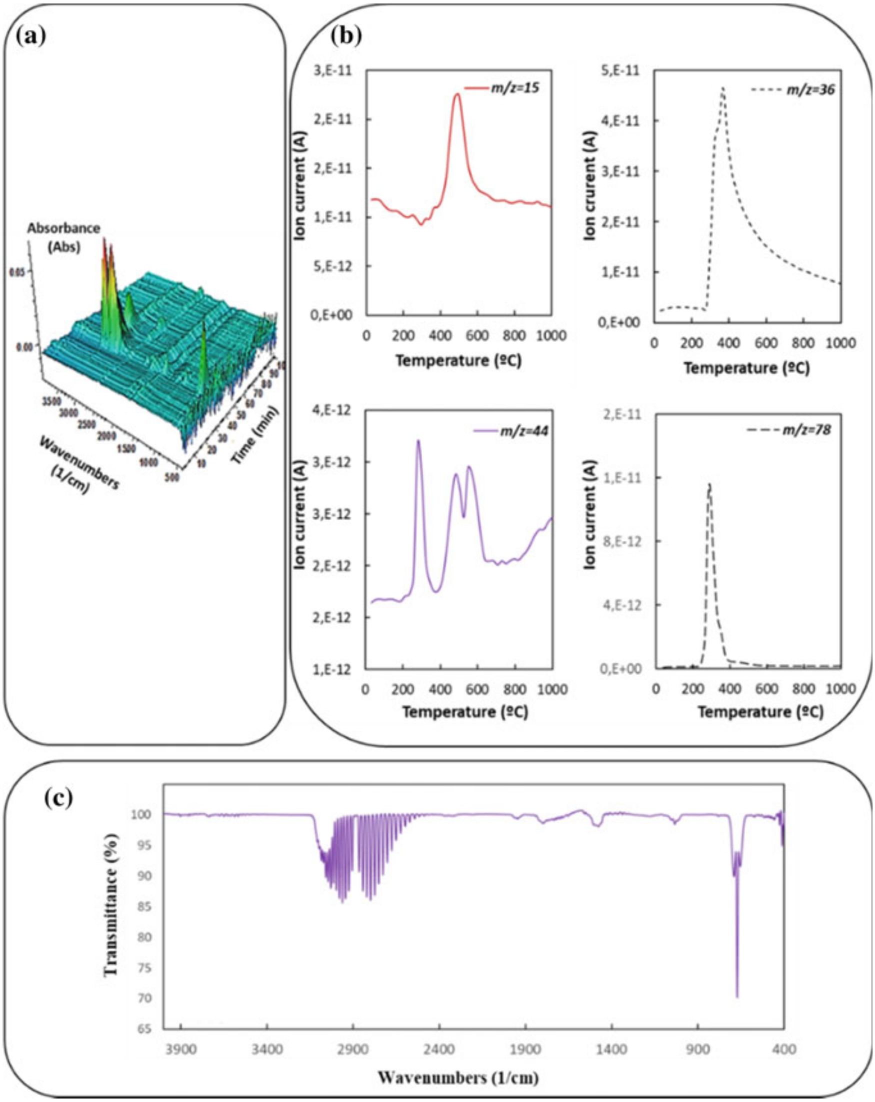

Fig. 3 Evolved gas analysis results of PVC degradation at 10 °C/min, **a** 3-dimensional FT-IR spectrum, **b** single-ion curves during MS analysis, **c** FT-IR spectrum at maximum degradation rate (at 285 °C) (Reprint with permission from [16, 36])

processing qualities by incorporating various processing additives [39–42]. During manufacturing of PVC-based composites, fillers are often employed to give plastics rigidity and strength. Although inorganic fillers like calcium carbonate, glass fiber, clay, mica, and talc now dominate the thermoplastic industry, wood-derived fillers have gained in popularity in recent years as a result of growing recycling awareness

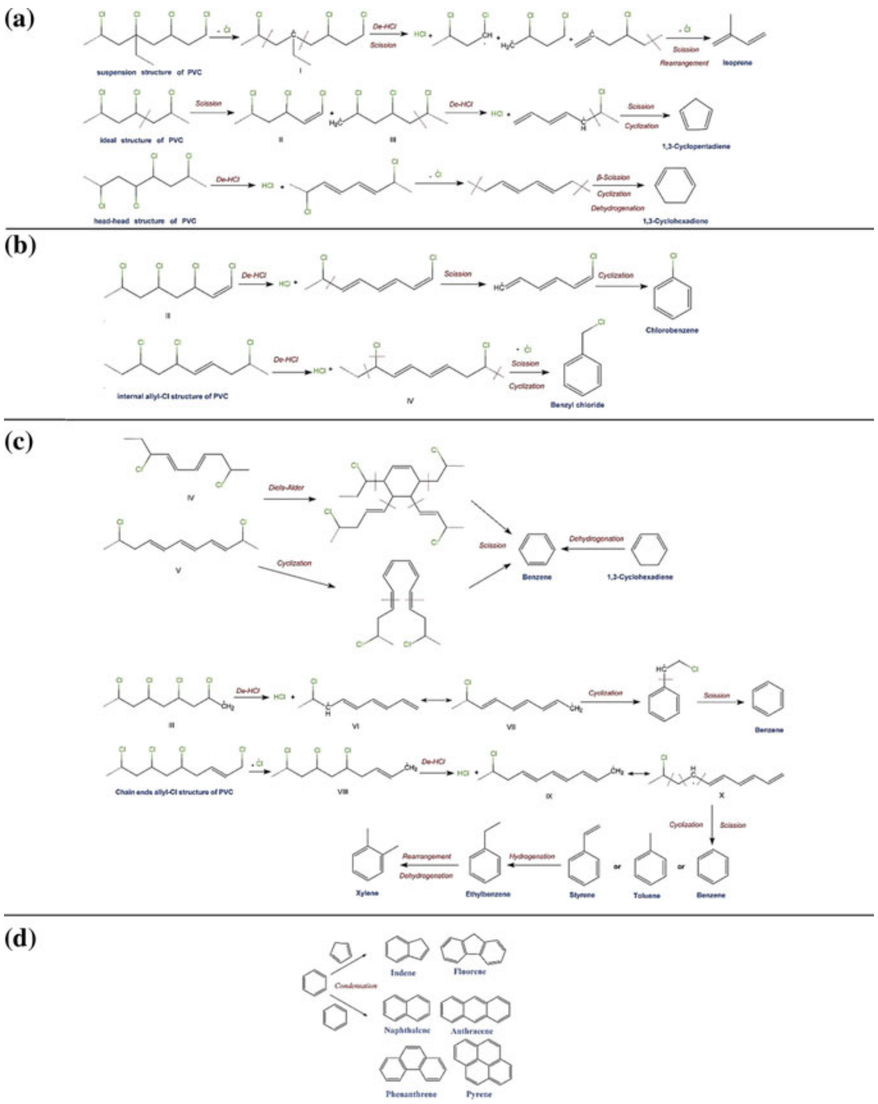

Fig. 4 Plausible reactions during PVC pyrolysis, **a** formation of alkenes, **b** formation of chlorinated hydrocarbons, **c** formation of monocyclic aromatics and **d** formation of PAH's (Reprint with permission from [37])

and the need for lower-cost precursors [43]. Especially, the use of renewable fillers in PVC composites, such as natural plant fibers, wood fiber, and lignin, results in materials with beneficial qualities that can be successfully employed as construction materials as well as in the automobile and furniture industry [44]. Natural wood fiber and other lignocellulosic biomass as a filler in thermoplastics lowers the cost of manufactured goods while also helping to conserve the environment [45]. However, thermal, and dynamic mechanical behavior research in wood, natural fiber-plastic composites is still lacking, particularly the impact of wood particles on polymer matrix molecular chain motions at elevated temperatures needs to be clarified.

Thermal and dynamic mechanical behaviors of wood plastic composites are generally characterized by using TGA, DSC, dynamic mechanical analysis (DMA) in the literature. For instance, Kabir et al. developed the bamboo fiber and PVC foam sheet composites via hot compression molding process. The thermal properties of the samples were monitored by a coupled DTA and TGA. TG-dTG results showed that there are two stages related to the significant deterioration. Dechlorination and depolymerisation are the first and second stages, respectively. The total mass loss during dechlorination was 39.9%, but during depolymerization, it was 25.6 percent, leaving 26.6 percent residue. The two endothermic peaks of DTA are found at 291.5 °C and 447.3 °C, respectively. The first is caused by melting, and the second is caused by PVC degradation [46]. Jiang et al. studied the thermal and dynamic mechanical behaviors of wood plastic composites made of PVC and surface treated, untreated wood flour that was characterized by using DSC and DMA. They showed the addition of untreated and Cu-treated wood flour to PVC resulted in small increases in T_g, but this effect was not as significant as T_g calculated from the peak temperature of observed by DMA analysis. The addition of wood flour and wood Cu-treatment significantly reduced heat capacity imparities between composites before and after T_g [47].

Fardausy et al. determined the physical, mechanical, and thermal properties of unidirectional jute fiber reinforced PVC film composites. Thermal characterization of PVC-jute fiber composites revealed that thermal degradation of the PVC film occurs earlier than that of the jute fiber. The degradation of composite occurred in two stages, according to the TG curve. Due to moisture content, the TG curve also indicated an initial loss of 1.1%. The endothermic maxima of the composite DTA curve were at 77.5 °C, 299 °C, and 451.5 °C. The dTG curve also confirmed the two main degradation stages at the temperatures of 299.0 °C and 444.9 °C, where the highest degradation occurred at 299.0 °C with a rate of 1.154 mg/min [48].

The influence of wood flour content on the thermal, mechanical, and dielectric properties of PVC was studied by Djidjelli et al. According to the results, wood fiber content had no effect on the T_g of plasticized PVC, which exhibited about 558 °C on DSC thermograms. They also discovered that wood fiber inhibits PVC thermal breakdown [49].

Xu et al. examined the effects on the thermal and rheological properties of PVC wood flour (WF) composites modified by adding chitosan (CS) of different contents and particle sizes. The thermal analyses of the Vicat softening temperature test (VST), DSC, and TGA revealed functional amino-groups in the molecular chains of natural chitosan which were indirectly established a "bridge" relationship between wood flour and PVC matrix. Heat resistance capacity, T_g of composites, and thermal stability at the early stages of degradation could be improved more effectively with an optimum addition amount (30 phr) and particle size (180–220 mesh). When compared to WF/PVC/SA composites with a 5 phr silane coupling agent (SA), the heat resistance capacity and thermal stability of WF/PVC/CS were superior at the early stages of deterioration, although the thermal stability of the entire compound system was slightly poorer [50]. In another study, Ge et al. examined mechanical and thermal properties as well as the morphology of PVC-WF composites with WF content ranging from 10 to 50 phr using silane coupling agent. The addition of WF decreased tensile strength and strain at the break, but did not effect on the T_g [51].

PVC-biomass composite was produced by PVC as a major matrix constituent, ethylene–vinyl acetate (EVA) as a polymeric plasticizer and wood flour (WF) and fly ash (FA) as filler in a study of Marathe et al. The addition of EVA resulted in an initial drop in T_g, showing its plasticizing effect. The miscibility of PVC and EVA was observed by the lower and single value of T_g in the analyzed temperature zone. The addition of WF to this matrix significantly raised T_g, demonstrating that the filler has a stiffening effect on the composite. The role of FA in increasing T_g was not significant. EVA was mostly used for its plasticizing properties and processing simplicity. The decrease in T_g caused by the addition of EVA was offset including by WF in the structure. As a result, the final composites had a T_g that is extremely comparable to PVC and thus a similar service temperature [52].

The effect of filler on the thermal characteristics of composites was investigated by Iulianelli et al. The increase in the amount of cumbaru filler did not affect the thermal characteristics of the produced composites. The homogenous distribution of motion within the individual components and the reduction of material stiffness at the molecular level were revealed by relaxation investigations of the molecular dynamic behavior [53].

Zaunidin et al. investigated the thermal stability of modified and unmodified banana pseudo-stem filled unplasticized polyvinyl chloride (BPS/UPVC) and PS/UPVC composites. The BPS filler disintegrated before the UPVC matrix formation, and the BPS/UPVC composites were more stable than both components. However, the thermal stability of BPS/UPVC composites decreased when the amount of BPS filler was higher. The decomposition temperature reduced as the amount of BPS filler was increased up to 40%. Acrylic-modified BPS/UPVC composites were found to have better thermal stability than unmodified BPS/UPVC composites [54].

It can be concluded that the usage of natural fillers in the preparation of PCV composite generally reduced the thermal stability of a thermoplastic polymer matrix, which is especially crucial in the case of PVC utilization. The manufacturing of PVC-based composites, particularly with natural fillers, is a complex technological challenge due to its relative multipart melt processing and high temperature and shear sensitivity. Other than wood-PVC composites, several composite structures were produced and thermally characterized using low-cost reinforcement agents from different origins such as fly ash, calcium carbonate [55], aluminum powder [56] and chicken eggshell [57]. As an example, Wang et al. described a method to fabricate high-performance geopolymer/PVC composite materials at a low cost by adding metakaolin-based geopolymers to PVC. They found that the thermal deformation temperatures of the composite materials were improved by 2–6 °C when compared to pure PVC. When the geopolymer percentage was increased to 4 wt. %, the T_g temperature increased by 1 °C, whereas there was little change when the geopolymer content was increased to 10 wt.%. TGA revealed that increasing the geopolymer content reduced the composite material's weight loss during thermal treatment. As a result, the presence of geopolymer considerably increased the thermal stability of the composite. The apparent activation energy of the geopolymer/PVC composite containing 4 wt.% geopolymer during thermal decomposition was higher than that of pure PVC [58].

4 Thermal Degradation of PVC Nanocomposites

Nanocomposites are a novel type of composite materials in which nanoscale dispersion in a matrix occurs. When compared to micro-and macro-composites, they contain at least one ultrafine phase dimension, often in the range of 1–100 nm, and usually display better characteristics. The modification of the polymer nature by incorporation of nanofillers has been a significant interest for researchers to enhance thermal properties to obtain better processing and a lifetime. Numerous studies reported that the resulting nanocomposites show improved thermal, mechanical, or optical properties. In recent years, different types, sizes, and ratios of nanofillers have been investigated to observe their influence on the decomposition behaviour of polymer nanocomposites, since they have strong influence on the characteristic properties [59]. Therefore, a proper combination of nano-characterization methods should be carried out to determine the main properties of polymer nanocomposites. Particularly, it is well-known that the thermal characterization methods offer a lot of information about the physical properties of polymer nanocomposites for their potential available application fields. TGA is a good choice to determine thermal and oxidative stability, water content and chemical composition in nanocomposite samples since it is a cost-effective and less time-consuming technique. TGA performed on several polymer nanocomposites presented those polymers prepared with the incorporation of different nanofillers showed enhanced thermal stability [60–64]. In this section different nanofillers such as metal/metal oxide, nanocarbon and nanoclay addition to the PVC structure is examined in detail in terms of the thermal properties of such composite structures.

4.1 PVC Nanocomposites with Metal and Metal Oxide Nanofillers

Metal and metal oxide nanofillers have gained a great attention for the preparation of PVC nanocomposites with improved thermophysical characteristics depending on various factors, such as type, ratio, and morphology. These metal and nanofillers can offer good chemical stability and compatibility, non-toxicity, antimicrobial activity, and bactericide and fungicide action [65]. PVC nanocomposites prepared with the most used metal or metal oxide nanoparticles (NPs) to apply in different areas are listed in Table 2.

