

Nano-structured Polymer-Based Composites



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Abstract Nano-structured polymer-based composites have gained much importance in recent years due to their improved and excellent properties compared to their bulk-sized equivalents. In nanostructured polymer composites, nano-sized particles are added to the matrix material as nanoparticles have a too high surface to volume ratio, resulting in improved composites' overall properties. In this chapter, various nano-structured polymer-based composites are discussed based on their suitable applications. The properties of nano-structured polymer-based composites such as thermal, mechanical, flame retardancy, electrical and optical properties, barrier properties, anticorrosive properties, and adsorption behaviour and factors affecting the properties are discussed. This chapter also presents the different manufacturing techniques of nano-structured polymer-based composites.

1 Introduction

Since ancient times advancement in material science is the root cause of technological development. The term nanocomposite is used in the early 1980s. These materials possess excellent mechanical, physical, biological, electrical, and chemical properties which make them superior to conventional materials. High surface area to mass ratio, large surface area, and high aspect ratio are some other attractive characteristics of nanomaterials [1]. The ratio of surface to volume increases with decreasing particle size, significantly affecting the material's properties.

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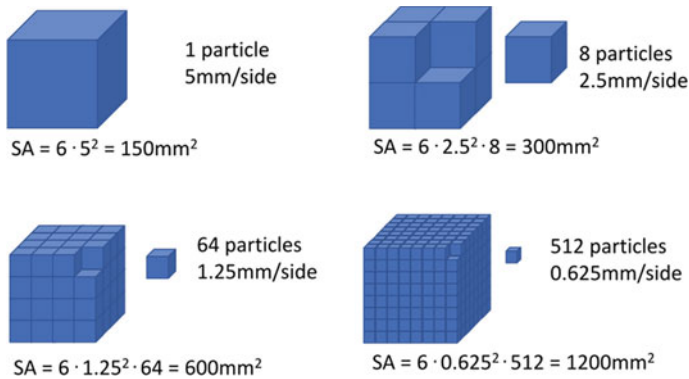


Fig. 1 Relationship between particle size and surface area [3]

The influence of the surface area had been demonstrated in the form of a particle [2]. The breaking of large particles into smaller particles results in an increased surface area. The rate of the reaction also increases as more surface area is available for the reaction. As shown in Fig. 1, the particle has an edge length of 5 mm. Therefore, the total surface area of the particle is 150 mm^2 . Reducing the particle's edge length to 2.5, 1.25, and 0.625 mm, the total surface area becomes 300, 600, and 1200 mm^2 .

When the composites' components have at least one dimension in the nanometre scale, they are termed nanocomposites. Most commonly it is the reinforcement phase which includes nano clay, nanotubes, or nanoparticles [4]. Nanostructured polymer composites can be obtained by using an appropriate polymer matrix and incorporating nanomaterials into it [5]. Few examples of nano-sized objects are DNA molecules having a diameter of 25 nm and proteins having a typical length of 10 nm.

Out of various nanocomposites, polymer nanocomposites are considered as a leading area of current research and advancement. It exhibits many beneficial properties (a) dimensional variability, (b) film-forming ability, and (c) activated functionalities [6]. Polymer nanocomposites have shown remarkable progress in electronics and communications, energy and data storage, aerospace, biomedical, agricultural sectors, food and water purification, environmental, sporting materials, automobiles, and packaging and defence applications [7]. The properties of polymers can be modulated precisely through the incorporation of nanofillers. Products made of nanocomposite in electronic and medical components, storage devices, stain-free fabrics, and nano paints are already commercialised. Nanocomposites are termed as 'materials of the future' as it has overcome present constraints of micro composites and monolithic.

Nanocomposites are used the first time in the early 1990s by Toyota Central R&D Laboratory to fabricate the car's belt cover using nylon-montmorillonite (MMT) clay nanocomposites [8, 9]. Nanoparticles, carbon nanotubes (CNTs), carbon nanofillers, graphene, nanocellulose, nanowires, nano-silica, and nano clay are extensively used engineered nanomaterials in medical, industrial, and consumer products. These are all tested for their reinforcing ability and showed tremendous improvement in the properties of nanocomposites [10–12]. Improved mechanical properties, high thermal

stability, and lower gas permeability are the few characteristics of polymer-matrix nanocomposites [13]. The market of polymer nanocomposites is anticipated to reach above USD 5100 million by 2020 [14].

2 Classification of Nanocomposites

Nanocomposites are categorized based on the type of materials (i.e., reinforcing and matrix material) employed for fabrication, as shown in Fig. 2 [15]. The different types of nanocomposites are (a) polymer-matrix nanocomposites, (b) ceramic-matrix nanocomposites, and (c) metal-matrix nanocomposites.

Both academicians and industrialists carry out extensive research activities in the field of polymer nanocomposites due to their outstanding properties such as (a) high modulus and stiffness, (b) high toughness, and (c) high strength with the incorporation of nano additives. Wear resistance, flame retardancy, barrier resistance, electrical, optical, and magnetic properties are also found excellent for polymer nanocomposites [16]. The properties of polymer nanocomposites are far better than conventional micro composites and metals. Thus, in this chapter, the discussion is focussed on nanocomposites that consist of the polymer as matrix material.

2.1 Polymer-Matrix Nanocomposites

In this type of nanocomposites, the polymer is used as matrix material, and different nano additives (nanomaterials) are used as reinforcements. The nanomaterials can be classified based on the number of dimensions in the nano range (=100 nm) where 1 nm

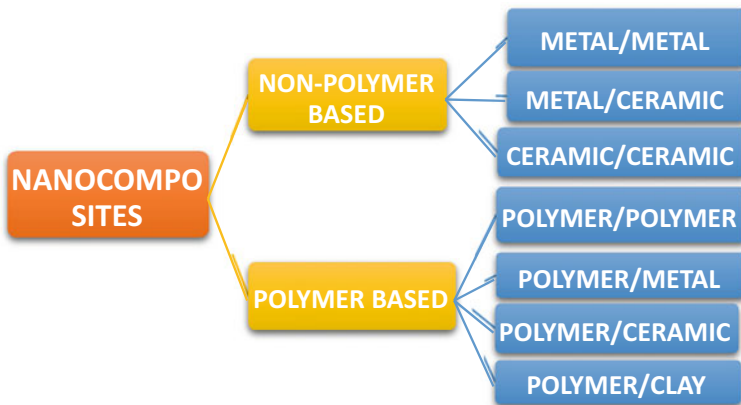
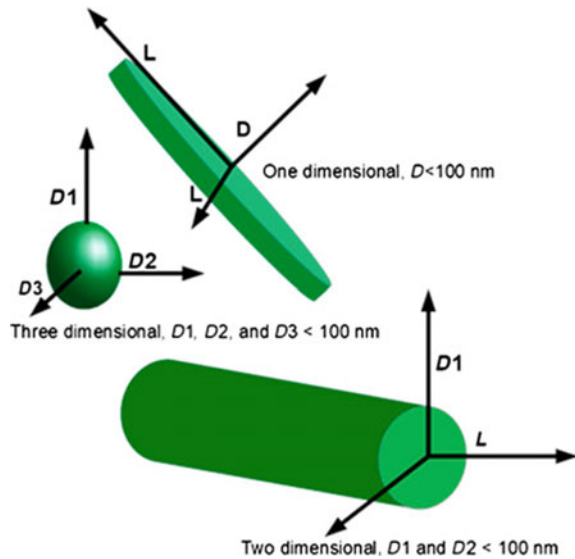


Fig. 2 Classification of nanocomposites [17]

Fig. 3 Classifications of nanofillers [20]



$= 10^{-9}$ m [18]. The nanofillers' applications in polymer composite are differentiated based on their dimensions, as shown in Fig. 3 [19].