Zinc oxide nanoparticles (ZnO-NPs) are one of the most studied and multifunctional inorganic nanofillers in polymer nanocomposites owing to their chemical stability, electrical, optical, effective antimicrobial properties, and high catalytic activity [66, 67]. Consequently, the incorporation of ZnO-NPs in PVC nanocomposites could provide better thermophysical, mechanical and structural properties in comparison to pure PVC, since it shows a large specific area, good interfacial interaction, and small size, thereby quantum effect. Elashmawi et al. utilized commercial ZnO-NPs (particle size <100 nm) to form ZnO/PVC nanocomposite films with different amount of nanofiller content (0, 2.5, 5, 10, 15 and 20 wt%) [68]. According to TGA thermograms, it was reported that the nanocomposite films exhibited higher thermal stability, specific heat, and T_g than that of neat PVC film related to strong interfacial interaction between PVC and ZnO-NPs. They also reported that the maximum decomposition temperature increased with the increasing mass change (wt%) of samples. In a different study, the increased T_g of PVC loaded with 2 wt.% ZnO-NPs was also reported with the increased molecular weight without any effect on the breadth of the transition zone of the sample [69]. In some studies, different polymers were introduced into PVC/ZnO-NPs nanocomposites. For instance, Hajibeygi et al. successfully prepared PVC/ZnO nanocomposites coated with new poly(amide-imide) (PAI) to test their thermal, combustion and mechanical properties [70]. It was reported that the PVC nanocomposites had better thermal stability than that of neat PVC samples. Additionally, surface modification via PAI coating could be used as a protective layer for PVC against thermal decomposition.

Silica nanoparticles (SiO_2-NPs) is another broadly studied amorphous nanofiller for the preparation of PVC nanocomposites. Especially, the influence of SiO_2-NPs

Table 2 PVC nanocomposites prepared with most used metal or metal oxide NPs

Metal/Metal oxide NPs	Property	References
ZnO	Antibacterial properties	[67]
	Thermal stability Translucency	[68]
SiO_2	Thermal resistance Mechanical stability Visible transparency	[71]
$CaCO_3$	Thermal stability Flexural strength Toughness	[72]
TiO_2	Compatibility with PVC Thermal stability	[73]
Ag	Thermal stability	[74]
Cu	Thermal stability Processability Antibacterial properties	[76]

on flame retardancy and thermal stability properties of polymer nanocomposites has been an important research area. Mallakpour and Nazari fabricated PVC-SiO_2 nanocomposite films which had been prepared with bovine serum albumin as a bio coupling agent [71]. They reported the effect of different weight percentages of the SiO_2-NPs (3, 6, and 9 wt.%) in the PVC matrix according to different analysis techniques. It was suggested that the encapsulation of SiO_2-bovine serum albumin gave the enhancement in thermal, mechanical, and optical properties of PVC nanocomposite films. TGA results indicated that the PVC nanocomposite films with 6 wt% of SiO_2-NPs presented the highest thermal stability.

Thermal properties can be improved by other types of metal oxide NPs. Bonadies et al. studied the effect of calcium carbonate NPs ($CaCO_3$-NPs) and surface modifiers on the thermo-mechanical and gelation properties of PVC nanocomposites [72]. A considerable increase in the thermal properties of PVC/$CaCO_3$ nanocomposites was reported with the addition of bare and stearic acid-modified $CaCO_3$ NPs. In another study, Lu et al. synthesized PVC nanocomposite films with folic acid modified TiO_2 NPs and characterized their thermal properties by TG-DTG and TG-FTIR techniques [73]. They concluded that the stability of the modified TiO_2 NPs-reinforced PVC nanocomposite films was enhanced due to a lower number of surface chlorine atoms and intermolecular attraction.

Recently, many studies have focused on the metal nanofillers in PVC nanocomposites because reinforcement of metal nanofillers into a polymer matrix can optimize the macroscopic characteristics of polymer material and provide new applicability for advanced applications. Among metal nanofillers, silver NPs (Ag-NPs) have been used in different potential application areas, especially medical device applications due to their broad-spectrum of antibacterial effectiveness. Shimoga et al. prepared PVC nanocomposites with different Ag-NPs concentrations and they analysed their thermal degradation by TGA [74]. From the TGA curves, they reported that the neat PVC and PVC/Ag-NPs nanocomposites presented two major degradation steps with onset decomposition at 240 °C. Due to the dehydrochlorination in the PVC chains forming long sequences of polyenes, the first degradation step was observed at around 240–415 °C. The second weight-loss step at around 415–475 °C was attributed to the main PVC chains with conjugated double bonds owing to the dehydrochlorination. They also concluded that the thermal properties improved with the increase in Ag-NPs (from 2.5 to 10 wt.%), which provides a positive effect on the thermal stability of PVC/Ag-NPs nanocomposites. Like Ag-NPs, the incorporation of copper nanoparticles (CuNPs) and their oxides have been extensively utilized to prepare polymer composites as they present antibacterial activity even with a small amount of nanofillers [75]. For example, Miranda et al. reported the incorporation of Cu-NPs into PVC matrix by a melt mixing method to illuminate the effect of NPs content on thermal, antibacterial, and rheological properties [76]. They investigated the thermal stability of PVC/Cu-NPs nanocomposites using TGA. It was reported that the weight losses were observed in two decomposition steps. The first weight loss was related to the dehydrochlorination process and the polyene formation in the temperature range of 150–325 °C, whereas the second weight loss was associated with the volatile aromatic products formation from cross-linking polyene intermediates, mainly benzene in the temperature range of 420 and 530 °C. It was concluded that the presence of Cu-NPs led to the formation of more char residues.

4.2 PVC Nanocomposites with Carbonaceous Nanofillers

Carbonaceous nanofillers such as nanocarbon black, graphene, graphene oxide (GO), reduced graphene oxide (rGO) or carbon nanotubes (CNTs) are good nanofillers for polymer nanocomposites. Particularly, graphene-like fillers and CNTs are of great interest to improve the thermophysical, mechanical and structural properties of polymer composites. Additionally, conductive polymer nanocomposites can be prepared by dispersion of carbonaceous nanofillers e.g., nanocarbon black, graphene-like fillers or CNTs.

The influence of various carbonaceous nanofillers on enhancing the PVC-based nanocomposite thermal properties at the nanoscale and the important role of their ratio have been extensively studied. Among them, PVC/graphene nanocomposites have emerged as an advanced material with improved thermal properties due to the superior intrinsic thermal conductivity of graphene. For example, Vadukumpully et al. prepared and characterized ultrathin PVC nanocomposite films with surfactant-wrapped graphene nanoflakes [77]. They used a simple solution blending and drop-casting followed by annealing route at 100 °C for 3 h to prepare PVC nanocomposites with graphene. The dispersion of graphene nanoflakes into PVC matrix with a few restacks was confirmed by SEM and AFM analyses. Further information on the thermal properties of prepared films was also characterized by TGA and DSC (in Fig. 5). As expected, the TGA curves of neat PVC and composite films followed two main weight loss steps. The first one in the range 250–360 °Cwas related to the loss of HCl. The temperature at which the thermal degradation starts (T_1) decreased to 230 °C with an increased concentration of graphene nanofillers from 0.5 to 2 wt.%, since they interacted Cl leading to form weaker C–Cl bonds in PVC at this temperature. Although graphene brings excellent improvements to the polymer matrix, it does not disperse well due to its hydrophobic nature. The dispersibility of nanofillers within the polymer matrix affects the forming of exfoliated or intercalated nanocomposites. GO and rGO include various functional groups like alcohol, or carboxyl groups, which make them more dispersible in the polymer matrix. Additionally, they are relatively inexpensive and easy to synthesize, and have layered structures and large surface area [78, 79]. Compared to bare PVC, PVC/GO and PVC/rGO films have presented improved thermal and mechanical properties. Moustafa et al. synthesized GO from graphite wafers via Hummer's method to prepare plasticized PVC (with average molecular weight (M_w ~ 43,000)) nanocomposites to be used as humidity sensor for advanced edible food packaging and other practical usages [80]. Several methods have been reported to disperse the nanofillers into PVC matrix, including solution process, in-situ intercalative process or melt blending to form a rigid and flexible nanocomposite films with high thermal stability [81, 82]. The thermal analysis of films obtained was investigated by TGA, in which PVC/GO nanocomposites prepared with different amounts of GO (1, 3 and 6 wt.%) by the *in-situ* method were heated from room temperature up to 550 °C under air by Moustafa et al. [80]. The increased thermal stability with the introduction of GO was reported, since GO nanosheets (exfoliated/or intercalated nanostructure) acted as a barrier and reduced the combustible volatile substances. Akhina et al. synthesized rGO and prepared plasticized PVC/rGO composite films via conventional melt compounding [83]. Expectedly, rGO nanofiller reinforced the thermal stability and dielectric permittivity. TGA results revealed that rGO showed no effect on the initial degradation temperature. It was also reported that the maximum mass loss temperature was shifted to a higher temperature.

Even though there have been several studies on graphene-reinforced polymer nanocomposites, today, carbonaceous nanofillers reinforcing materials developed in this research area are dominated by CNTs. These studies mainly focus on understanding how significant the classification of CNTs and their ratio are in determining the characteristics of polymer matrix composites. CNT, which are identified as coaxial graphitic cylinders, exists in two classes: (i) single carbon nanotubes (SWCNTs) and (ii) multi-walled carbon nanotubes (MWCNTs). Although some researchers underlined the cytotoxic effect of CNTs on human skin cells when in contact, various studies propounded that these nanofillers are great additive to prepare PVC-based polymer nanocomposites with high thermal and physical properties.

Saeed and Khan used SWCNTs purified/functionalized by acid treatment as reinforcing material for the preparation of PVC/SWCNT composites via solution casting method [84]. The increased dispersibility of SWCNTs due to the introduced carboxyl (–COOH) group by acid treatment into the PVC matrix was confirmed by SEM images. According to TGA results, the bare PVC and the PVC/SWCNT composites (3, 7 and 10 wt % of SWCNTs) showed two degradation steps. The first step, which occurred at 280–380 °C, was related to the dehydrochlorination during the

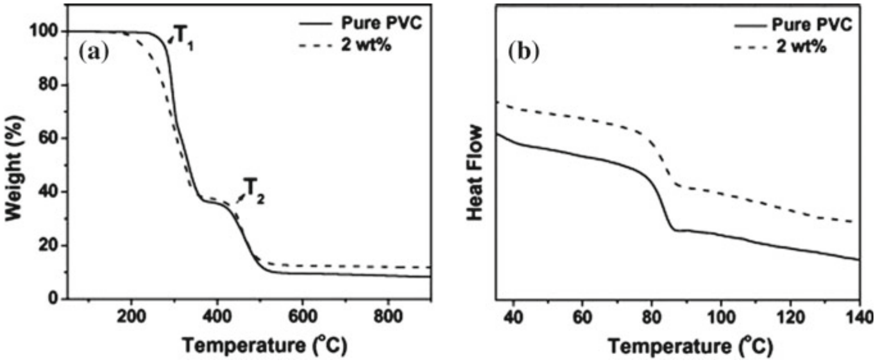

Fig. 5 TGA (**a**) and DSC (**b**) curves for graphene/PVC composite films (Reprint with permission from [77])

thermal degradation of PVC, whereas the second one (420–520 °C) was for the secondary decomposition. It was concluded that the thermal stabilities of PVC/SWCNT nanocomposites were increased by about 20–25 °C in comparison to bare PVC samples. Although the effect of SWCNTs on the improved properties of polymer nanocomposites is quite significant, MWCNTs are preferable due to their low-cost production and higher dispersibility without any functionalization procedure. For example, Naim et al. used the solvent blend technique for the preparation of PVC nanocomposites with high purity (>95%) commercial MWCNTs (length 10–20 mm, diameter >50 nm) without any physical or chemical treatment [83]. They reported the effect of the blending ratio on the thermal, optical, and electrical properties of PVC/MWCNTs. The non-isothermal kinetics measurements for PVC/MWCNTs nanocomposites prepared were determined by TGA at five different heating rates of 5 to 40 °C/min. It was reported that a clear improvement in the thermal stability of PVC nanocomposites was achieved with the addition of MWCNTs (0.45 wt%). In another study, PVC/MWCNT and PVC/graphene nanocomposites were compared in terms of their morphological and thermo-mechanical properties by Hasan and Lee [86]. They revealed that PVC nanocomposites prepared with graphene resulted in smoother surface morphology and greater thermo-mechanical stability than that of PVC/MWCNT films since MWCNTs aggregated in PVC matrix due to van der Waal interactions. In summary, these reports clearly prove the possible usage of carbonaceous reinforcements in PVC matrix for different advanced applications.

4.3 PVC Nanocomposites with Nanoclays

Today's main requirements is to provide thermally stable along with electrically conductive and mechanically stable PVC nanocomposites with a small amount of nanofillers. Recently, many studies have been reported on the use of nanoclays to reach this goal [87, 88]. Polymer nanocomposites prepared with the incorporation of nanoclays have been receiving a significant attention for the fabrication of advanced composite films, since these nanofillers have platelet-like structures, which lead providing tortuous paths in polymer matrix increasing the barrier properties of composite films. According to studies reported, it is also well established that these nanoclays are well-dispersed in the polymer matrix to prepare compact composite films [89, 90]. The well dispersion of the nanoclay layers into polymer matrix can successfully enhance the thermal, mechanical, and gas barrier properties. Nanoclay family covers different types of clays, which involves four main classes depending on their chemical composition: (i) montmorillonite (MMT)/smectite, (ii) kaolinite, (iii) illite, and (iv) chlorite [91]. Among them, the use of MMT, halloysite, and bentonite dominates most of the research in this area.

MMT has been widely used to develop polymer/nanoclay composites because it is earth-abundant and low-cost material. Additionally, MMT has a three-layer sandwich structure with a thickness of 1 nm, a length of about 200 nm and an interlayer space of around 1 nm, which could be extended through polymer chains using proper physical and chemical process conditions [92]. Therefore, it was revealed that MMT can be used in pristine and/or modified form with various ionic surfactant, in the presence of different types and amounts of plasticizers [93]. Peprnicek et al. studied the effect of the modification of MMT nanofillers and the processing conditions on the thermal stability of final PVC/nanoclay composites [94]. They used natural $-$ Na^+ MMT and two organophilic MMTs (30B and 93A) modified with two types of quaternary ammonium salts. TGA results proved that the thermal properties depend on the interactions between PVC and nanoclays. In comparison to nonmodified natural MMT, organophilic MMTs were better nanofillers to achieve higher thermal and mechanical stabilities. The main degradation temperature was shifted to a higher value with the presence of organophilic MMTs. The TGA curves also showed that the preparation method did not affect the thermal stabilities of PVC/MMT nanocomposites. Zheng and Gilbert investigated the effect of different types of stabilizers (calcium/zinc, barium/zinc, organotin, and an epoxy co-stabilizer,) and different grades of Cloisite nanoclays on the thermal properties of PVC/nanoclay composites [95]. They used Cloisite Na (a natural MMT), Cloisite 10A (MMT modified with dimethyl benzyl hydrogenated tallow quaternary ammonium chloride), and Cloisite 30B (MMT modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium chloride) as reinforcing materials. The addition of epoxy co-stabilizer improved the thermal stability and the presence of Cloisite Na developed a catalytic effect on PVC dehydrochlorination. It was also reported that the thermal stability of PVC nanocomposites was reduced with the addition of ammonium-modified MMT. They revealed that some phosphonium-modified MMT provided better thermal stability than that of ammonium-modified MMT, since the onset degradation temperatures of allyl-PMMT and methyl-PMMT were about 320 °C, while it was about 250 °C for Cloisite 30B. The best thermal stability results were obtained from PVC/hydroxyethyl-PMMT nanocomposite.