2.1.1 One-Dimensional (1D) Nanomaterials

Nanofiller with at least one of its dimensions < 100 nm is considered one-dimensional (1D). It is in the form of a sheet. It has various applications in microelectronics, biosensors, sensors, biomedical, and coatings. It possesses extraordinary electrical, magnetic, and optic properties—examples: nano clay, nanoplatelets, nanosheets, and montmorillonite (MMT) clay.

a. Polymer–clay nanocomposites

C.A. Bower in 1949 first mentioned polymer–clay nanocomposites during conducting DNA engross from the montmorillonite clay [21]. The advancements in polymer–clay nanocomposites result in their usage in numerous applications. Polymer–clay nanocomposites are termed as multiphase systems. It consists of a contentious phase of polymer and dispersed phase of silicate (filler) with at least one dimension in the nanometre scale—the chemical bonding between filler and polymer results in the composites' superior properties. To achieve high strength, smectite clay (saponite, montmorillonite, and hectorite) are used as filler materials out of which the most common is montmorillonite (MMT) [22]. When dimensions of the filler are in nanoscale, their properties also change significantly [23]. Tests are conducted on various nanofillers like graphene, CNTs, nano-silica, and nanocellulose to find their strengthening ability (reinforcing). Currently, clays are the most demanded layered silicates used for the fabrication of polymer nanocomposites.

b. Structures of polymer–clay nanocomposites

The polymer–clay nanocomposite properties’ improvement depends on the extent of the clay particles’ dispersion in the polymer matrix. The dispersion of clay nanoparticles in polymer mainly depends on two parameters. These are:

1. Physical and chemical compatibility between polymer and clay nanoparticles, and
2. The method used for the production of polymer–clay nanocomposite.

The microstructure of polymer–clay nanocomposites is dependent on the inter-phase bonding between polymer and clay nanoparticles. The possible types are described below, and the same is presented in Fig. 4 [24].

1. **Phase-separated structure:** This structure is produced when the interface bonding between polymer and clay nanoparticles is very delicate. It is difficult to obtain the polymer intercalation in the clay layers during mixing between the organic polymer and inorganic clay (unmodified clay). As a result, clay is scattered as lump or particles stacked in aggregation with the polymer. The structure of composites is achieved because of phase separation. The properties

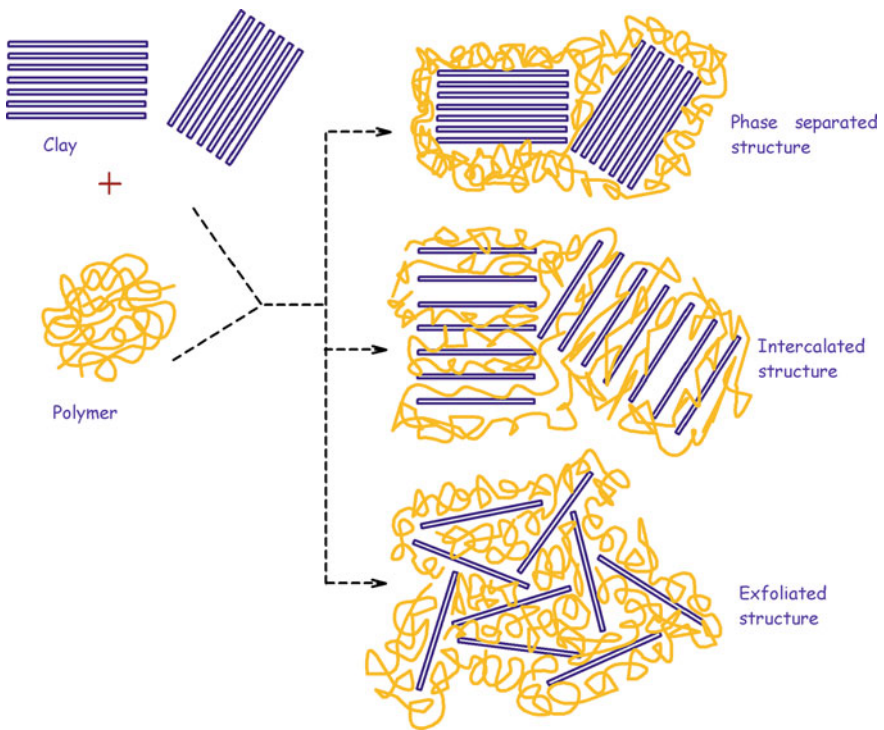


Fig. 4 Structures of polymer–clay nanocomposites [24]

of phase-separated composites are similar to conventional micro composites. Hence, it is anticipated that polymer–clay nanocomposites of such category show a downturn in their properties [25].

2. **Intercalated structure:** When the polymer–clay nanocomposite polymer chains are intercalated to a limited extent between the clay layers, it produces intercalated structure. The distance between the interlayer and clay layers increases due to the polymer intercalation, and it is termed as intercalated polymer–clay nanocomposites.
3. **Exfoliated structure:** The delaminated or exfoliated structure is obtained when individual clay layers randomly separated as sheets are dispersed in the continuous polymer at a suitable gap that relies on the clay charge. If the interlayer spacing increases more than 8–10 nm due to polymer chains, the structure obtained is considered as exfoliated structure. Improvement in the mechanical, barrier and thermal properties of the resultant nanocomposites depend on the uniform dispersion of exfoliated clay in the polymer. It is challenging to achieve complete exfoliation. In exfoliated nanocomposites, better dispersion of individual clay layers can result in lower clay content and higher aspect ratio. Large surface interaction between polymer and clay is the main reason behind the most notable advancement in polymer properties [26].