Polymer/nanoclay composites can be prepared by bentonite as another type of MMT organic nanofiller. Bentonite is identified as layered hydrophilic aluminium magnesium silicate materials. As mentioned, it has a structure with a thickness of 1 nm. Usually, bentonite contains lattice iron and catalytically active cites [96]. In literature, growing attention has been placed on PVC/bentonite composites, since the incorporation of bentonite nanoclays into plasticized PVC was resulted in an improvement of the thermal stability. Several routes such as the direct mix or pre-gel method of the components have been used to decrease the degradation of PVC/nanoclay composites, [87] with the choice of organic modifier chemistry [97]. Benderly et al. adopted two different mixing methods (direct mix and pre-gel method) for the preparation of PVC/diisodecyl phthalate plasticizer/nanoclay (bentonite or hectorite) composites [98]. Thermal, mechanical, barrier, and dispersion properties of PVC composites were examined using a wide range of analysis methods. The results exhibited that the bentonite nanofillers caused a significant increase in mechanical and barrier properties as well as smoke reduction. It was also reported that the mass-loss rate and the peak heat release rate of PVC/nanoclay composites were reduced in comparison to bare PVC. In another study, important enhancements in thermal stability of PVC/bentonite nanocomposites were achieved by melt blending method [99]. They studied the effects of preparing temperature (160, 170, and 180 °C) and the organically modified and unmodified bentonite content (1 and 5 wt.%) on the structural properties of resulted nanocomposites. It was suggested that the T_g of PVC nanocomposites prepared with organically modified bentonite shifted to a higher value in comparison to bare PVC sample. It has been reported that the thermal degradation temperature of PVC/organically modified bentonite nanocomposites increased up to 60 °C with not only the increased bentonite content, but also increased particle size of bentonite.

Halloysite nanotubes (HNTs) are one of the other most popular nanoclay reinforcing materials, which are natural aluminosilicate ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$) having a high amount of 1D hollow tubular structure with length up to 1000 nm [100]. In literature, it has been reported that polymer/HNTs nanocomposites presented good mechanical and thermal stability, as well as biocompatibility and fire retardancy [101, 102]. Liu et al. adopted the melt blending technique for the preparation of PVC/HNTs nanocomposites [103]. The role of HNTs concentration on the structural and thermal properties of nanocomposites was determined by TGA and SEM. They suggested that the addition of HNTs into the PVC matrix successfully delayed the decomposition of PVC due to the interference effect. It was also revealed that HNTs can be used to improve flame retardancy of PVC, since HNTs showed a barrier effect, preventing the diffusion of the volatile decomposition products, thus providing thermal insulation properties. Consequently, the smoke production was significantly reduced with the presence of HNTs. In some cases, halloysite nanoclay and nanofillers, which are abundantly available and eco-friendly, are utilized together in the PVC matrix. For instance, Senthilvel and Prabu successfully prepared a polymer composite of acrylonitrile butadiene copolymer (NBR)/PVC, which is a miscible physical blend of commercial importance, by carbon black-HNT hybrid fillers to test the synergistic effect on the mechanical and thermal properties for automotive applications [104]. It was reported that the NBR/PVC-carbon black-HNT nanocomposites showed good thermal stability and superior mechanical properties due to the formation of intercalated structures and improved interfacial interactions. According to the TGA thermograms, the composites exhibited two degradation steps, in which the first and second mass losses occurred at 260–310 °C and 310–500 °C, respectively. The HNT reinforcing shifted the degradation peaks towards higher temperatures indicating the improved thermal stability.

5 Conclusions

With the explosive growth of polymer science and composite manufacturing techniques, numerous combinations of PVC-based composites and nanocomposites are of interest. The thermal characteristics and degradation behavior of PVC have been critically assessed within the scope of this study. Moreover, composites and nanocomposites have been highlighted in recent developments using state-of-the-art signs of progress on aspects of the PVC matrix. By this way, the improvement in the thermal characteristics of PVC composites and nanocomposites is deeply expressed in this chapter. It is inevitable to conclude that viability and opportunity for manufacturing and commercialization of PVC-based composites and nano-composites are closely linked with their temperature-dependent thermal characteristics. Systematic studies are also required that will show the effects of the different reinforcements and additives together with the production methods to investigate thermal stability and heat transfer mechanisms within the composite structure. The use of thermal analysis techniques such as thermogravimetry makes the prospects of such composites much more feasible for the next applications. The advancement of polymer materials science would benefit greatly from the effective creation of multifunctional PVC composites and nanocomposites. In order to achieve reasonable results in terms of thermal stability and thermal characteristics, it is preferable to support the results of thermogravimetry with distinct thermal tests using various analytical apparatus. Additionally, materials characteristics should be properly designed such as mechanical expectations and their integrated results with thermal characteristics should be satisfied for the specific applications of such PVC-based composites.

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Dielectric Properties of Polyvinylchloride (PVC) Composites and Nanocomposites

Vijayalekshmi Vijayakumar and Sang Yong Nam

Abstract Over the last 20 years, polyvinyl chloride (PVC) based composites have garnered attention in the dielectric material research owing to their excellent insulating properties, mechanical strength, flexibility, chemical and thermal stabilities. The influence of various nanoparticles on different dielectric properties of PVC and their applicability in electronic industry are briefly discussed in this chapter. The nature of polymer-filler interface, concentration, type and chemistry of nanoparticles are critical in the final dielectric properties. The influencing factors and improvements of dielectric properties such as permittivity, dielectric loss and break down voltage in PVC polymer composites from mechanism, single and multi-nanoparticles, surface functionalization and ionization are overviewed in this review. This review is expected to help the readers to comprehensively understand the fabrication of PVC composite dielectrics with high performance for various applications.

Keywords Break down voltage · Dipole moment · Nanodielectrics · Permittivity · Polarization

1 Introduction

In these decades, flexible polymer composites have emerged as an excellent candidate for dielectric applications in the electronic industry especially from portable electronic devices to high-efficiency hybrid electric vehicles owing to their cost-effective industrial-scale processability, light weight, superior service life, and environment-friendly nature, excellent flexibility along with high breakdown strength, energy

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density and dielectric constant, as well as low dielectric loss. The polymer dielectric composites also demand actuators, sensors, capacitors, telecommunication and pulsed power systems [1, 2]. Polyvinylchloride (PVC) is an inexpensive polymeric material, that exhibit excellent insulating properties, wide bandgap, high mechanical strength and flexibility, thermal as well as chemical stability making it a promising candidate in the dielectrics. The miniaturization and integration of electronic gadgets constantly demand flexible energy storage materials with high dielectric constant and minimum loss. Currently, various ceramic fillers owing to their intrinsic high dielectric constant have been utilized in polymer composites to enhance the dielectric properties but, the high volume requirement and low interfacial interaction resulted in a high dielectric loss as well as poor flexibility and process ability to the composites. In fact, conductive nanomaterials are preferable on account of ease of processability, and very low filler dosage for enhancing dielectric properties [3].

Incorporating low loading nanoparticles into polymer matrix owing to their high surface area with homogeneous distribution and structure–property relationship can achieve significant improvement in the dielectric, thermal and mechanical performance of nanocomposites than the conventional composites [4–6]. The influence of various nanoparticles such as graphene oxide, Fe_2O_3, NiO, silica, etc. on dielectric properties and their correlated parameters for PVC based nanocomposites were studied by many researchers. The purpose of this review is to demonstrate various dielectric property requirements and comprehensively summarize various PVC based composites for different dielectric applications.

2 Various Dielectric Properties

As per the dielectric theory, for every material whether conducting or insulating, upon applying a direct or alternating current, there is a range of migration of electric charges. This movement of charges is limited in a dielectric or insulating material, forming a dipole moment between them, consecutively polarizing the material. An electric dipole consists of two equal and opposite charges that are separated by a space or distance. The quality of the system to behave like a dipole refers to the dipole moment and the total dipole moment within a volume occupied is called polarization. The number of dipole moments per unit when all the dipole charges are arranged in one direction determines the polarizability of the material. The dielectric responses in a polymer are mainly associated with dipolar, atomic and electronic polarization over different time and length scales. The dipolar or orientation polarization is closely determined by the relaxation of electric dipoles responding to the alternating electric field in the frequency range up to 10^8 Hz and exhibiting high dielectric constants. Atomic polarization caused by nucleus displacement and electronic polarization by electron movement in response to the alternating electric fields operates in the infrared or far-infrared frequency range (10^{13} Hz) and ultraviolet frequency domain (10^{15} Hz) respectively. Generally, electronic polarization and dielectric responses are closely related to the bandgap of the dielectrics [7, 8].

Dielectric constant

The charge density or dielectric displacement (D) generated in a dielectric medium is proportional to the dielectric field (E) and the proportionality requires an introduction of a constant, k(ε) where k is called the dielectric constant or permittivity of the material placed between the parallel plates.

$$\mathrm{D} = \varepsilon\, \mathrm{E} \tag{1}$$

An absolute permittivity (ε_0) is found in vacuum when electric field is supplied and is represented as

$$\mathrm{D} = \varepsilon_0\, \mathrm{E} \tag{2}$$

The value of ε_0 is 8.854×10^{-12} F/m.

Therefore, the dielectric constant or relative permittivity is the ratio of electric field density produced in the medium to that produced in a vacuum by a constant electric field. It can also be defined as the ratio of capacitances of a capacitor filled with given material to the capacitance of an identical capacitor in a vacuum without the dielectric material.

The dielectric material is subjected to an electric field to study its properties and the most important properties are polarization, dissipation, conduction and breakdown. When direct current is applied to a dielectric material, dipoles are aligned in the field direction. Moreover, the applied charge will migrate from one end to the other end, resulting in the phenomenon called polarization. The dielectric material allows charge storage within the material, acting as a capacitor by neutralizing the charges at the electrodes and the capacitance value will be used to determine the permittivity of the material. However, there are two different current types, charging or polarization current I_C and loss or conduction current I_L in an AC electric field applied across the parallel plate capacitor. Both contribute to determining the dielectric constant. It can be represented as:

$$\mathrm{I} = \mathrm{I}_C + \mathrm{I}_\mathrm{L} \tag{3}$$

The charge storage can be represented in terms of dielectric constants [9] and the above equation can be written as:

$$\mathrm{I} = \mathrm{V}(\mathrm{i}\omega \mathrm{C}_0)(\varepsilon - \mathrm{i}\varepsilon'') \tag{4}$$

The dielectric behaviour of polymer composites is the result of the interaction of matter with an applied electric field that oscillates at different frequencies (f) at a given temperature and is generally described in terms of the complex relative permittivity (ε_r) corresponding through the equation:

$$\varepsilon_\mathrm{r}(\omega) = \varepsilon'(\omega) - \mathrm{i}\varepsilon''(\omega) \tag{5}$$

where, $\varepsilon' = t \times C_p/(A \times \varepsilon_0)$ reflects material polarizability due to dipole reorientation, deformation of delocalized electron distributions or interfacial polarization (dielectric constant related to the stored energy), $i = \sqrt{-1}$, angular frequency $\omega = 2\pi f$ and $\varepsilon'' = t/(\omega \times R_p \times A \times \varepsilon_0)$ is dielectric loss or energy dissipated inside the material as heat. Here, t is the thickness of the material, A is the area of electrodes, ε_0 is the permittivity of free space, C_p and R_p are the equivalent parallel capacitance and resistance of the samples, respectively measured from LCR meter. The inability of a material to polarize and the rate of change in the oscillating period of the applied ac electric field cause to occur dielectric loss. The relaxation time, time is taken for the dipoles in the material or a displaced system to return to their original orientation or equilibrium value entirely depends on the electric field oscillation that causes dielectric loss. When an alternating electric field is applied to a material, there is a delay between the change in the field and the change in polarization represented by the angle δ. The ratio of energy dissipated to the energy stored in the dielectric is called the dissipation factor or loss angle ($\tan \delta = \varepsilon''/\varepsilon'$) [4, 10]. Broadband dielectric spectroscopy (BDS) represents a powerful tool to measure electrical behaviour in polymer nanocomposites. The feature of broadband frequency ranging from 10^{-6} to 10^{12} Hz allows the investigation of various physical phenomena such as molecular mobility, polarization, relaxation, conductivity effects as well as interfacial effects, etc. in composites [4].

3 Preparation of PVC Based Composites and Nanocomposites

Numerous methods such as ultrasonic mixing, solution blending, and melt blending are used to fabricate the PVC based composites. High-speed mixing of raw materials followed by melt mixing in a twin-screw extruder is also applied to prepare PVC composites for proper dispersion of nanofillers [6]. The simplest ways to make PVC nanocomposites are ultrasonic mixing and solvent casting [3]. In the former process, after the initial stirring of the mixtures of polymer and filler, ultra-sonication is applied for some time to achieve proper filler dispersion. In the solvent casting, both polymer and filler are dissolved/dispersed in suitable solvents separately with the help of a magnetic or mechanical stirrer, then both the solutions are mixed together and finally after dispersion casting, evaporation is necessary for removal of the solvent systems used [11]. Melt mixing is another method to prepare PVC based composites, in which all materials are dry mixed at room temperature to form a uniform mixture followed by a melt mixing process at high temperature using an internal/Brabender mixer [12].