2.1.2 Two-Dimensional (2D) Nanomaterials

In 2D nanomaterials at least two dimensions of nanofillers should be <100 nm. Filaments, fibres, or tubes are generally used as 2D nanomaterials. In energy, sensors, catalysis, electronics, and optoelectronics, 2D nanofillers are extensively used. Examples: CNTs, nanofibers, nanowires, nanorods, whiskers, and 2D graphene [27].

a. Polymer-carbon nanotube (CNT) composites

In 1985, buckminsterfullerene (C_{60}) which is the latest form of carbon, was discovered [28]. CNTs comprising long and thin cylinders of carbon were first discovered in 1991 by employing an arc-discharge method [29]. CNTs differ from other carbon materials like fullerene, diamond, and graphite. It has carbon with an aspect ratio of >1000 [30]. CNTs are divided into two types based on the fabrication process [31]. The essential properties of different CNTs are shown in Table 1.

Table 1 Physical properties of different CNTs [32]

Properties	SWCNTs	MWCNTs
Density (gcm^{-3})	0.8	1.8
Electrical conductivity (S/cm)	$10^2\text{--}10^6$	$10^3\text{--}10^5$
Thermal conductivity (W/mK)	6000	2000
Thermal stability in the air ($^{\circ}\text{C}$)	>600	>600

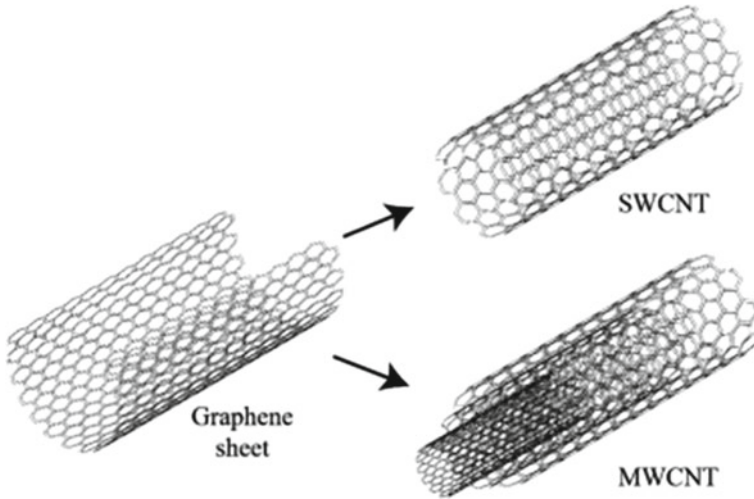


Fig. 5 Schematic presentation of SWCNT and MWCNT produced from graphene sheets [33]

- **Single-walled CNTs:** SWCNTs comprise a graphene layer rolled into a seamless (smooth and continuous) cylinder (Fig. 5). The diameter of an SWCNT is approximately 0.5–5 nm [34].
- **Multi-walled CNTs (MWCNTs):** MWCNTs are a special form of fullerene comprising two or more than two concentric cylindrical graphene sheets (Fig. 5) separated by Van der Waals forces. Inner and outer diameter reported for an MWCNT is 1.5–15 nm and 2.5–50 nm. The most usual interlayer distance is in the range of 0.32–0.35 nm and can vary slightly due to defects and other several factors [35, 36].

It is made up of large macromolecules having a unique shape, size, and exceptional mechanical properties. Nanotubes are differentiated based on their diameter, length, chirality, or twist. By employing different processing techniques, CNTs can be fabricated into various aspect ratios, and their lengths can also be varied. Superb mechanical properties, lightweight characteristics, and high specific surface area of CNTs have attracted researchers to use them as reinforcements in polymer composite [37–40]. Its diameter is <100 nm and can be thinner than 5 nm. CNTs are used for several purposes such as (a) fabrication of energy and hydrogen storage systems, (b) manufacturing of automotive and aerospace components, (c) creation of nano filters and sensors, (d) identification of cancer cell and tissue engineering, (e) drug and gene delivery, (f) production of electronics devices and microchip, artificial implants, hard and flexible materials, and (g) solution of environmental problems [41]. The global CNTs market is forecasted to reach USD 6.8 billion by 2023 from USD 1.6 billion, the market valuation in 2016 [42].

An investigation is performed to determine the effect of CNT pre-localisation on the properties of ultra-high-molecular-weight polyethylene (UHMWPE) nanocomposites [43]. It is concluded that a high concentration of CNT results in enhanced strain-hardening and yield stress of CNT-UHMWPE nanocomposites. Another study showed that the mechanical properties like tensile strength and impact toughness of graphene-polyvinyl chloride (PVC) composites could be improved remarkably by steady dispersions at very low loading graphene (i.e., 0.3 wt%) [44]. A study was conducted on multi-layered graphene-reinforced polymer composites to analyse the nano-indentation properties through molecular dynamics (MD) simulation. The results revealed that the indentation resistance is considerably using single and multi-layered graphene sheets [45]. Arash et al. [46] employed the MD simulation method to record the nanocomposites' total potential energy for calculating CNT-polymer nanocomposites' properties. The results showed that Young's modulus of (polymethyl methacrylate) (PMMA) strengthened by infinite long CNTs is remarkably increased compared with pure PMMA. The mechanical properties of graphene-polymer composites are evaluated by applying MD simulation [47]. The results showed that shear modulus, hardness, and Young's modulus increased approximately 27.6, 35, and 150% by reinforcing graphene nanosheets into the polymer.

b. Structure of carbon nanotubes (CNTs)

The electronic configuration of carbon atom is $1s^2 2s^2 2p^2$ which shows that in 1 s orbit it has 2 strong bound electrons. In 2 s and 2p orbitals, 4 relatively weak bound electrons are called valence electrons. Carbon atom enters different hybridization stages like sp, sp^2 , and sp^3 in different materials due to a slight difference in energy between 2 s and 2p levels. The hybridization flexibility allows the atomic orbitals to organize themselves in the structures of various dimensions such as nanoparticles (3D), CNTs (2D), and nano clays (1D) [48, 49].

Defects such as pentagons and heptagons sometimes formed on the external layer to form curved and spiral-type nanotubes. The longest grown CNTs currently are above 0.5 m [50] and cycloparaphenylene is considered the shortest CNT [51]. The thinnest CNT with a diameter of 0.3 nm is armchair CNTs [52]. CNTs are observed to hold the maximum density of 1.6 g cm^{-3} (generally, $1\text{--}1.4 \text{ g cm}^{-3}$) [53]. MWCNT's tensile strength is 63 GPa (9,100,000 psi) [37], for stainless steel it is 0.38–1.55 GPa. Pressure up to the level of 25 GPa can easily withstand by standard SWCNTs without permanent deformation. The geometry and most of the properties of CNTs depend on the diameter and chiral angle (θ), also known as helicity [54]. There are three conditions to differentiate SWCNT based on the chiral index. According to the conditions given below, SWCNT is also named armchair, zigzag (achiral nanotubes), and chiral (Fig. 6).