4 Dielectric Insulation Materials

High voltage cables insulated with plasticized PVC (p-PVC) based nanocomposites are widely used in nuclear power plants, various power apparatuses as well as industrial applications. The insulators surround and protect the wire and cable from coming into contact with outside conductors, prevent the wire material from environmental threats such as water, heat and resist electrical leakage as well as fire hazards [13]. Distortion and complete breakdown as a result of carbonization of polymers at the region of sparking can generally happen that may lead to large outages therefore, high rating cables with good insulating properties are essential to keep the system reliable [10]. Compared to the conventional additives, incorporating different nanofillers such as clay, silica, nano metal oxides, carbon nanotube, graphene, etc. can increase the service life of the insulator against degradation. The dielectric behaviour of p-PVC/aluminium oxide (n-Al_2O_3) prepared by melt mixing under DC biasing field studied by Nikam et al. exhibited an intense frequency and DC bias voltage-dependent parameters such as dielectric constant (ε'), dielectric loss (ε''), and loss tangent (tan δ). The maximum degree of dispersion was reported as up to 4 phr of nano alumina. The unique dielectric behaviour in terms of increased dielectric constant for high dosage (>2 phr) owing to the restricted mobility of dipolar groups by polymer-filler interaction as well as a decrease in dielectric constant with increase in DC bias due to the decrease in grain boundaries activation energy was also reported in their work [5]. The performance of PVC based composites is affected by filler type and concentration in the matrix and numerous studies have explored the effects of filler on the dielectric properties of the composites. The effect of various nanomaterials such as clay, SiO_2, ZnO, and Al_2O_3 on the dielectric properties of PVC composites studied by Thabet et al. revealed that 10 wt% Al_2O_3 contributes the highest dielectric constant upon other nanoparticles [14]. Mansour et al. investigated the effect of ZnO on the dielectric properties of PVC based nanodielectrics prepared through sonication-solution casting technique and found an enhanced break down strength and decreased dielectric constant (ε') as well as loss tangent up to 0.14 vol% ZnO indicate good polymer-filler interaction. The improvement in dielectric properties due to good filler dispersibility is qualified for electrical insulation applications [15]. A decrease in dielectric constant (ε') with an increase in frequency due to less number of dipoles which contribute to polarization is observed for PVC/SiO_2 nanocomposites. Moreover, the addition of silica owing to their large surface area along with a change in PVC morphology as well as the space charge distribution caused a reduction in the internal field and dielectric constant to the composite. The α-relaxation due to micro Brownian motion at around glass transition temperature was also observed from the dielectric loss behaviour [16]. Similar behaviour of reduction in permittivity and dielectric loss with frequency owing to the inability of the dipole to follow the field variation at high frequencies was also reported in the case of PU/PVC/CNT as well as multi-walled CNT filled PVC nanocomposites [17, 18]. PVC modified with TiO_2, SiO_2, and Al_2O_3 showed variation in dielectric properties based on the chemistry of different oxides and their availability to react with evolved hydrochloric acid. A high value of permittivity in silica filled composite due to the polarizability owing to the hydroxyoxide generation, lack of formation of units susceptible to be polarized due to the acidic behaviour of titania, no significant effect on dielectric permittivity and loss attributed to the amphoteric characteristic of alumina were observed by Ciuprina et al. γ-irradiation on these PVC composites assured good dielectric insulation characteristics especially for the high-frequency regimes as the nanostructures don't involve difficulties over the frequency domain 10^2–10^7 Hz [19]. Mamunya et al. explored the effect of multiwalled carbon nanotube (MWCNT) percolation threshold (φ_c) on the dielectric properties of PVC based composites. They observed that, below $\varphi_c = 0.045$ vol.%, the dielectric constant (ε') and loss (ε'') values are frequency-independent while ac conductivity (σ_{ac}) has a slope close to 1 that demonstrates their insulating properties. However, above φ_c, Maxwell–Wagner-Sillars (MWS) polarization contributed to a complex dielectric permittivity that resulted in an increase of dielectric constant and loss with frequency drop. Simultaneously, an increase in conductivity that gives a higher contribution to dielectric parameters was also reported [20]. The effect of copper oxide on the dielectric properties of PVC showed an increase in real dielectric permittivity (ε') with CuO content and a decrease with frequency due to interfacial polarization. The imaginary dielectric permittivity (ε'') curves displayed relaxations, a combined effect of both crystalline chain relaxation as well as interfacial polarization. Increased percentage of CuO resulted in an enhancement of both static and high-frequency dielectric constant but a decrease in the relaxation time (τ_0) [21].

Surface modification of nanoparticles is a common method to reduce their surface energy as well as improve the compatibility with polymer and dispersion inside the matrix which has a positive impact on dielectric properties. Ahmad et al. measured the influence of sodium dodecylbenzene sulfonate (SDBS) modified graphene oxide (GOSDBS) nanosheets on the electrical properties of PVC/rice straw (RS) composites prepared by melt mixing. The dissipation factor of the composite was about 0.174 and 0.015 at 20 Hz and 10^6 Hz respectively. The various functional groups on the basal plane and edges of GOSDBS nanosheets acted as sites for macromolecular-filler interaction as well as scattering points for charge carriers and the composites are useful for electrical insulation in cable industries [12]. Improvement in ac and dc breakdown strength of PVC after incorporating γ-amino propyl triethoxy silane functionalized silica (SiO_2) also encourages using these composites as high voltage power cables in a wide application range. 0.5 wt% amino-functionalized SiO_2 imparted an ac and dc break down strength of 63.8 $kVmm^{-1}$ and 75.5 $kVmm^{-1}$ respectively, corresponding to an enhancement of 14.1% and 16.3% over pristine PVC respectively [10]. The strong interfacial area between vinyl tris (2-methoxy ethoxy) silane functionalized titanium dioxide (TiO_2) and PVC owing to the closest surface tension of vinyl silane ($\gamma_{vinyl} = 41.1$ dyn cm^{-1}) and PVC ($\gamma_{PVC} = 41.9$ dyn cm^{-1}) enhances the breakdown strength (55.4 $kVmm^{-1}$) and decreases ε_r and tan δ revealed better insulation properties suitable for cable insulation [22]. Sodium montmorillonite (Na^+-Mt) functionalized with different alkoxysilane, N-(2-aminoethyl-)-3-aminopropyl-trimethoxy-silane (NH_2-Mt) (AEAPTS) or 3-mercaptopropyl-trimethoxy-silane (SH-Mt) (MTPS) promoted good exfoliation and high complex permittivity owing to the increased polar group mobility of both intercalants, ammonium salt in the clay or mercapto group in MTPS which is suitable for high voltage devices [23]. Silica micro-powder (SMP), a kind of ultrafine quartz powder has strong insulation characteristics, good chemical resistance, excellent thermal stability and physical properties as well as an environmentally friendly nature without radiation. However, the strong polarity makes interfacial problems and poor compatibility with hydrophobic PVC polymer. The use of isopropoxy trioleate acyl titanate (KTTO), a monoalkoxy fatty acid acyloxy titanate coupling agent significantly improved the interfacial bonding between polymer and filler, hydrophobicity and overall dispersity of silica micro-powder as well as the performance of PVC composites [6]. Incorporating graphene oxide (GO) nanoparticles into polyvinyl chloride (PVC)/polyvinylidene fluoride (PVDF) blend using a pulsed laser ablation technique can also disperse nanoparticles without aggregation resulting in lower hydrophilicity to the composites. Further, an increase in dielectric constant with the addition of GO and a charge hopping conduction mechanism that obeys Jonscher's power law were also observed [24].

The dielectric constant value depends on the number of polarizing dipole per unit volume and their dipole moment. Effect of temperature on the dielectric constant value of PVC/lead oxide (PbO) nanocomposite demonstrated that the huge number of dipoles become ready to orient with an external electric field at a temperature higher than the glass transition owing to the drop in viscosity that enhances the dielectric constant. The authors reported that the presence of lead oxide leads to an improvement of the dielectric constant at a concentration higher than 5 wt%. The restricted dipoles owing to the molecular restriction at the polymer-filler interface interaction zones due to good nanoparticle dispersion cause a reduction in dielectric constant up to 5 wt% PbO loading. However, some restricted dipoles attain sufficient energy to remove the restriction group at high temperatures. The dielectric loss (tan δ) value related to the charge mobility through the polymer backbone was increased with an increase in frequency up to 50 kHz and became constant for further frequency. The maximum value of tan δ occurs when hopping frequency and external field frequency are the same. Pure PVC, as well as PVC/PbO composites, exhibited a decrement in dielectric loss with an increase in frequency due to the tunnelling transition rates of the charge carriers [25]. The morphology and space charge distribution affected by the surface area of the nanoparticles can leads to a reduction in the internal field. The incorporation of $La_{0.95}Bi_{0.05}FeO_3$ nanoparticles into PVC contributed a reduction in relative permittivity as well as dielectric loss to the composites [26]. Thabet et al. reported the usage of different nanoparticles strategy as more effective to reduce the dielectric losses than the singular nanoparticles technology. The electric field distribution in three-phase belted power cables is important to be used as an insulator. Figure 1a, b shows the electric field distribution in PVC based three-core belted power cables with an individual as well as multiple nanocomposites. The multi-nanocomposite of clay (0.1 wt%) + zinc oxide (0.2 wt%)/PVC is more efficient in insulation to withstand electrostatic field distribution due to its low dielectric constant [27].

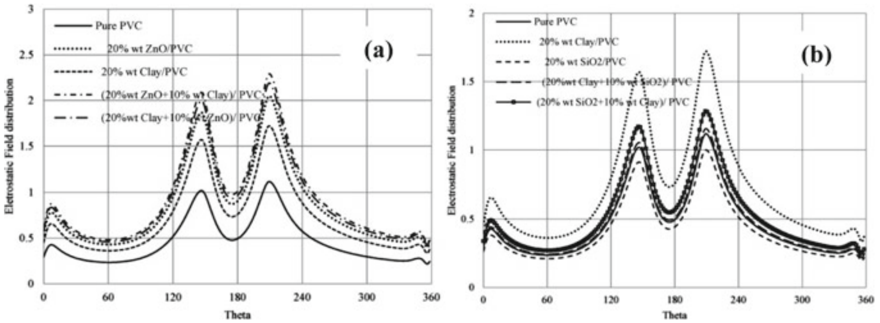

Fig. 1 **a** and **b** Effect of individual and multi nanoparticles on electric field distribution in PVC [27]. Reproduced with permission from Elsevier

5 Dielectric Composites for Energy Storage Applications

Conductive nanomaterials offer an enormous network of nanocapacitors extended over the entire insulating polymer matrix resulting in an improved dielectric performance of the polymer nanocomposites through interfacial polarization. The main factors affecting the dielectric properties of the polymer and its composites are polarizability, free volume and conducting-insulating-conducting network [7]. The dipole, atomic and electronic polarizations which arise in response to the applied electric field contribute much to enhancing the dielectric performance of polar polymers. Therefore, polarizability related to the basic polymer structure and free volume is important which is explained by Clausius–Mossotti equation. In dipole polarization, the relaxation time, time is taken by the mobile charge carriers in returning to their original steady-state equilibrium condition determines both dielectric loss and constant. Polymer nanocomposite dielectrics reinforced with two-dimensional materials involving carbon materials, MXenes, oxide ceramics, clays, boron nitride and so on exhibit remarkable properties and great potential in dielectric and energy storage applications. Incorporating ideal electrically conductive MXene flakes, a 2D filler to boost the dielectric performance while maintaining super flexibility of PVC nanocomposites promoted interfacial polarization which endowed high dielectric properties. MXene facilitated the formation of numerous dipoles at the interfaces (number of micro-capacitors) and contributed to the improvement of the energy storage capacity of the composites. 10 wt % MXene displayed a high dielectric constant of 11,800 at 25 Hz and the value decreased to 6100 with an increase in frequency to 1 MHz due to the reduction in charge density or the number of dipoles at high frequency by the rapid and periodic changing of applied ac electric field. The inability of a material to polarize with changing rate of the oscillating electric field resulted in dielectric loss. Minimum dielectric loss with a high dielectric constant is much preferred for dielectric applications. PVC/MXene with 10 wt % filler displayed a minimal dielectric loss of 1.31 at 25 Hz [3].

The combined advantages of high electrical conductivity of filler and dielectric permittivity of hosting polymer with its mechanical flexibility make the polymer composites recommended in charge storage capacitor applications. Compared with batteries and electrochemical capacitors, dielectric capacitors exhibit high working voltage and power density, longer lifespan and greater cycling stability. Many researchers incorporated graphene nano-platelets (GnP) into the PVC matrix to improve its dielectric and mechanical properties and most of the reports included the change in dielectric properties, but lag behind the detailed temperature dependence on dielectric behaviour. Motivated with this Ahmed et al. presented a study on the effect of GnP on PVC nanocomposites prepared by solution casting technique. Both GnP content and increase in temperature made an increase in both permittivities (ε') as well as dielectric loss (ε'') due to the generation of strengthened interfacial polarization as well as dipole relaxation respectively. At high frequencies, a decrease in the value of $\varepsilon'(\omega)$ owing to the lag of dipoles behind the applied electric field was also reported. The mechanical strength and conductivity were improved with the increase in GnP dosage [11]. The dielectric spectroscopic studies at different temperatures of PVC/silicon dioxide (SiO_2)/montmorillonite (MMT) composites also agreed on the improvement in dielectric constant up to the glass transition temperature. The high dielectric strength for PVC/4 wt% MMT (37) and low value for PVC/4 wt% SiO_2/4 wt% MMT (26) nanocomposites were observed because comparatively very higher dielectric constant for nanoparticles than the polymer causes a very low dielectric field to be acted on the nanoparticles and its interface region. As a result, a homogeneous electric field exists and the decrease in a number of quasi-mobile charges as well as dipole moment leads to a low dielectric constant. Decay in dielectric constant with an increase in frequency on account of both interfacial polarization as well as electrical conductivity was more pronounced at high temperatures (90, 110 °C). The TDC α-peak near the glass transition region due to the reorientation of the dipolar main chain segment and Maxwell–Wagner–Sillars (MWS) relaxation at high temperature associated with the charge trapping at the interface of nanocomposites supported the temperature dependency on their dielectric properties. The capacitance of the nanocomposites explored their application as a capacitor. [2]. Akhina and their co-workers have shown that reduced graphene oxide (RGO) incorporated into plasticized PVC through conventional melt compounding also resulted in an increased dielectric constant making it well suited for applications in the dielectric as well as energy storage devices. The increased number of polymer-filler interface contacts provided numerous sites for the reinforced Maxwell Wagner Sillars (MWS) effect and interfacial polarization that lead to a high dielectric constant of the PVC/RGO composites. Moreover, the dipoles responsible for this polarization couldn't keep their orientation in the direction of an alternating electric field at high frequency causing a deterioration in the dielectric constant [7]. PVDF/PVC/GO nanocomposite prepared by Elashmawi et al. also yielded an amorphous rich phase and a decrease in dielectric constant (ε') and dielectric loss (ε'') with an increase in frequency. The polarization due to Maxwell Wagner interfacial polarization resulted in small dispersion in dielectric loss and high dielectric constant at low frequency. More number of polarons (electrons) with an increase in GO and their hoping with an increase in frequency gives rise to an improvement in conductive properties of the composite [28]. Strong dipole–dipole interaction among dodecylbenzene sulfonic acid (DBSA) doped polyaniline (PAND) and PVC at low frequency and room temperature caused an increased dielectric loss factor and permittivity with a decrease of frequency between 0.5–10^6 Hz. The reduction in charge trapping centres and thereby more number of conducting channels participating in the relaxation process observed resulted in an improved conductivity to the composites [29].

The addition of NiO nanoparticles synthesized by sol–gel method using nickel nitrate hexahydrate and egg white into the PVC polymer matrix owing to their good dispersion in the polymer matrix, semiconductor behaviour, high dielectric constant ($\varepsilon' > 10$), electrochemical activity and chemical stability has grown great attention for application in energy storage capacitors, solar cells, sensors, display devices, and lithium-ion batteries, etc. [4]. The dielectric property study on PVC/NiO nanocomposites using a broadband dielectric spectrometer in the frequency range of 0.1 Hz to 20 MHz at different temperatures showed the highest value of dielectric constant (ε') at low frequency side and the value decreased with increase in frequency. At low frequency, the rate of electric field oscillation is smaller than the oscillating frequency of molecules ($\omega << 1/\tau$) and thereby dipole arises from C–Cl bond and dipole–dipole interaction among PVC chains reoriented themselves with the applied electric field. At moderate frequency ($\omega > 1/\tau$), the dipoles are not completely oriented because of change in electric field direction and hence dielectric constant (ε') onset to decrease. As the dipoles have no response to the electric field at high frequency ($\omega >> 1/\tau$), the dielectric constant (ε') decreased and reached a constant value. An increase in temperature increased the dielectric constant. At low temperatures, the energy absorbed by molecules is small and a minor number of dipoles contributed to the polarization process. As the temperature increased and reached the glass transition temperature, the intermolecular energy absorption, decrease in polymer viscosity as well as increase in the number of dipolar groups contributed to the increase in ε' value [4]. Silicon carbide (SiC) owns good thermal, chemical and dielectric properties. Alghunaim et al. introduced silicon carbide (0.02 to 0.06 wt%) into PVC/poly (N-vinyl carbazole) (PVK) blend that showed a sharp increase in both ε' (2×10^6) and ε'' (3.6×10^6) with filler content towards low frequencies (from 20 MHz to 0.1 Hz) attribute to the orientation of dipole by themselves in the direction of an applied electric field [30]. Incorporating a giant dielectric constant material, calcium copper titanate (CCT) ($CaCu_3Ti_4O_{12}$) (~700 at room temperature) in PVC revealed a high dielectric constant to the composite and the value decreased with increase in frequency and increased with temperature rise. Dielectric loss increases with filler content and frequency but dropped with an increase in temperature [31]. Multiphase and multilayer systems can also improve the dielectric as well as energy storage properties of two-dimensional material reinforced nanocomposites [32]. Anti-static multi-layer graphene (MLG) (3.5 wt%) filled PVC composite films prepared by the conventional melt-mixing method exhibited a surface electrical conductivity lower than 3×10^8 Ω per square [33].