1. If chiral indices are equal (i.e., $n = m$), then the chiral angle is 30° .
2. If anyone of the chiral index is 0, i.e., $(n, 0)$ or $(0, m)$, then the chiral angle is 0° .
3. In the last case, $n \neq m$, if the chiral angle is $0^\circ < \theta < 30^\circ$ [55].

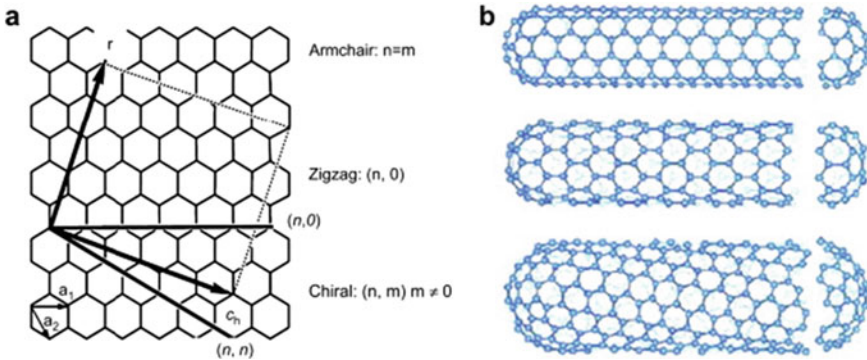


Fig. 6 **a** Representations of rolling of a graphene sheet and **b** different types of CNTs [48]

2.1.3 3D Nanomaterials

In 3D nanomaterials, all three dimensions are in nano range and mostly in cubical and spherical shapes. It is also referred to as iso-dimensional nanoparticles or zero-dimensional nanoparticles. To fabricate nanocomposites, it is essential to find the inherent properties of 3D nanofillers. Applications in which 3D nanomaterials are applied when combined with suitable matrix (polymer) are coatings, filtration, and biomedicine. Examples: nanoparticles (nanocellulose), nanogranules, and nanocrystals.

a. Polymer-nanocellulose composites

Nanocellulose can be explained as particles with diameters below micrometre ($0.1 \mu\text{m}$ or 100 nm). In other words, nanocellulose is considered as particles whose size defines its optical, electrical, or magnetic properties [56]. Nanocellulose is extracted from a plant cell wall which is known as a natural nanomaterial. Nanocellulose has some striking features such as (a) high strength, (b) high surface area, and (c) excellent stiffness. Cellulose fibre combined with hydroxyl groups and strong hydrogen bonding networks renders into outstanding mechanical and physical properties [57]. Nanocellulose, which is a natural fibre, can be extracted from cellulose. Nanocellulose fibre gained special attention due to its size as its diameter is less than 100 nm and length is several micrometres. Nanocellulose holds outstanding strength property, low density (around 1.6 gcm^{-3}), and is considered as biodegradable nanofiber. It has high stiffness (220 GPa) which is better than the Kevlar fibre. It also has a high tensile strength (10 GPa) which is better than cast iron and strength to weight ratio is about eight times higher than stainless steel. Nanocellulose can be functionalized into various surface properties as it is transparent and consists of a reactive surface of hydroxyl groups [58].

b. Structure of polymer-nanocellulose composites

Cellulose is an extensive, renewed, natural organic polymer. The primary origin of cellulose is cotton that contains 95% pure cellulose. The primary material properties can enhance by accurate dispersion of cellulose in nanocomposites [59]. Cellulose nanocrystals or nanowhiskers are extracted from cellulose fibres through acid hydrolysis. Nanocellulose can be divided into two types:

- i. nanostructured materials (cellulose microfibrils and cellulose microcrystals), and
- ii. nanofibers (cellulose nanocrystals, cellulose nanofibrils, and bacterial cellulose) [60, 61].

Several nanocellulose forms can be produced using different methods from various cellulosic sources, as shown in Fig. 7 [62]. Characteristics like morphology, size, etc. of nanocellulose depend on the (a) isolation and processing conditions, (b) cellulose origin, and (c) possible pre-treatment or post-treatment. Nanocomposites fabricated using nanocellulose comprises of exceptional properties like (a) lightweight, (b) high mechanical strength, (c) transparent, and (d) high thermal properties [63].

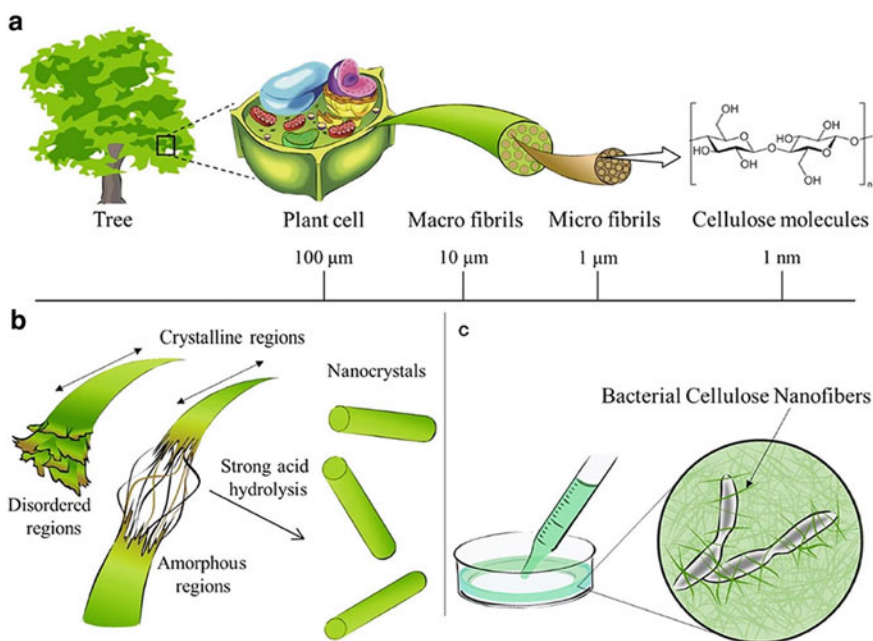


Fig. 7 **a** Extraction of cellulose from trees, **b** reaction between cellulose and strong acid to obtain nanocellulose, and **c** representation of bio nanocellulose cultured from cellulose-synthesizing bacteria [64]

3 Properties of Composites Reinforced with Nanofillers

Nanofillers are incorporated in a matrix (polymers) to improve the structured nanocomposites' characteristics for suitable applications. Nanofillers also hindered the drawbacks of polymers used for the manufacturing of nanocomposites. The improvement in the property is challenging as it may affect the other characteristics. The study revealed that the polymer's nature and properties, fabrication conditions, and methodology affect the final characteristics of nanocomposites [65]. The different properties of polymer nanocomposites are discussed in the following sections.