High breakdown strength and dielectric constant are the key parameters required for high energy density in capacitors. However, both are generally contrary to each other. To solve this trade-off, Feng et al. prepared a PVC based ternary composites bearing V_2C MXene-Cu_2O hybrid filler that exhibited a high dielectric constant of 55 and a low loss of approximately 0.085 at 100 Hz as well as a high breakdown strength of 332 MV/m. Quantum sized high polarity micro-regions at the V_2C MXene-Cu_2O interface imparted a high dielectric constant to the material. The very strong dependence of the dielectric constant on the low-frequency region was also noticed owing to the interfacial polarization due to the electric dipole pairs present at PVC/V_2C interface. However, no favourable interfacial dipole orientation could catch up with the change of high-frequency electric field; therefore decrease in dielectric constant was observed. The linearity in conductivity data with elevated frequency supported the electric insulation feature of the composite [34].

High dielectric constant (high-k) polymer composites under integrating high dielectric constant nanofiller with high breakdown voltage, flexibility and ease of processing of matrix have received increased research interest nowadays for various dielectric applications [35]. High-k dielectric nanocomposites based on PVC/multi-walled carbon nanotube (MWCNT) with 4% nanoparticle exhibited a dielectric constant value of 13,066 with low dielectric loss ranging between 0.05 to 1.28 can be useful for capacitive sensors and supercapacitors. Dielectric relaxation measurement showed that the polarity of the PVC matrix and interfacial polarization at PVC and MWCNT strongly affected the dielectric properties [36]. Even though the desired dielectric properties have been realized in many organic–inorganic nanocomposites, achieving high permittivity with low loss at high frequencies is still challenging. To achieve this, neat beta-SiC nanoparticles owing to their low intrinsic bandgap (~2.2 eV) and high inborn conductivity were used in PVC and the produced high-k nanocomposite dielectrics achieved a permittivity of 239 and loss of 0.0074 at a high frequency of 1 GHz [37].

Ionizing radiation is an advanced tool in the scientific community for the functionalization of specific properties to the polymer-based system. Energetic electromagnetic radiation as well as particles with higher energy than the polymer chain dissociation energy is used as an ingenious tool for this purpose. Gamma and 90 meV carbon ions irradiations on the dielectric response of PVA/H_3PO_4/SiO_2 nanocomposites showed an improvement in electrical properties such as ac conductivity, dielectric constant and dielectric loss with the dosage of irradiation, attributed to the formation of low molecular polymeric macromolecules. The effect of 90 meV carbon ions irradiations on electrical properties was higher than that of gamma irradiation. The real and imaginary parts of complex permittivity are related to the capacitance that determines the dipole alignment or polarization as well as the energy needed to align the dipoles respectively. The value of dielectric response is high at low frequency due to the existence of ion pairs that can perform long-range migration and act as localized dipoles. The high electrical conductivity after irradiation proposed the potential applicability of the composite for battery applications [38]. Poly(vinylidene fluoride) (PVDF)/Poly(vinyl chloride) (PVC) blend doped with palladium nanoparticles (PdNPs) prepared by laser ablation technique exhibited an improved segmental motion and the number of ions and charge carriers built on the blend were increased with increasing conductivity of the composite system, which makes it suitable for battery and electronic applications. Palladium nanoparticles have remarkable supramolecular and catalytic activity. The dielectric constant and loss values were high at low frequency and the values were decreased with a rise in frequency, besides an increasing trend of both the properties observed with an increase in the dosage of PdNPs. Both these behaviours are due to the high contribution of charge accumulation in the composite assigned to the polarization effect [39].

Dielectric Composites for Other Applications

The high driving voltage requirement of several kilovolts associated with dielectric elastomer actuators (DEAs) directed PVC gel, a kind of electroactive polymer actuator as a promising dielectric material for soft robotics. Moreover, PVC gel exhibited high electrically induced bending deformation as well as amoeba-like creep deformation with high stability and durability. The actuator consists of a PVC gel membrane placed between two electrodes and when an electric field is applied, electrons migrate from cathode to anode through the PVC gel and a layer with high a density of negative charges in gel near the anode is formed. The Maxwell force between this layer and the anode surface led the gel to asymmetric deformation, resulting in creep deformation along the anode. The PVC actuator proposed by Yi et al. displayed a minimum strain of 21%, and maximum output stress of 600 kPa only at a low voltage of 120 V and a continuous actuation of 1 million times, a sign of high durability [1]. PVC gel plasticized with dibutyl adipate (DBA) also showed an efficient electrically induced bending deformation due to the electrochemical formation of the solvent-rich layer and its deformation from the Maxwell stress [40]. There have been reports of the potential application of PVC nanostructure-based ultra-flexible biosensors prepared using the dielectric heating assisted nanoimprint lithography (NIL) method for wearable health monitoring devices [41]. A 6% PVC/PVA blend owing to the extended chain length of the blend showed high conductivity of about 2.59×10^{-6} Scm^{-}1and low tangent loss of 0.9 that is suitable for low k-dielectric materials, gas sensor encapsulation device and other electronic applications [42]. PMMA/PVC/m-SiO_2 (hexamethyldisilazane modified silica) composite prepared by Lavina et al. yielded low-k composite dielectric films with electrical dispersion up to a frequency of 1 MHz which is promising for organic microelectronic systems such as OTFT devices. Film with 20 to 35 wt% m-SiO_2 exhibited ε' values lower than that of SiO_2 ($\varepsilon' = 3.9$) and a $\tan \delta < 0.05$ [43]. Dielectric behaviour of PVC/lithium triflate polymer electrolytes showed a sharp rise of both real and imaginary parts of dielectric constants towards low frequencies as a result of electrode polarization effects and a decrease in polarization due to the charge accumulation as well as a drop in ε' and ε'' at high frequencies [44]. The dibutyl phthalate (DBP) plasticized PVC/lithium triflate electrolyte showed much higher ε' as well as dissipation factor ($\tan \delta$) values at room temperature Higher lithium triflate content (40%) was dominated by conductivity and mask any dielectric process [45].

6 Summary and Conclusion

Flexible polymer composites are frequently used in the design of various dielectric applications ranging from portable electronic devices to high-efficiency hybrid electric vehicles. PVC based composites are characterized by excellent insulation properties, flexibility, and mechanical, thermal as well as chemical stability making them a promising candidate as dielectrics. Flexible energy storage materials with high dielectric constant and minimum loss are highly demanded the miniaturization of various electronic gadgets. Various ceramic fillers with high intrinsic dielectric constants have been utilized to enhance the dielectric properties but the high volume requirement and low interfacial interaction results in high dielectric loss and poor flexibility to the composites. The application of low loading nanoparticles owing to their high surface area with homogeneous distribution and structure–property relationship is appropriate and various nanocomposites are designed with different techniques for dielectric applications. Filler type and concentration as well as polymer matrix-nanoparticle interface have a significant impact on the dielectric properties of PVC nanocomposites. The effect of various nanoparticles such as SiO_2, Al_2O_3, ZnO, CuO, PbO, palladium, CNT, clay, GO, etc. on the dielectric properties of PVC composites and their applicability for high voltage cable insulation, energy storage, actuators, sensors, telecommunication systems, and so on are discussed in detail.

Advantages such as high resistance and dielectric breakdown strength as well as low dielectric loss make PVC based nanocomposites suitable for high voltage insulators. High breakdown strength and dielectric constant, both contrary to each other are the key parameters required for high energy capacitors. In this regard, high-k composites have been developed by integrating high dielectric constant nanofiller with a high breakdown voltage of matrix. Composites have various advantages depending on the microstructure and interface between polymer and filler. Even though the desired dielectric properties have been realized in many PVC nanocomposites, achieving high permittivity with low loss at high frequencies is still challenging. Therefore, attention should be given to the PVC-nanofiller interface.

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Possible Interaction of PVC with Micro-and Nano-fillers

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Abstract Undoubtedly, polyvinyl chloride (PVC) is one of the most produced synthetic polymers globally and is used in all areas of life. Its general structure consists of hydrocarbon and chloride as well known. The main reasons for its widespread use in our life are low production cost, high mechanical strength, and chemical stability. The PVCs have significant problems such as low thermal resistance or weak impact strength. Thus, nowadays, the current studies are noteworthy on the PVC-matrix composites reinforced with micro-/nano-based fillers. The primary purpose of this studies improves the mechanical, physical, or chemical properties of PVC. Of course, the essential feature of a composite structure is the matrix/reinforcement interface and its interactions. In addition to the production method, the selection of matric and reinforcement fillers is the main factor affecting the adhesion and interactions between the interface. In this chapter, an overview of the possible interaction of PVC with micro- and nano-fillers is presented.

1 Introduction

Polyvinyl chloride (PVC), composed of 42% hydrocarbon and 58% chloride, was first discovered by the scientist Regnault in 1835. After polyethylene (PE) and polypropylene (PP), the PVC is one of the thermoplastic polymers we use primarily in everyday life, such as construction, packaging, medical, or clothing. Some application areas of PVC can be listed as pipes, electric wires, window profiles, credit cards or bags, and tubing for blood transfusion [46]. More recently, wood fiber PVC has become

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more popular, with good mechanical properties, moisture, fungal resistance, long life, wood-like surface performance, and recyclability [16, 46].

The primary reasons for PVC's widespread use are its low cost, high mechanical strength, and high chemical resistance [5, 76, 78]. Moreover, good insulation and fire resistance may be considered as their other vital features [5]. However, the PVCs have major problems such as low thermal stability, low impact strength, and low strength [83]. Current studies in this field have focused mainly on the addition of impact regulators and coupling agents to improve composite properties [46]. Many researchers have conducted numerous studies on PVC matrix composites and/or nanocomposites to enhance PVCs' properties [16, 78].

The fillers reinforced into the PVC matrix can be divided into PVC matrix composites and PVC matrix nanocomposites. However, different fillers are reinforced into the PVC matrix beyond size. These can generally be categorized as organic and inorganic fillers, but this classification is very generic. To make an understandable classification for fillers reinforced into the PVC matrix, these fillers can be classified as follows: (i) carbon-based fillers, (ii) natural fillers, (iii) mineral and metal oxide fillers [24]. Carbon-based fillers reinforced into the PVC matrix include carbon nanotubes (CNTs), graphene oxide (GO), carbon black, graphite, etc. Natural fillers include rice husk, bamboo fiber, coconut shell, banana pseudostem, etc. Even though plenty of metal oxide fillers is used in the PVC matrix, the most commonly used ones are SiO_2, TiO_2, ZnO, MgO, etc. The most common mineral clays are bentonite, kaolinite, talc, etc. [24, 35, 78] (Fig. 1).

The type and size of fillers used to improve the properties of the PVC matrix are essential. However, another equally important parameter is figuring out and intervening with matrix/filler interaction. Interfacial interaction of PVC matrix/fillers can be enhanced so that an effective improvement can be seen in many properties of composites, particularly the mechanical properties [87, 88], as well as the wettability and adhesion between PVC matrix/fillers can be developed with the surface modification of fillers [29].

Filler materials can be used as particle or fiber reinforcements. Filler materials are particles when geometric axes have a similar order of magnitude in two or three dimensions, depending on the Aspect ratio (for example, a spherical or discoid shape).

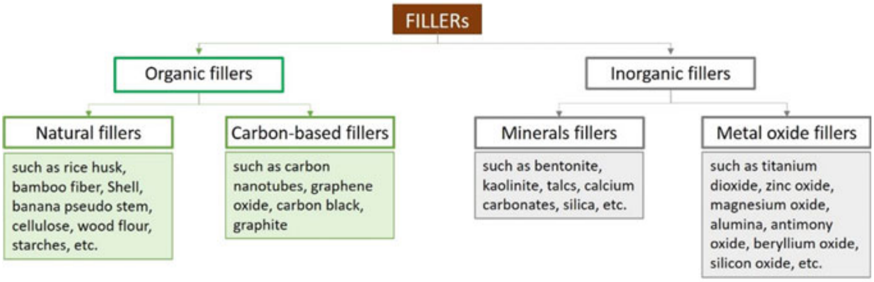

Fig. 1 Fillers types added to the PVC resin

The aspect ratio of particle filler plays an important role. The higher the aspect ratio, the higher the strength of the composite. The aspect ratio must be obtained above the critical value for better stress transfer [50]. Fibers can be defined when one dimension is considerably larger than the other two dimensions (e.g., carbon nanotubes have approximately 1000 nm in length only compared to ~ 1 nm diameter). Fiber-reinforced composites have been widely used in applications such as construction for many years, and their market share is increasing in many other industries. Fiber-reinforced composites consist of fibers that act as reinforcements or fillers and a polymer matrix. In fiber-reinforced composites, the matrix protects fibers against external environmental harmful impacts [9].

As stated above, the bonding formation in the composite structure is explained with the concept of “wettability” or “interface adhesion” [26]. Interface adhesion is the other important parameter that should be considered after selecting the matrix and filler elements, which are the main elements of the composite that will produce the desired properties. Because in the absence of a good interface adhesion, the charge from matrix phase-to-filler phase is not effectively transferred on composite materials [25].

Polymer matrix composites (PMCs) may be exposed to stresses in operating conditions. Stress concentration can be caused in the composite for two reasons (i) thermal processing due to different thermal expansion coefficients for fiber and matrix and (ii) mechanical stresses due to different strength properties of both materials. When an adhesive with a low interface is subjected to composite loads, micro-cracks develop on the interface and spread to the matrix. Consequently, the composite suffers damage in the form of stripping or fracture [52].

Although composite materials are produced by joining macro grade matrices and fillers in different ways, they are expected to act as a single material when subjected to physical, chemical, or mechanical impact. In this respect, the value of the bond strength or adhesion on the interface determines the behavior of the composite [99]. Mechanical interlocking, electrostatic interaction, molecular interaction, and chemical bonding are all bonding methods at the interface [29].

However, the high adhesive strength at the interface does not certainly lead to optimal composite properties. It is crucial to figure out the role of physicochemical interactions at the fiber-matrix interface and to establish quantitative correlations between the nature and level of those interactions and the ultimate mechanical behavior of composite materials [37]. In other words, the effect of interface adhesion (W) on the magnitude of stress transfer capacity from fiber to matrix must be analyzed [91]. This interface stress transfer capability is measured through a fragmentation test on single-fiber composites and is defined as shear strength, τ, in the interface. τ is expressed as follow (Eq. 1) [49].

$$\tau = \frac{\mathrm{d} \cdot \sigma_{f(l_c)}}{2 \cdot l_c} \tag{1}$$

where d is the fiber diameter, l_c is the critical length of the fiber part at the end of the decomposition process, and $\sigma_{f(l_c)}$ defines the fiber stress strength at the length of the measurement equal to l_c. The extent of theoretical and experimental approaches leading to the establishment of such relationships is discussed [49]. Layers that exhibit physical and mechanical properties different from mass, i.e., the presence of the interface, affect the results. Therefore, it is of primary importance to comprehend the role of physicochemical interactions at the fiber-matrix interface and to establish quantitative relationships between the nature and level of those interactions and the ultimate mechanical behavior of composite materials.