3.1 Mechanical Properties

Nanofillers as reinforcing agent play a significant role in improving the mechanical properties of polymer nanocomposites [66]. While reinforcing soft matrix with rigid nanofiller, the considerable amount of applied load is borne by nanofillers subject to adequate interactions between filler and matrix [67, 68]. Increased value of modulus can be attained by increasing the ratio of filler in the nanocomposites. Nanocomposites possess better mechanical properties than the neat polymer. CNTs demonstrated exceptional mechanical properties with Young's modulus of 1.2 TPa and tensile strength of 50–200 GPa. CNTs are considered as the most suitable candidate as reinforcement because of their superior properties including (a) low density, (b) high surface area, and (c) high aspect ratio [32]. A study showed an increase in clay content results in higher storage modulus of polyvinylidene fluoride/clay nanocomposites at 100–150 °C [69]. Research conducted on nylon-6-clay nanocomposites showed significant improvement in the properties as its modulus doubled and strength increased by 50% at clay loading of 4.2 wt.% [70, 71].

3.2 Thermal Properties

Many researchers reported that polymer structured nanocomposites have superior thermal stability than pure polymers due to nanofillers' incorporation into the polymer matrices [72, 73]. Polystyrene-clay nanocomposites have higher degradation temperature, i.e., around 30–40 °C in comparison to pure polystyrene under nitrogen and air heating degradation conditions [74]. Outstanding thermal conductivity of CNTs attracted many researchers to fabricate nanocomposites with improved thermal conductivity by reinforcing CNTs into various polymer matrices [75, 76]. Thermal conductivity in the case of CNTs-polymer nanocomposites relies on several factors (a) CNTs content, (b) aspect ratio, (c) dispersion, (d) CNT-polymer interfacial interactions, and (e) existence of metal impurities. According to the report,

thermal conductivity at room temperature increases by 300% and magnetic alignment increases by approximately 10% with a SWCNTs loading of 3 wt.% in epoxy [77]. Similarly, in an infiltration method, the thermal conductivity is increased to 220% by combining epoxy and SWCNTs (2.3 wt.% l) [78]. CNTs can improve the thermal stability of the polymer due to its better heat dissipation characteristic. The thermal property of nylon-6-clay thermoplastic nanocomposites is enhanced with an increase in the heat distortion temperature (HDT) by 80 °C when compared one-on-one with pristine polymer [70–74].

3.3 Flame Retardancy

Polymers are extensively used in domestic applications, and thus, their flammability needs to be reduced. Presently common chemical additives are used as flame retardants to reduce the ignition and control burning. Conventionally, phosphorous and several halogen-based compounds are used as a flame retardant without affecting the other properties and quality of polymer [79, 80]. Polymer nanocomposite is investigated for high-temperature applications using epoxy, nylon-11, etc. Nano clay plays a significant role in decreasing the flammability as flammability is considered an important aspect for many applications [81]. Nanocomposites produced from the nylon, polystyrene, epoxy, or vinyl ester possess low flammability compared with pure polymer.

3.4 Electrical and Optical Properties

Many research groups study the influence of adding nanotubes in polymers to improve electrical properties. In some studies, nanotubes are employed to improve relatively low-cost polymers' conductivity as an alternative to presently used filler like carbon black. Other studies investigated the incorporation of nanotubes in conducting polyaniline polymer. However, further work needs to be performed, aiming specific applications such as photovoltaic devices or supercapacitors. In many cases, improvement in mechanical properties is an additional advantage of the incorporation of nanotubes.

3.5 Barrier Properties

The addition of clays in polymer improves the barrier properties of the polymer as clay sheets are impermeable. Barrier properties are enhanced due to the maze or tortuous path that slowdown the gas molecule diffusion through polymer [82, 83]. The degree of advancement in barrier properties directly relies on the degree of tortuosity

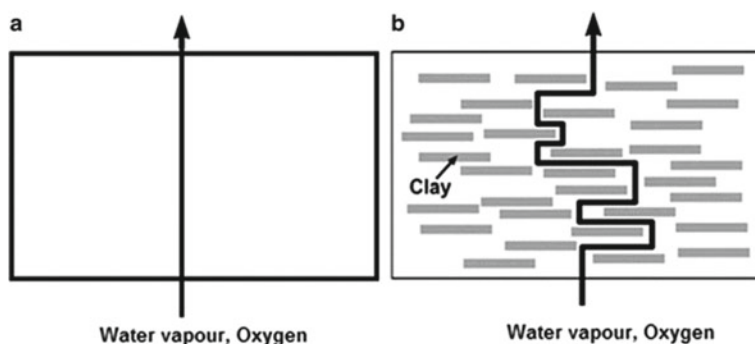


Fig. 8 Illustration of the tortuous pathway [86, 87]

produced by clay layers in the diffusion way of molecules through polymer film. The ratio of actual distance covered by diffusive molecule to the shortest distance to diffuse is a tortuous factor. It is mostly influenced by the aspect ratio of clay dispersed in the matrix. Barrier properties in the polymer can be further improved by increasing exfoliation or dispersion and the clay sheet's lateral length. Many researchers have reported that barrier properties are against diffusion of gases and vapours in polymer-clay nanocomposites [84, 85]. Figure 8 shows the tortuous path formed in polymer film due to the incorporation of exfoliated clay nanoplatelets.

- Pathway taken by migrating gas molecules is perpendicular to the film orientation when average diffusion occurs.
- Diffusing molecules must navigate impenetrable particles or platelets and through interfacial zones with distinct permeability features than those of virgin polymer. The mean gas diffusion length increased due to the tortuous pathway.

3.6 Anticorrosive Properties

Anticorrosiveness of the polymer can be improved by incorporating platelet fillers like layered silicate as it increases the length of the diffusion pathways. Clay reduces the permeability of polymer coating films by increasing the diffusion pathways shown in Fig. 8. The structured polymer nanocomposites of different polymers such as polystyrene, polyimide, polyaniline, and epoxy with unmodified and organically modified clays are investigated as anticorrosive coatings on metals [88].

3.7 Adsorption Behaviour

Incorporation of nanoparticles in polymer matrix turns polymer nanocomposites into highly tuneable adsorptive material. The adsorptive behaviour of nanocomposites

can be utilized for many applications such as (a) water purification, (b) fuel cell technology, (c) drug delivery, and (d) chemical sensor. Toxic materials like metal ions, dyes, and microorganisms from water or wastewater can be removed using polymer nanocomposites due to their adsorptive behaviour.

Apart from the properties discussed above, polymer structured nanocomposites possess few more properties. The properties of nanocomposites depend not only on the properties of individual components but also on the structured polymer nanocomposites' properties. These are (a) process used to fabricate nanocomposite, (b) types of filler material, (c) orientations of filler material, (d) degree of combining two phases, (e) interfacial adhesion, (f) volume fraction, (g) nature of the interphase, (h) shape and size of nanofiller materials, and (i) system morphology [89].