The physical attraction between electrically neutral bodies is best described as the wetting of solid surfaces by liquids. Wetting-related bonding involves very short-range interactions of atom-scale electrons that develop only when the atoms of the components approach or come in contact with each other within a few atomic diameters [73]. For continuous fiber composites, in particular, weak adhesion may result from insufficient physical contact between the resin and the fiber due to incomplete wetting. Contact between a liquid and a solid can be established provided that the liquid is not too viscous and a thermodynamic driving force is present. Therefore, wetting must be done for any adhesion to occur. A high value for a liquid surface free energy prevents the spread of a liquid droplet from covering the surface. The wetting or contact angle (θ) is achieved by a balancing force (Young equation). Most of polymeric surfaces can be described as low energy while fillers surface is described as high energy. The total surface energy of a material is (γ_i. It can be considered that this value consists of two parts; Lifshitz-van der Waals (γ_i^{LW}) and acid–base component (γ_i^{AB}) [17]. The first section represents long-distance dispersion forces, orientation (Keesom), and induction (Debye), while the second section represents short-distance H-bond or Lewis's acid–base interactions. Ideally, it is necessary to characterize the solid resin (polymer) and filler (fiber) surface energies with proper probe fluids for LW and acid–base components and to calculate adhesion for any resin-solid system.

Consequently, methods such as roughening the matrix-reinforcement interface and modifying the matrix and fillers may be employed to ensure good wettability in the interface. These surface modification effects are attributed to thermodynamic driving forces and have been shown to affect polymer adhesion and other characteristics depending on the surface and interface forces.

2 PVC Matrix Composites Reinforced with Micro/Nano-fillers

In micro filler/polymer composites, surface modification of particles has already been a broadly applicable technique for minimizing particle/particle interaction and increasing particle/matrix interaction. Along with the latest advances in nanoscience and nanotechnology, the correlation between polymer nanocomposites' properties and nanoparticles' surface modification has also become a significant interest [74].

Polymer matrix nanocomposites (PNCs) represent a radical alternative to the conventional filler polymers or polymer mixtures, which are the fiber of the modern plastic industry. Unlike the traditional composites where the reinforcement is at the micron level, PNCs are sampled with separate components at several nanometres levels [96]. In recent years, it has been observed that the addition of the low content of these nano-filler agents to the polymer may lead to improvements in the mechanical, thermal barrier, and flammability characteristics without affecting their machinability.

PNCs are classified by the size of nano-filler agents. One-dimensional nano-fillers are: plates, laminas, and/or shells; two-dimensional nano-fillers are in the form of nanotube and nano-fibers that are smaller than 0.1 in diameter, and three-dimensional nano-fillers are isodimensional nanoparticles such as nanometric silica [56].

In a PVC matrix, the capabilities of the interfaces stand out to transfer stresses from matrix to fiber in the interaction of nano-filler. Theoretically, the composite's strength increases as the filler agent's particle size reduction for a given particle volume fraction. A smaller particle size with a higher surface area yields higher strength by transferring more efficient stress [87, 88]. The matrix can completely cover the filler agent surface under optimum particle loading, while the small particles lead to good distribution and strong particle–matrix interaction [50].

As a result, interface control is critical to obtaining a good bond between the inorganic filler and the polymer. The ratio of particle volume to interface volume changes drastically in favor of interfaces with decreasing filler size (Fig. 2). The emergence of new properties with nano−, meso− and micro-material interactions will also be the subject of recent studies.

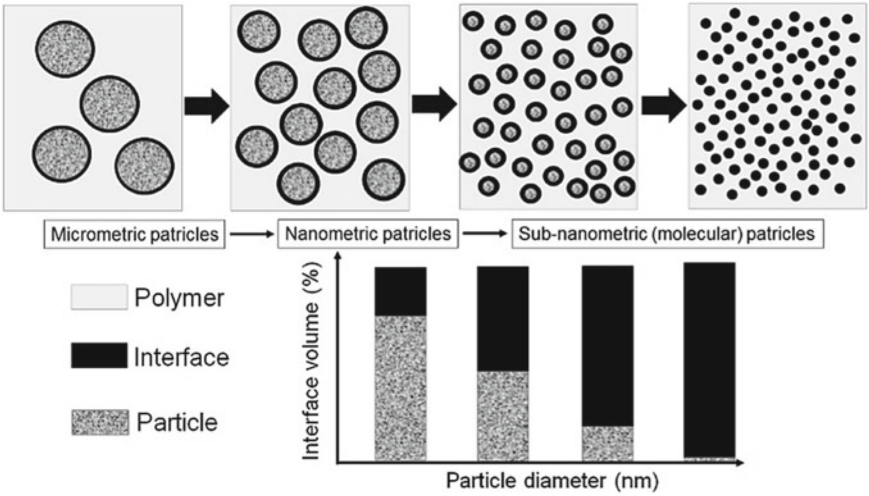

Fig. 2 Schematic representation of the ratio particles/interfaces changes with the size of the filler [71]

3 Interaction of PVC Matrix with Organic Fillers

3.1 Interaction with Carbon-Based Fillers

In recent years, the addition of carbon-based nanofillers into PVC, such as graphite, graphene (Gr), graphene oxide (GO), and carbon nanotube (CNT), is very frequently referred to in the literature [4, 5, 68]. In general, the approach for obtaining nanocomposites is primarily based on generating a large interface between the nanosized building blocks and the polymer matrix. However, this approach alone is not sufficient. Improvement in the physical and chemical properties of the PVC nanocomposites with carbon-based fillers mostly depends on the components' characteristics like their composition, concentration orientation, and structure. The interfacial interactions between the composite matrix and the filler are of prime importance in this respect that characterizes the interphase [30, 101]. The interphase is the immobilized polymer layer that covers the surface of the filler particles. Therefore, the effect of the interphase is directly related to its homogeneity, the quantity of material used, and the characteristics of the mixing components, particularly particle sizes. The influence of the interphase can be insignificant for larger particle sizes due to their lower surface areas to allow significant amounts of interphase to form. However, nanoparticles have very large surface areas that can make up interphase of a substantial volume fraction of the total composite. For that reason, while using nanoparticles, the composite properties are determined by the interphase. Both the amount of material attached to the interphase and the interaction resistance due to mixing can affect the properties of the nanocomposites significantly [74].

In some cases, they use appropriate surface modifications when necessary, resulting in good interfacial adhesion and leading to the success of developing new nanocomposites. As a matter of fact, many of the distinctive features of the nanocomposites that high modulus of elasticity, high yield strength, low permeability, etc., are influenced mainly by the interphase. This part discusses the interactions of the carbon-based fillers such as graphite, Gr, GO, and CNT with the PVC matrix.

As it is known, graphite comes from the Greek word *graphein*, which means to write. Graphite can be seen in powder, flake-like, flat, fibrous, and spherical forms with various particle sizes. Flake-like graphite consists of a thin layer less than 100 nm in thickness. Carbon atoms in graphite are arranged in hexagonal sheets, and the distances between the two carbon atoms of each sheet's hexagon are 1.42 Å [5]. Carbon atoms are linked to each other by a covalent bond in these layers. In graphite, each layer of the hexagonal sheet of carbon is connected by Van der Walls forces.

Another carbon product, graphene, was obtained more than a decade ago by graphite exfoliation by Andre Geim and Konstantin Noholev. Then its synthesis techniques, properties, and potential applications were investigated worldwide [70]. Graphene is known for its superior properties. It is considered two-dimensional because it is only one atom thin and formed by the perfect arrangement of covalently bonded carbon atoms in a hexagonal honeycomb lattice [30]. The carbon–carbon bond length in graphene is 0.142 nm. Graphene has attracted a lot of interest owing to its lightweight, high young modulus (~1.100 GPa), high electron mobility at the room temperature (250.000 $cm^2 \cdot V^{-1} \cdot s^{-1}$), high thermal conductivity (5000 $W \cdot m^{-1} \cdot K^{-1}$), large specific surface areas (2630 $m^2 \cdot g^{-1}$), and good compatibility with polymers [8, 51, 106]. In addition, it has also been used as a high-performance lubricant in various regions due to its flexible graphitic layers, high strength, and atomically smooth surface [97].

Graphene oxide (GO) is generally synthesized by Hummers, Staudenmaier, and Brodie methods by the oxidation of natural graphite flake to various levels [5, 106]. Strong acids and oxidants are used for the oxidation of graphite. However, oxidation levels of the graphite are related to graphite precursor, reaction conditions, and method used. Oxidation, epoxide, hydroxyl groups, and the carboxylate of some polar groups are linked with each layer. While carbonyl groups are placed near the edges, other groups stay above and below of each graphene layer [5].

Carbon nanotubes (CNTs) are known for their unique properties such as thermal, optical, and mechanical properties. Various methods that are widely used for the synthesis of carbon nanotubes are laser ablation, arc-discharge, thermal chemical vapor deposition, chemical vapor deposition (CVD), plasma-enhanced chemical vapor deposition, and chemical vapor deposition with microwave plasma, hydrothermal synthesis, solar oven and electrolysis method, etc. [67]. In CNTs structures, atoms form hexagonal geometry, and atoms bond with each other by planar sp^2 configuration (as in graphite plate). Carbon nanotubes can be of single-layer (single-walled) or multi-layered (multi-walled). Single-walled nanotubes are formed by one-layer cylinders of graphite, while multi-walled tubes are composed of around 50 [1]. In short, a single-layer carbon nanotube can be described as a form of graphite wrapped in a cylinder of the atomic plane resembling a honeycomb without creating any defects. Despite their very thin structures, they are very strong and rigid and can be used as excellent conductors if properly fabricated. Diameters of carbon nanotubes can be in the order of nanometres and lengths of micrometres. In multi-walled tubes, the distance between the two tubes is usually greater than the bond distance between the carbon atoms forming the tube. In nested tubes, if the distance between the walls of the tubes is small enough (0.15 nm) to allow the carbon atoms to bond, the carbon atoms bond tetrahedrally by sp^3 configuration. In other words, each carbon atom has four tetrahedrally bonded neighbors. The rods consist of completely hollow or partially filled tubular structures. The flexibility of these structures is less than the tubes; they also show different mechanical and electronic properties than single-walled tubes [62].

Graphite enhances the multifunctional features of nanocomposites like thermal, mechanical, electrical, and lubricating properties while in use as fillers due to its sigma bond, delocalized pi bond, and Vander Waals forces between graphite sheets. Addition of graphite filler into the PVC composites with conventional polymer processing methods like compression and injection molding are known. The properties of the PVC/graphite composites depend on various parameters such as the composition of the PVC and its production method, the structure of the graphite, and interactions and level of dispersion in the polymer matrix [5]. Polymers are used as insulators in the electrical industry due to their high specific electrical resistance. If electroconductivity is desired, the conductive fillers are added to the polymer matrix. With electroconductive properties, nanocomposite materials are widely used in the electronics field, particularly in power for electrical-conductivity, conductive adhesives, electromagnetic interference shielding, conductive paints, gas and pressure sensor [6, 65].

Other than graphite, the addition of carbon black has also been studied. It was reported that carbon black with a high surface area improved the electrical current percolation at lower concentrations due to a conductive network. Still, its weak interactions and porous structure decreased the mechanical properties [65]. However, the advantage of the addition of graphite is its good conductivity and its lubricating effect in the melt. In some cases, the graphite is coated with some elements such as Cu. It was found that the metalized graphite significantly increases the viscosity of compositions. For that matter, the compositions exhibit superior heat transfer characteristics due to the strong adsorption interaction of the binding agent to the filler surface. The use of more conductive copper-plated graphite makes it possible to create electroconductive polymer composites with high adhesive strengths [10, 64, 65]. The effects of the graphite-filler on the PVC/styrene-acrylonitrile composites, in respect of electrical, morphological, and hardness, were investigated. Analysis of the composites by microscopy revealed the formation of a conduction network at the interfacial regions in a well-dispersed graphite-polymer matrix. Improvement in conductivity and hardness even at a very low filler loading was reported by Sachdev [77]. Graphite is used as electronically conducting filler in various proportions to polyethylene oxide (PEO)/PVC nanocomposites using the solution casting technique. It was noted that the increase in filler loading increased the electrical conductivity. But, increasing the amount of graphite also impaired the young modules and tensile strength of the nanocomposites. 5 wt% of graphite loading was found to be adequate for that matter, whereas its higher level of usage between 15–25 wt% caused agglomerations [32]. To enhance the electrical conductivity of the PEO/PVC, the addition of graphite together with $FeCl_3$ in PEO/PVC by solution casting method has been found beneficial. As per the method described elsewhere [85], graphite and 6 wt% $FeCl_3$ were mixed in toluene with stirring and then washed and dried for 5 h in an oven at 60 °C. The $FeCl_3$ doped ground graphite powder was then blended with the tetrahydrofuran (THF) solution of PEO/PVC and casted on a glass mould and dried at room temperature. It was seen that electrical conductivity performance was enhanced with addition of fillers however, it adversely effected the tensile strength of the nanocomposite films. The THF blend of the sonicated dispersion of graphite in N-methyl-2-pyrrolidinone (NMP) was also used as fillers for the PVC composites by solution blending method. With this method, the uniform distribution and interaction of graphite nanosheets and polymer increased Young's modulus by 63%, and it also increased the tensile strength by 19% [63]. The addition of graphite nanosheets into the PVC matrix improves the electrically conductive of the nanocomposites. It also increases the thermal stability, dielectric constant, and absorption of the magnetic waves at microwave frequency [6].

Graphene/PVC nanocomposites possess very high elasticity modules, and graphene addition to polymers improves the thermal, mechanical, and electrical properties of the nanocomposites [45]. The superior properties of the graphene doped polymer matrix, such as strength and toughness, were due to the prevention of the propagation of microcracks [97]. As a result, the mechanical and wear resistance of the nanocomposites increases significantly. The synthesis method of graphene/PVC nanocomposites is based on the solvent evaporation method. Tetrahydrofuran (THF) is generally used as a solvent for PVC that forms thin polymer films (foils) and fibers. The advantage of this method is the dispersion of nanoparticles in the solvent can be enhanced by sonication. However, secondary aggregation of the nanofiller due to solvent evaporation should be considered. A method such as mixing with molten polymer and in situ polymerization is also used for the graphene/PVC nanocomposites [101]. The homogenous dispersion of the graphene filler into the PVC was investigated by using various dispersants such as oleic acid, polysorbate 80, and Curcuma longa L. rhizome. The improvement in dispersion stability and disaggregation of the filler was observed with Curcuma longa L. rhizome [101]. Wang et al. [98] studied the synthesis of the multi-layer graphene (MLG)/PVC composites by using melt-mixing technics.

The improvement in mechanical properties was attributed to the uniform-homogenous dispersion and interactions of the MLG and PVC. The interactions and reinforcing mechanisms of MLG/PVC composites are shown in Fig. 3. It can be noticed how the strong interactions between entangled PVC chains enhance the mechanical strength and tensile modules. With the use of plasticizers, e.g., DOP (dioctyl phthalate), the distance between PVC chains gets enlarged, weakening the interactions between the polarized groups resulting in the decrease in mechanical properties. However, when MLG added, the interaction between components and the mobility of the PVC chains decreases. Owing to high structural integrity and low surface energy of MLG, DOP molecules absorbed easily improving the compatibility of the MLG and PVC matrix. The uniform dispersion and effective stress-transfer among the components cause to enhance the tensile modules of the nanocomposites.