Nanomaterials play a critical role in enhancing nanocomposites' properties by dispersing and distributing nanofillers in the matrix. Sometimes, if it is not appropriately dispersed, agglomeration of particles takes place, and thus, nanocomposites' characteristics deteriorate, affecting the nanocomposite's performance improvement. Figure 9 shows different types of distribution and dispersion of nanoparticles in the matrix.

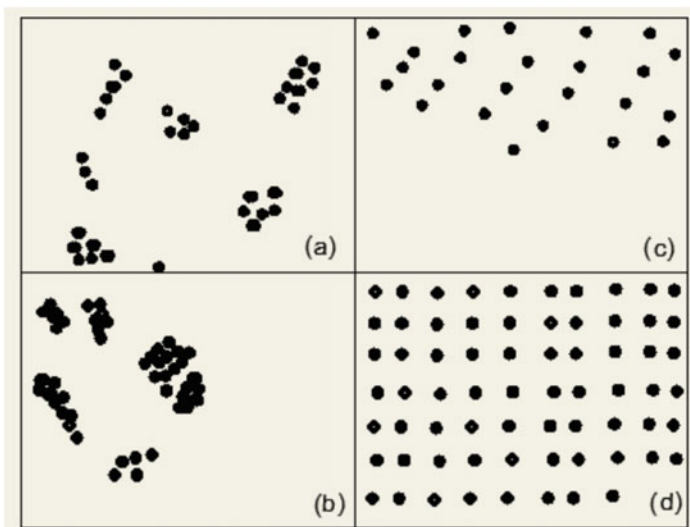


Fig. 9 Representations of distribution and dispersion of nanoparticles in matrix **a** good distribution but low dispersion, **b** poor distribution and poor dispersion, **c** poor distribution but good dispersion, and **d** good distribution and good dispersion [90]

4 Manufacturing Techniques of Nano-Composites

Manufacturing of polymer nanocomposites can be done either by mechanical or chemical processes. The difficulties associated with polymer nanocomposite manufacturing are uniform and homogeneous dispersion of nanoparticles in the polymer. Intricate polymerization reactions, chemical reactions, and surface modification of filler are approaches to solve this problem [91]. The processes used for the manufacturing of nanocomposites depend on the matrix material types, i.e., organic or inorganic [92]. The different methods involved in the fabrication of polymer nanocomposites are:

1. In-situ polymerization
2. Intercalation method.
 - a. Chemical technique
 - b. Mechanical technique.
3. Sol-gel method (other emerging synthesis methods)
4. Direct mixing of nanofillers and polymer [93].
 - a. Melt compounding/blending
 - b. Solvent method.
5. Latex technology
6. Ex-situ Synthesis
7. Other methods.
1. **In-situ polymerization:** It is considered the first evolved method moderately used to dispersion nanoparticles in the monomer. The process is schematically shown in Fig. 10. It is an efficient method that improves the compatibility between the nanofillers and polymer [94]. In this technique, the formation of the polymer occurs between the intercalated sheets [95]. This technique provides

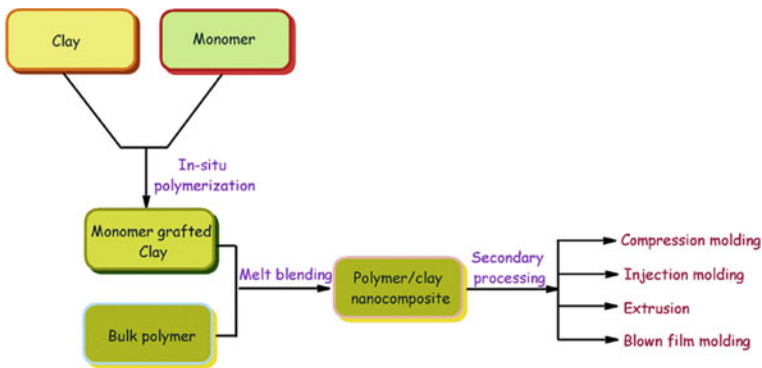


Fig. 10 Schematic representations of the stages of the in-situ polymerization method [16–24]

uniform dispersion of nanoparticles in the matrix. Swelling of nanoparticles takes place in monomer solution when low-molecular-weight monomer solution is discharged between nano clay layers [96]. Monomers are polymerized after mixing with nanoparticles through addition or condensation reactions with the help of an initiator and/or the catalyst at an elevated temperature either in presence or absence of solvent. The benefit of using this method is the formation of covalent bonding between polymer and functionalized CNTs, resulting in improved composites' properties. The reports showed the application of in-situ polymerization method for manufacturing of epoxy-based nanocomposites [97–99]. High-temperature synthesis causes decomposition of polymer, and slow rate of reaction is the disadvantage of the process [100].

2. **Intercalation method:** In this method, the nanoplatelets type of nanomaterials disperses into the polymer. Properties like flammability, shrinkage, and stiffness improved due to the addition of clays (nanomaterial) into the polymer. Swollen of clay takes place in solvent and intercalation of polymer chains occurs between the layers. Precipitation or vaporization method is used to obtain intercalated nanocomposite by removing the solvent [101]. Two different techniques can be used to disperse nanoplatelets homogeneously [102].
 - a. **Chemical technique:** It uses the in-situ polymerization method in which polymerization reaction occurs after the dispersion of nanoparticles in the monomer. In this method, nanocomposites are produced through chemical reactions in a liquid environment. It holds an additional polymerization process after nanoplatelets are distributed into the polymer. Nanoplatelets are swollen in the monomer solution, and the emergence of the polymer takes place between the intercalated sheets due to polymerization method. It results either in compact nanocomposite material or nanocomposite particles [103, 104].
 - b. **Mechanical technique:** It involves polymer and nanoplatelets direct intercalation using solution mixing. Co-solvent is used to dissolve polymer and solvent to swollen up the nanoplatelet sheets. Mixing of these two solutions allows the polymers chain to intercalate into the nanoplatelets layers and displace the solvent [16].
3. **Sol–gel method:** It is also termed as template synthesis [105]. The bottom-up approach is employed in the sol–gel method, and its principle is different from the preceding methods. The dispersion of solid nanoparticle in monomer solution results in a colloidal suspension of solid nanoparticles termed sol. In the gel, 3D interconnecting network formed between phases by polymerization reactions followed by hydrolysis procedure. In this method, the polymer is considered a nucleating agent assisting in developing layered crystals. As it grows, the polymer is oozed between layers and nanocomposite is formed [96]. Various other methods are applied for preparing polymer nanocomposites includes electrospinning, self-assembly, and phase separation. The method used

to manufacture nanofibers with the help of electrostatic force is known as electrospinning. The nanofibers in the range of 40–200 nm in diameter are manufactured using this unique synthetic method [106, 107]. Producing nanofibers with the electrospinning help is based on the polymer's viscoelastic behaviour and the electrostatic forces [108, 109]. Electrospun nanofibers possess special properties such as (a) cost-effectiveness, (b) permeability, (c) superior directional strength, (d) low basis weight, (e) high porosity, (f) flexibility, (g) layer thinness, and (h) high surface area per unit mass [110]. The molecule-mediated technique used for fabricating several nanocomposite films with desirable thicknesses is self-assembly [111]. Nanoparticles are connected by weak van der Waals hydrogen bond and electric/magnetic dipole interactions, rather than strong chemical bonds [112]. Production of nanofibrous matrices from polymer solutions requires thermally induced gelation, solvent exchange, and freeze-drying called phase separation [113].

4. **Direct mixing of nanofillers and polymer:** In nanocomposite fabrication, direct mixing of nanofillers and polymer transpire as a top-down approach. It is based on the breaking of cluster nanofillers during mixing. This method is most suitable for fabricating polymer nanocomposites as it necessitates two common ways of blending the polymer and nanofillers.
 - a. **Melt compounding/blending:** In this method, polymer and nanofillers combine in the absence of solvents above the polymer's glass transition temperature. In melt compounding/blending shear stress or hydrodynamic force instigate viscous drag to melt polymer and breakdown the aggregates of nanofiller using shear stress, which boosts homogeneous and uniform distribution of nanofiller in the polymer (Fig. 11).
 - b. **Solvent method:** In the solvent method, nanoparticles are distributed in solution employing solvent and polymer is dissolved in co-solvent (Fig. 12). Solvent evaporation or solvent coagulation is used to retrieve resulting nanocomposites from solvent methods. The shear stresses induced in the polymer during the solvent method are lower than melt compounding. The sonication method is employed to pre-disperse nanofillers in the solvent

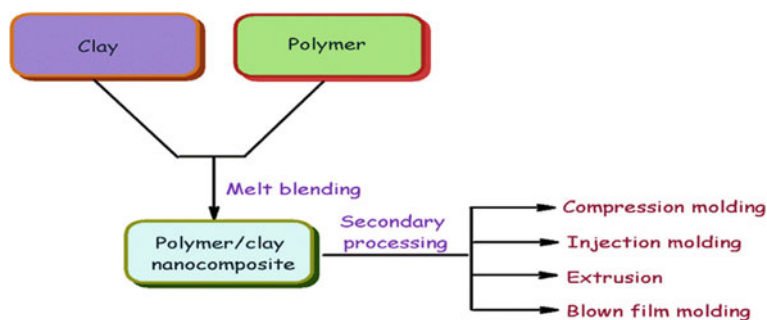


Fig. 11 Schematic of the steps involved in melt-blending [16–24]

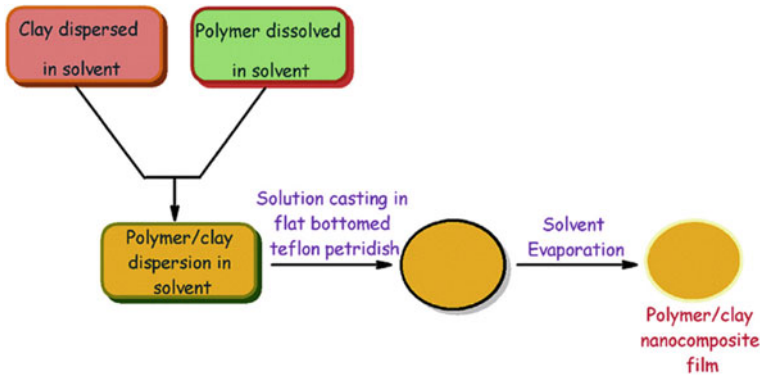


Fig. 12 Schematic representations of stages involved in solution-blending [16–24]

and breakdown aggregates of nanofiller. This method is also known as solution mixing.

5. **Latex technology:** It is a new technique to incorporate CNTs into polymer [114, 115]. In this method, distinct polymer particle colloidal dispersion occurs in an aqueous medium. It is used in polymers produced by emulsion polymerization or brought into the emulsion to disperse CNTs. It is an easy process as it comprises two simple aqueous components, flexible, reproducible, dependable, and permits integration of individual CNTs into a highly viscous polymer matrix. The procedure is safe, environmentally friendly, and economical as water is used as a solvent for CNT dispersion.
6. **Ex-situ synthesis:** It is also termed a blending or direct compounding technique in which nanofillers are synthesized by the external synthesis process and then added or combined to a monomer or resin. This is also used to fabricate polymer nanocomposites when mass production is desired. The process is economical and has operational convenience. At first, nanofillers and polymer are individually produced and compounded by solution melt blending, emulsion, or mechanical forces [116, 117]. The nanoparticles show a significant tendency to form large clusters during blending.
7. **Other methods:** To obtain nanocomposites with high CNT content, the latest processes developed are (a) pulverization, (b) spinning of coagulant, (c) layer-by-layer deposition, and (d) densification. Table 2 provides a summary of the technique, benefits, and CNTs used in these methods. It should be noted that many researchers have conducted tests to devise the latest processing methods that can develop nanocomposites with unique structure and properties for specific applications.

Table 2 New techniques for manufacturing of CNT-polymer nanocomposites

No	CNT	Fabrication technique	Benefits	Method
1	As received CNTs	Polymer and CNTs are mixed and pulverized by pan mill or twin-screw	Possible grafting of polymers on CNTs, easy scale-up, and solventless process	Pulverization [118, 119]
2	Pre-distribution of CNTs using surfactant solution	Coagulation of CNT into mesh by wet spinning into polymer solution and transforming the mesh into the solid fibre by slow draw procedure	Used to fabricate CNT-polymer fibre	The spinning of coagulant [120]
3	Pre-distribution of CNTs in solvent	Dipping of a solid substrate of CNTs into polymer solutions by the following curing	Structural flaw arises from the phase segregation of polymer	Layer by layer deposition [121]
4	As grown CNTs forest	CNT forest is produced and shifted to a pool of uncured epoxy. The matrix is infused into CNT forest and then cured	CNT vol.% can be controlled by varying the densification of CNT forest and aligning CNTs in nanocomposites	Densification [122]

If the polymer nanocomposites are prepared by using any one of the above techniques then they have to go for final processing by employing conventional manufacturing methods like (a) injection moulding, (b) calendaring, (c) casting, (d) compression moulding, (e) blow moulding, (f) rotational moulding, (g) extrusion moulding, and (h) thermoforming.