Graphene oxide (GO) is attracting researchers worldwide due to its exceptional properties in various areas such as chemical sensors, composite materials, energy

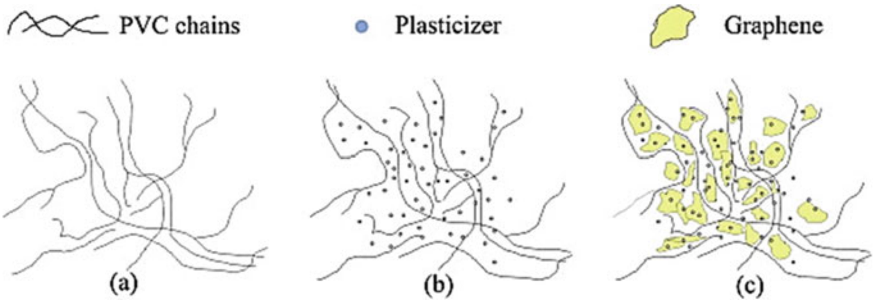

Fig. 3 Structural schematic of MLG/PVC composites **a** neat PVC, **b** soft PVC containing DOP plasticizer, **c** MLG/DOP/PVC composites (Reprinted with permission from ref. [98], Copyright 2015, Elsevier)

storage, and optical and electrical devices. However, to exploit the structure and physical properties of the carbon materials derived from graphite such as graphene, GO, chemically reduced GO (CRGO) or thermally reduced GO (TRGO), or functionalized graphene sheets (FGS), the degree of dispersion, orientation and interfacial adhesion are very important for the manufacturing of polymer nanocomposites. Various surface-modified functionalized GO of all allotropic modifications can be developed with its functional groups. These functionalized GO sheets show strong hydrophilic properties and easily disperse in water or other aqueous media to form stable colloids. Due to its hydrophilic nature, GO sheets can only be distributed in aqueous media, which is incompatible with organic polymers [19]. In the Hummers method, the graphite is oxidized by potassium permanganate ($KMnO_4$) and sulfuric acid (H_2SO_4), while in Brodie and Staudenmaier's method, the combination of potassium chlorate ($KClO_3$) with nitric acid (HNO_3) is used to oxidize graphite [106]. The use of GO as a filler in thermoplastics and the importance of its dispersion in a polymer matrix, and interfacial interactions between the filler and polymeric matrix are briefly discussed as follows. To improve its homogenous dispersion in the PVC matrix, GO are functionalized. Thus, strong hydrogen-bonding interaction between the PVC chain and hydroxyl, carboxyl and epoxy groups of GO sheets can be obtained [5]. In studies by Li et al. [55], enhancement of the interfacial interaction of the PVC and reduced graphene oxide (rGO) was achieved by hybridizing rGO with zinc oxide (ZnO) nanoparticles. Synthesis of the rGO filled with ZnO nanoparticles (rGO-ZnO) by one-pot chemical route was done by mixing GO and zinc nitrate ($Zn(NO_3)_2$) in water and adding sodium hydroxide and hydrazine hydrate. TEM, SEM, and XRD methods analyzed the obtained rGO-ZnO hybrid. rGO-ZnO/PVC composites were obtained by a simple solution mixing and drop-casting. Tensile strength, interfacial tension, and glass transition data evaluated interfacial interaction between PVC and rGO-ZnO. It was found that the ZnO nanoparticles acted as a bridge to connect PVC via electrostatic attraction and hydrogen bonding linking rGO by a p–$\prod$ stacking/electrostatic interaction. Significant enhancement in mechanical properties and glass transition temperature was observed due to very strong interfacial interaction between PVC and nanofillers.

In another report, the synthesis of GO reinforced PVC-waterborne castor alkyd (WCA) nano-composites (PVC/WCA/GO) films via solution blending technique was discussed. For the GO synthesis, the natural graphite and $NaNO_3$ were dissolved in H_2SO_4, and then $KMnO_4$ was gradually added into this suspension as an oxidation agent. The suspension was filtered and washed with a warm HCL solution. In the last stage, it was filtered and dried. The obtained GO was then added to PVC/WCA using the solution blending method. It was noted that the samples with proper dispersion in the composite matrix showed significant improvement in tensile strength and elastic modulus of the nanocomposite. 260 and 185% improvements in tensile strength and elastic modulus were achieved by adding 0.5 wt% of GO compared to the neat polymer [102]. GO reinforced PVC nanocomposites can be obtained by the colloidal blending method too. Likewise, GO powder synthesized via the Hummers method is also used in this method. Before preparing PVC/GO composites, GO was separately dispersed in THF and sonicated. Then the mixture was sonicated for homogenous dispersion. Significant improvements in mechanical strength, thermal stability, and electrical properties were observed due to the homogeneity of the nanocomposites and their strong interactions between covalently bonded PVC matrix and GO [18]. Lee et al. [53] studied the synthesis of flexible PVC nanocomposites with fillers of hyperbranched polyglycerol (HPG) with functional graphene oxide (HGO). The production of the HGO via ring-opening polymerization of glycidol was seen in Fig. 4.

GO was first obtained with Hummers method, treated with glycidol mixture, and yielded HPG-grafted GO. Then, the hydroxyl groups were esterified by using butyric anhydride. It was indicated that the hyperbranched polyglycerol (HPG) and functionalized graphene oxide (HGO) caused uniform dispersion of the fillers and resulted in strong interactions between the HGO and PVC [53]. In another work, a significant improvement in mechanical properties of the PVC nanocomposites was reported using various GO derivatives. Firstly GO, poly (methyl methacrylate) (PMMA) grafted GO, polydopamine coated GO (rGO@PDA), reduced by dopamine (rGO@PDA-g-PMMA) were synthesized by Hummers method and then blended with PVC to form nanocomposites. Superior mechanical and thermal properties were reported for the nanocomposite thus formed, and this was due to the homogenous distribution and interfacial interactions of the fillers in the PVC matrix [36].

The effect of both multi and single-walled CNTs on the PVC matrix was also discussed in the literature. Especially nowadays, CNTs have become one of the most attractive materials in nanocomposites due to their properties such as high aspect

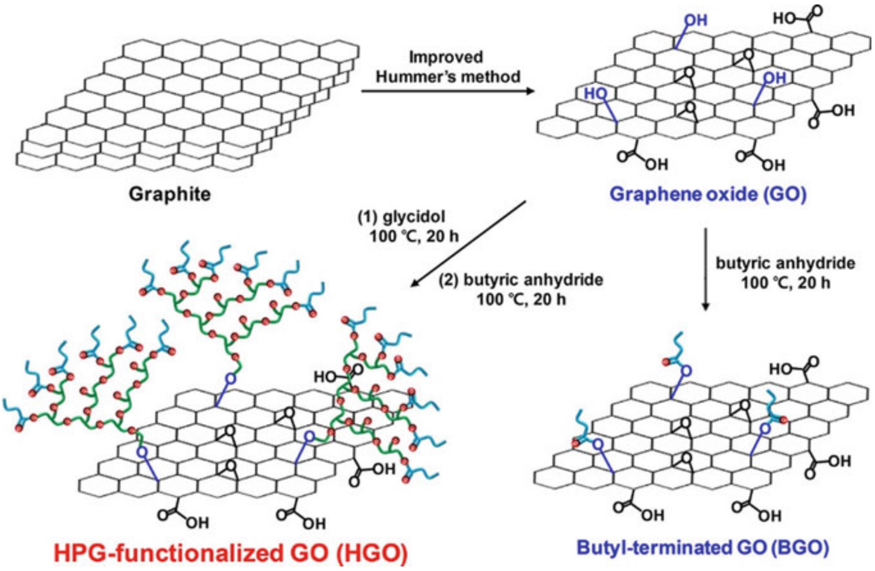

Fig. 4 Synthesis of HGO by Surface-initiated polymerization of Glycidol followed by esterification with butyric anhydride (Reprinted with permission from [53], Copyright 2017, American Chemical Society)

ratio, low density, and high electrical conductivity with excellent mechanical and thermal properties. Even using a very small amount of CNTs in the polymer matrix provides very good mechanical strength and electrical conductivity of the composite material compared to the conventional fillers. The CNTs-based nanocomposites are being used in various areas such as field emission, electromagnetic interference shielding, and actuators. Manufacturing CNT-based nanocomposites are difficult due to the Van der Waals interactions between CNTs, hindering effective unbundling. As a result, inhomogeneous dispersion of CNTs due to segregation adversely affects the properties of the nanocomposites. The successful fabrication of CNTs based nanocomposites depends on the high degree of dispersion of CNT in the main polymer matrix. Since the carbon nanotubes tend to self-associate into microscale aggregates, the surfactants such as sodium dodecyl sulfate, sodium dodecylbenzene sulfonate, and N-methyl-2-pyrrolidone are used to make a uniform dispersion of CNT in polymer matrix [57, 95]. Interfacial interactions can be maximized by chemical modification of CNTs to disperse or to make them compatible with the various polymer matrices. A synergy between the solvent and polymer was reported due to the high solubility of the long alkyl-chain modified multiwalled carbon nanotubes (MWNTs) and PVC in cyclohexane. The increase in thermal stability, conductivity, and improved young modules was attributed to the modification of CNTs and cooperative effects between solvent/polymer/CNTs [79]. The effects of the various amounts of single wall carbon nanotubes (SWCNT) in PVC composites revealed improved mechanical and thermal properties. The homogenous dispersion and interfacial adhesion between the PVC/SWCNT matrix consist of 0.25–0.75 wt% of fillers, resulting in increases in Young's modulus, tensile strength, elongation to break, and toughness. In composites including 1 wt% of the nanotubes agglomerated, decreases were observed in mechanical properties due to agglomeration acting as stress concentrators during the stress loading [105].

4 Interaction with Natural-Based Fillers

Synthetic fiber-reinforced polymer composites are widely used in high-performance applications such as the aerospace and automotive industries due to their superior mechanical properties and lightweight. However, their common usage can cause major ecological problems if they are not adequately recycled [50]. These reasons have led researchers to investigate using natural fibers as polymer reinforcements. PVC is a well-known contaminant due to the release of harmful substances into the atmosphere, such as hydrogen chloride and dioxins, during processing or decomposition. The combination of PVC and natural fibers is an exciting alternative as natural fibers are 'ecologically friendly' [13].

PVC composites made of natural fibers are preferred because of their low cost, renewability, recyclability, biodegradability, corrosion resistance, thermal and electrical insulation, and good mechanical properties [9, 40, 61]. Given the relatively low impact resistance of the PVC matrix, however, it is more practical to develop impact

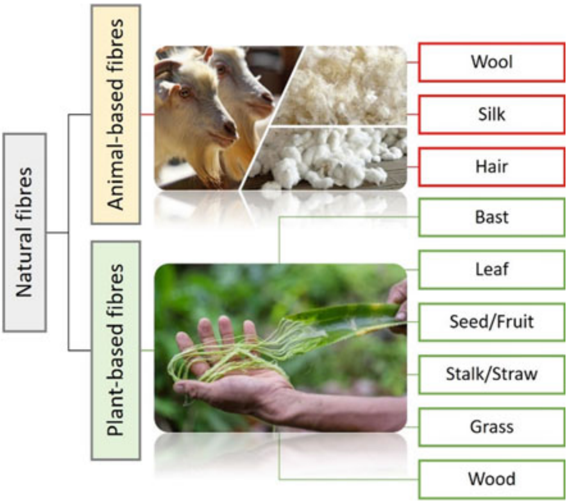

Fig. 5 Classification of natural fibers

strength. Current studies on PVC/natural fiber composites have focused mainly on the addition of impact regulators and the use of coupling agents to improve composite characteristics [46]. Natural fibers may originate from animal wool, hair, silk, and plant (wheat, hemp, sisal, jute, kenaf, coconut) or less used mineral origin [9, 13]. Figure 5 shows the classification of the natural filler agents [13].

The vegetable fibers are natural compounds made from cellulose, bonded to a hemicellulose and lignin matrix. Lignin-rich fibers (e.g., coir fiber, kenaf) are flexible and have high deformation [23]. Cellulose-rich fibers (e.g., banana, pineapple leaves, rice husk, potato peel, and canola straw) are used as fillers for high-performance materials [90]. Stalk fiber is obtained from the straw of cultivated plants, such as wheat, oat, maize, barley, or rape [7]. Stalk fiber and straw improve the strength of PVC composites without increasing their weight [12, 58]. Kenaf Hibiscus cannabinus is a plant known as deccan hemp and java jute from the Malvaceae family. Kenaf is one of the allied fibers of jute and displays similar characteristics. Jute is a bast fiber obtained from the trunk stripes of Corchorus species plants. Jute fibers have good mechanical properties, such as high tensile strength and thermal/insulating properties [75].

Sisal fibers are obtained from the leaves of the sisal plant. Sisal fibers are complicated and have a rough texture. Gomuti fibers are usually black and stiff fibers. Arenga is obtained from the sugar palm tree. Hemp and jute fibers have a thinner texture and a smaller diameter than coir, gomuti, and sisal [93]. Reinforcing kenaf, jute, and sisal fibers into the PVC matrix improves its mechanical properties [2, 20, 47]. Bamboo is an essential source of forest that grows abundantly in many tropical and subtropical regions, particularly in Asia. It has easy machinability with fast growth, high strength, and surface hardness. Thus, PVC/Bamboo composites are widely used in furniture production and construction materials [72]. Around 2000 different plant fibers are used in various applications, including composite [14]. The physical and mechanical properties of some of these fibers are given in Table 1.

The natural fiber structurally contains cellulose, hemicellulose, lignin, pectin, and wax materials [69]. The plant fiber (Fig. 6) wall consists of three main layers: middle lamella (lumen) and primary and secondary walls (PW, SW1, SW2) [21, 52]. The middle lamella connects the single fibers as the fiber bundle. Therefore, extraction processes can separate single fibers from fibers. In-plant fiber, the S2 layer is the part that determines the longitudinal mechanical properties. The helical structure of long cellulose chains makes up most of the microfibrils. Amorphous regions composed of lignin and hemicellulose are packed with cellulose chains. Microfibrils have a diameter of 10−30 nm [69].

A high aspect ratio (length/width) in cellulose-based fiber composites is very important, indicating potential strength properties. Continuous fibers have a high

Table 1 Mechanical and physical properties of several natural fibers [13, 40, 41, 50, 66, 92]

Fiber	Diameter of fiber (μm)	Length of fiber (mm)	Density (gr·cm^{-3})	Tensile strength (MPa)	Young's module (GPa)	Chemical treatment
PVC	–	–	1.35	48	3.3	–
Cotton	12–35	15–56	1.5–1.6	287–800	5.5–12.6	Silane
Coir	6.8–13.6	20–100	1.15	131–175	4–6	Alkaline
Flax	5–38	10–65	1.5	345–1035	27.6	Silane, MMA
Hemp	10–51	5–55	1.47	690	70	Silane, trimethoxy silane
Jute	5–25	0.8–6	1.3	393–773	26.5	Alkali benzoyl chloride
Kenaf	12–36	1.4–11	1.4	930	53	Alkaline, PMPPIC
Sisal	7–47	0.8–8	1.33–1.5	363–700	9.0–38	Alkaline, stearic acid
Pineapple Leaf	20–30	3–9	0.8–1.6	180–1627	34–82	NaOH, KOH
Ramie	18–80	40–250	1–1.55	400–1000	44–128	NaOH, NaOH silane
Soft wood	33	3.3	1.5	600–1020	18–48	Titanate, polyurethane, Hydroxide, chitin, chitosan
Bamboo	14	2.7	0.91	503	35.91	Sodium bisulfate, sodium hydroxide, sodium silicate

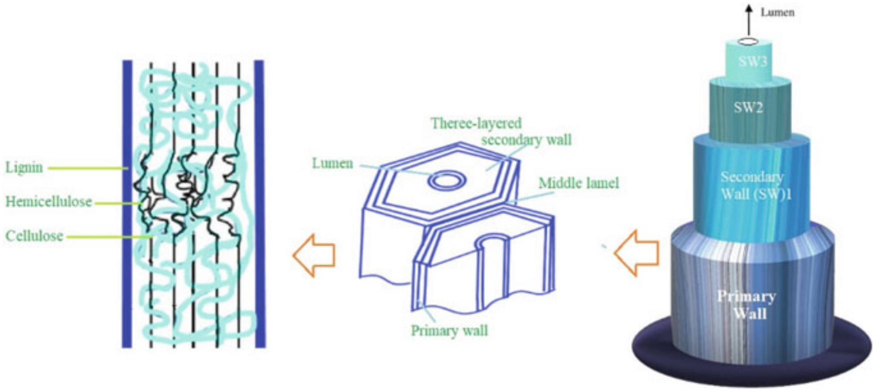

Fig. 6 Schematic representation of plant fiber structure: primary Wall, middle lamella, lumen, S1-external secondary wall, S2-middle secondary wall, and S3-internal secondary Wall (derivated from refs [52, 69])

aspect ratio and provide the composite with good strength properties. Low aspect ratio discontinuous fibers are suitable for complex parts and large-scale production [21].

Natural fibers are inherently hydrophilic, poorly resistant to moisture, and incompatible with the hydrophobic PVC matrix [40]. The incompatibility of natural fibers results in a weak fiber/matrix interface leading to a decrease in the mechanical properties of the composites. Reinforcing natural hydrophilic fibers in the PVC matrix leads to a heterogeneous system with lower properties due to poor fiber-matrix adhesion. Because of the cellulose and lignin hydroxyl (OH) groups found in the structure of natural fibers, these fibers have a good potential for chemical treatment. -OH group's reaction can alter the surface energy and polarity of natural fibers [52]. Chemical treatment of fibers or surface modification improves fiber and matrix adhesion, which is critical in developing further composites.

Fiber modification may be alkali, silane, acetylation, benzoylation, acylation and acrylonitrile grafting, malleated coupling agents, permanganate, peroxide, isocyanate, stearic acid, sodium chlorite, triazine, fatty acid derivate (oleoyl chloride) and fungal, etc. [92]. Additionally, as an alternative coating technique, plasma surface treatment and plasma polymerization were used mainly for the surface modification of fibers [86]. Various coupling agents used are titanate, silane, betaine, malleated PP (MAPP)]; compatibilizer, for example, polypropylene-grafted-maleic anhydride (PP-g-MAH), maleic anhydride; and surface modifier usages such as stearate, stearic acid, [11]. As a result, adhesive strength determines the effectiveness of stress transfer between PVC and filler materials. These processes have improved homogeneity, and as a result, the distribution of the particles has improved to provide a better bond between the fillers and the matrix.

Alkali or mercerization treatment is one of the standard chemical treatment methods applied to natural fibers to strengthen the thermoplastic PVC matrix, which removes certain amounts of wax, oil, and lignite covering the outer surface of the cell wall [22]. Also, alkali treatment is cheaper than other chemical treatment methods. Upon alkali treatment, the crystallinity of Cellulose increases, and the impurities and swelling decrease in wood fiber, resulting in a smaller number of -OH groups [42].

If it is looked at binding agents and surface modification in natural fillers, we can see that they increase the cross-bonding rating. It has been reported that the tensile strength of PVC reinforced with cellulosic fibers (wood pulp) decreases with the use of untreated fibers, whereas the strength of the composite increases by 51% with the wood pulp reinforcement developed with silane. The PVC/ sawdust composite study with three different silane agents revealed enhanced mechanical properties compared to untreated composites [46]. This is because the silane is a dispersion agent. The titanate and aluminate coupling agents (ACAs) are improving interface compatibility and enhancing the mechanical properties of WPC. In this case, the effect of the aluminate is weak, and the effect of the titanate is apparent [54]. Adding up to 7% lignin as a bonding agent in PVC/rice straw composite enhanced its tensile strength and reduced the weight gain percent and the swelling. The main reasons behind these trends were the binding of hydrophobic lignin to the hydroxy surface of lignocellulose materials, improvement in the bonding between rice straw particles, and the reduction of gap content [46].

Strong interface adhesion between PVC and amino groups containing chlorine on the WF (Wood filler) surface is encountered, resulting in significant increases in the mechanical properties of composites [82]. The properties of PVC matrix natural fillers composites depend on removing non-cellulose components from the fiber surface and forming a clean and rough surface for better interface adhesion [38]. Coupling agents or compatibilizers are used to promote the bonding of functional groups to enhance interface adhesion binding between fiber/matrix [104]. The studies have also revealed that reduced fiber hydrophilic ability and polarity increase the angle of contact with water, but vice versa for fluids without polar [84]. Samajpati and Sengupta [80] investigated the wettability of five plant fibers on different polymer matrices. Finally, he found that fiber/matrix wettability is governed by the physical and chemical properties of the fiber surface and polymer surface tension. Consequently, the classic contact angle method plays an informative role in wettability and interface adhesion.

5 Interaction of PVC Matrix with Inorganic Fillers

5.1 *Minerals and Metal Oxide Fillers*

Good modulus, strength, rigidity, durability, hardness, and particularly low-price composites have been obtained by adding mineral nano-fillers to the PVC matrix [94]. Mineral fillers that are frequently used in PVC matrix are mineral clays such as montmorillonite (MMT), sodium montmorillonite (NaMMT), organophilic montmorillonite (oMMT), other mineral clays such as laponite, bentonite, hectorite, kaolinite, and halloysite, mica, vermiculite (a similar mineral), calcium carbonate, $CaCO_3$-silica, talc-layered double hydroxides (LDHs) [24].

It is available in two crystal forms: Calcium carbonate ($CaCO_3$), calcite (rhombohedral), and aragonite (orthorhombic) [35]. Calcium carbonates are mainly used along with polyvinyl chloride (PVC) for their hydrophobic character. Nanosized calcium carbonate and silica filler improve toughness, electrical properties, heat resistance, radiation resistance, and other properties in the matrix and reduce the cost of composites [87, 88]. Talcs are alumina silicates. They are usually reinforced into the PVC matrix with $CaCo_3$. Bentonite, a form of montmorillonite clay, is a mono aluminum layer consisting of an octagonal plate inserted between two layers of silicone and tetrahedral plates [103]. Many researchers have studied the reinforcement of bentonite and derivative clay minerals to develop thermal, mechanical, and flame retardant features in a PVC matrix [33, 43]. Also, montmorillonite and organophilic montmorillonite are reinforcing elements frequently used in PVC matrix. These clays are added in different morphologies from micro to nano levels as aggregated, intercalated, and exfoliated in the matrix [15]. In the aggregated structure, clay tactoids are well dispersed in the polymer matrix, but single clay layers are not delaminated. In the Intercalated structure, clay tactoids exhibit delamination to a certain degree. Therefore, polymer chains may diffuse into the galleries between them. In the exfoliated structure, clay tactoids are completely decomposed apart into single layers that are homogeneously distributed in the matrix [89]. In particular, exfoliation structures are preferred for storage modulus, increased tensile and flexural properties, heat distortion temperature, decrease in gas permeability, and unique properties [27]. Mica is aluminum silicate in terms of chemical composition. It can also contain Al, Si, K, Mg, and Li elements. They are also called as potassium, magnesium and lithium mica when compared to other elements. Mica is used as filler to improve Young's modulus, hardness and dielectric properties of some polymeric materials, including PVC. Silica (SiO_2) is preferred in a PVC composite material as it is fuel efficiency, dielectric properties, improvement of mechanical properties, and resistance to heat and moisture [35].

Metal oxides are another group of fillers that are reinforced with PVC polymers. These reinforcements are used to prevent thermal degradation of PVC in particular [31]. Zinc oxide is a white pigment with a UV barrier, providing good electrical conductivity and high heat resistance to the resins. The addition of metal oxide in PVC, such as ZnO particles, was preferred as ZnO particles strongly interact with PVC chains resulting in mechanical improvement [55]. Furthermore, the nanosized ZnO stands out in improving PVC's structural, optical, and thermal properties [59]. Titanium dioxide is a white pigment that enhances the UV barrier and provides aging, water, and heat resistance. Titanium dioxide is primarily used in thermoplastics and unsaturated polyesters [35]. The addition of TiO_2 into a polymer may significantly affect the polymer's electrical, optical, and photocatalytic properties. It is anticipated that it will be one of a wide range of technological applications in the future as a nanocomposite [59].

Magnesium oxide (MgO) increases polymer resins' strength, creep resistance, and thermal conductivity. Today, ceramics such as alumina and silicon oxide are widely used in many engineering applications such as automotive, electronics, and aerospace. Among these ceramics, alumina or aluminum oxide (Al_2O_3) at various purity levels is one of the most cost-effective materials in the engineering ceramics family due to several desirable properties, such as excellent hardness and abrasion resistance good dielectric properties. It also has good acid resistance and the resistance to alkali attack at high temperatures and high thermal conductivity, providing benefits in PVC micro and nanocomposites in particular. In the polymer, beryllium oxide was used as microspheres. It was determined that the electrical and thermal conductivities of the polymer have increased [35].

The interface interaction of PVC/mineral fillers and their effect on the performance of polymer nanocomposites are affected by four factors. These factors are the properties of the components, the composition, the structure, and the interface interactions. In Fig. 7, the formation of a surface layer of varying thickness, different from the matrix, is schematized due to the adsorption interaction of the polymer with the solid surface. In this case, the interaction of polymeric molecules with a solid surface should lead to a redistribution of intermolecular bonds at the surface or transition layer and the formation of new physical junctions in the physical network.

The effect of the interphase depends on the amount and properties of the interphase. This is why nano-fillers stand out. This is since their interactions in the matrix are only atomic in places. However, nanoparticles often have issues with homogenous dispersion, which means that the large surface area expected of them is not always achieved. The conditions of interface interaction between the matrix and fillers determine the free surface energy of the filler agent and the ratio between the filler and the matrix. These materials are divided into two groups high surface energy (metals, oxides, and other inorganic materials) or low surface energies (polymers, organic compounds) [44].

PVC polymers have acidic qualities and may interact with fillers with basic properties (SiO_2, CaCO, mineral, etc.). If there is no special interaction at the phase boundary, the thermodynamic adhesion work is determined by the phase's thermodynamic cohesion work, which has lower cohesion energy. In this case, the adhesion can be improved by boosting the polymer cohesion strength. The surface is the simplest way to alter interface interactions. For this purpose, the surface should have

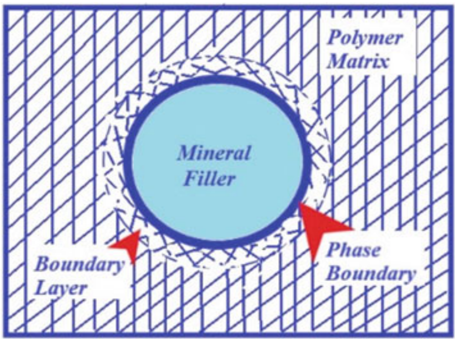

Fig. 7 The scheme of types of filled systems (redrawn with permission from ref [44], Copyright 1995, Elsevier)

interaction of fillers with each other and matrix-filler agent interaction. Agglomeration refers to the interaction of the filler agents with one another, and when the size shrinks, agglomeration becomes simpler [60]. PVC mineral matrix is supplied by interface development modifiers (coupling agents, surfactant, etc.) in composites, and these modifiers can be selected based on the composition of the components. Coating the surface of filler agents with a low molecular weight organic compound is the oldest and most used modification. Amphoteric surfactants are generally used with one or more polar groups and a long aliphatic chain. The surface treatment of $CaCO_3$ with stearic acid is a typical example [74].

The principle of the process is the preferential adsorption of the polar group of the surfactant on the surface of the fillers. High-energy surfaces of inorganic fillers are usually able to interact mainly with the polar group of the surfactant. Reactive surface treatment assumes that the coupling agent undergoes a chemical reaction with both components. However, coupling agents are considerably more complex than non-reactive agents; the coupling agent polymerization makes the development of chemically bonded and physisorbed layers difficult to define surface chemistry, characterize the interlayer and optimize the operation. Mica, silicate, $CaCO_3$, and $Mg(OH)_2$ fillers are examples of fillers and reinforcements that contain reactive OH groups on their surface and have been effectively employed with silane coupling agents [39, 60]. Natural bentonite is considered a hydrophilic agent. Therefore, it is incompatible with organic compounds like polymers and plastics. It may be converted into organo clay and hydrophobic by employing quaternary ammonium, a nitrogen-containing surfactant [28]. Figure 8 shows the modified clay and its incorporation into the polymer.

The surface of metal oxide NPs can be modified using physicochemical interactions between the NPs and the modifiers. The matrix can occur through a combination of different mechanisms in the material, such as the distribution of metal or metal oxides, complexation/chelation, electrostatic interactions, and precipitation or reduction reactions. The parameters that control the nature of the nanostructured metal oxide/polymer composite are (i) the nature of the functional polymer, (ii) the type of nanoparticle precursor, (iii) the reaction that forms nanoparticles, and (iv) the composition of the metal and metal oxide nanoparticles [81].

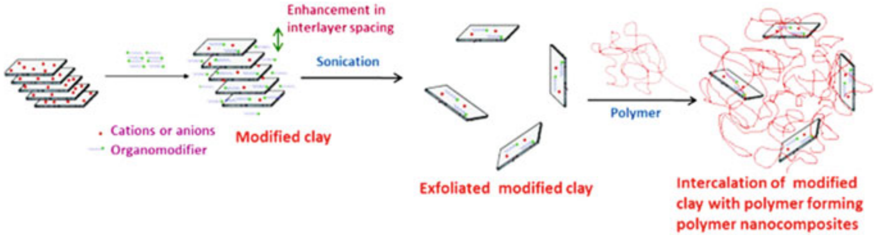

Fig. 8 Schematic diagram showing clay modification and intercalation of polymer to form polymer nanocomposites (Reprinted with permission from ref [48], Copyright 2015, Elsevier)

The modifiers have weak van der Waals forces or hydrogen bonds on the NP surface in the physical modification approach. Recently, surface modification of NPs such as TiO_2, Fe_2O_3, Al_2O_3, and Al_2O_3-CuO has been done using surfactants. Chemical surface modification is an effective method to improve nanomaterial surface properties. This technique is based on the covalent bond between the modifier and the NP surface. Various coupling agents, Thiols, amines, organophosphorus molecules, carboxylic acids, polymers, and silanes have improved NP dispersion in various media [3]. The behavior of treated and untreated nanoparticles in the composite varies under operating conditions. When the nanocomposite is subjected to mechanical stresses, a stress concentration appears around it. Cavitation (voids) occurs at the polymer/nanoparticle interface in unmodified/uncoated particles. Surface coating of nanoparticles with terminal alkyl groups causes cavitation to occur at higher stresses due to the high interfacial adhesion achieved by increasing the adhesion work and the interfacial surface area [34].

Consequently, the interaction of polymeric molecules with a solid surface (including the polymeric one) should result in a redistribution of intermolecular bonds on the surface or in the transition layer and the formation of additional physical joints on the physical network [44].

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