5 Applications of Nanocomposites

With nanotechnology, polymer nanocomposites came into limelight as it possesses many advanced features and improved properties. Nanomaterials have extensive applications in various sectors, as discussed below [123, 124]:

1. **Aerospace:** The primary concerns for the aerospace structure are weight, strength and stiffness, performance, thermal stability, retardancy, and durability [125]. Nanocomposites have exceptional structural properties, including favourable coefficient of thermal expansion. These properties are critical in aerospace research focusing on telescopes and antennas [126].

Weight reduction: Reduced vehicle weight can increase payload capacity and reduce fuel consumption and emissions. In aircraft and spacecraft industries, the current trend is to maximize the use of lightweight composites. Boeing 787

is made up of a large volume of composites (50%) in comparison to Boeing 777 in which only 7% is used. A nano porous polymers density is 1/5th of a fully dense polymer, i.e., 0.2 g cm^{-3} . Enhancement in mechanical properties like strengthening nanopore walls is achieved by adding nanofillers (CNTs, nano clay, and graphene). Composite weight can be reduced by using CNT fibres that possess higher tensile properties [127].

Strength and stiffness: Organic polymer-nanocomposites possess remarkably higher modulus and strength. The fracture toughness of composites is increased from 3.4 to 4.2 MPa/m², i.e., 24% with the incorporation of 10 vol% MWCNT in alumina composites [128]. The addition of 1% nanotubes increases the elastic stiffness of CNT-polystyrene composites by 36–42% and tensile strength by 25% [129].

Thermal stability and fire retardancy: It is considered an essential property to meet market-driven performance and cost requirements. It plays a vital role in many applications, such as aircraft, military applications, and many sensing systems. Experimental results showed enhancement in the flame retardant, thermal, and mechanical properties of the polymer nanocomposite and confirmed their use in aerospace applications [130, 131].

2. **Automobile:** Polymer–clay nanocomposites are first used to fabricate car parts as they possess high stiffness and thermal stability. The first industry used nanocomposites in the automobile was General Motors. The use of nanocomposites resulted in the reduction of component weight by approximately 1 kg [132]. Toyota Central R&D Laboratory performs extensive research in 1986 to determine the properties of nylon-6-clay nanocomposites used as timing belt covers in automobile [133, 134]. In recent times, nanocomposites are the most commonly used material for manufacturing of car parts like side moulding, doors, seatbacks, console, cargo bed bridge, panels, trim, handles, rear view mirror, components of the gas tank, engine cover, bumper, etc. as it produces stiffer, lighter, less brittle at cold temperature, and more scratch-resistant parts. The weight of any part fabricated using 5 wt% clay can be reduced by 25% compared to glass fibre reinforced nylon. The addition of nano clays also results in increased thermal distortion temperature from 65–152 °C. In the late 1990s, CNTs were found in most automobiles' fuel system where they are typically blended with nylon to prevent static charge build-up. The whole automotive world is currently using polymer nano clay-composites as a potential substitute because of low emission, low cost, and high performance. The use of nanomaterials in automobile tires is one of its earliest applications. Future applications of nanocomposites to the automotive industry include (a) sensors and switches, (b) fuel cells, (c) batteries, (d) hydrogen storage, (e) fire-retardant interiors, (f) LED lighting, and (g) miniaturized systems based on NEMS.
3. **Nanostructured membranes:** Membranes possesses internal nanostructures that are termed as nanostructured membranes [135]. In recent years, the advancement of nanostructured membranes in the different field covers:

Nanostructured membranes for reverse osmosis: CNTs and graphene oxide are considered the most favourable nanomaterials for reverse osmosis application. These materials can be synthesized to have non-tortuous pores in a few nanometres to transport water molecules in the desalination process [136–139].

Nanostructured membranes for ultrafiltration: Ultrafiltration is basically for water treatment based on the membrane separation process. The phase inversion method is used to fabricate ultrafiltration membranes whose pores are generally in the nanoscale range (1–100 nm) [140].

Nanostructured membranes for gas separations: Nanomaterials like silica (SiO_2) and CNTs are incorporated into the polymer to prepare nanostructured membranes for gas separation. The selection of nanomaterial and polymer is the subject of extensive research [141–146]. Silica can improve the thermal and mechanical stabilities as well as gas separation property of membranes. CNTs have excellent mechanical and thermal stabilities and potentiality to minimize the compaction effect in high-pressure gas separation. The improvement is attributed to the ability of MWNTs to improve the mechanical strength and anti-compaction property of the mixed matrix membranes.

4. **Water treatment processes:** In water treatment, nanostructured polymer composites are employed in diverse roles and capacities (like catalyst, adsorbents, and membrane filters) and as monitoring purposes and detecting microbial agents. Nanomaterials and polymers used in composites play a crucial role in determining its utilization for the treatment process. Methods of preparation and synthesis polymer nanocomposites also influence the performance of the application for water treatment [147].

Polymer nanocomposites as photocatalysts: Application of polymer nanocomposites as catalysts during wastewater treatment has received enormous attention among researchers. Polymer nanocomposites have great potential as catalysts due to the unique characteristics such as superior influence on the rate of chemical reactions, specific surface area, and inherent electronic properties. Studies revealed that polymer nanocomposites could function as photocatalysts in chemical reactions when light is absorbed, bringing excitation in higher energy levels¹⁴⁵. The suitability of polymer nanocomposites as efficient photocatalysts for water treatment purposes is based on the quality of nanocomposites used and their ability to irradiate light source [146].

Polymer nanocomposites as adsorbents: The most straightforward and efficient procedure of separating water and contaminants is adsorption [148, 149]. When substances like liquid, solid, or chemical species gather and transform into a solid surface is termed as adsorption [150]. When transferring the adsorbate molecule from solution to the available binding sites on the adsorbent, the procedure is considered adsorption. According to various reports, numerous sorbents used to remove contaminants are activated carbons sourced from different precursors like clay [151]. It showed tremendous results in the water treatment process, and its efficiency is based on its intrinsic properties [152]. To enhance the wastewater remediation process's efficiency, nanosorbents are used to eliminate contaminants that are difficult to remove during wastewater treatment.

Studies in previous reports showed polymer nanocomposites efficiency as adsorbents to remove contaminants such as heavy metals, pesticides, pharmaceuticals, perfluoroalkyl acids, etc. [153].

Polymer nanocomposites as filtration membranes: Designing and fabricating efficient filtration membranes are purposely done to exclude specific predetermined molecules or species like oils [154], dyes [155], solutes/salts [156], and heavy metals [157, 158]. Polymer nanocomposites were also employed to eliminate antimicrobial [159], flocculation/dewatering of sludge [160], removal of chlorinated byproducts [161], and natural organic matter [162]. To eliminate all these various sorbents, promising remediation capabilities are synthesized and utilized. Filtration membrane is widely used for water treatment due to its adaptable nature. It also has few inherent qualities like high sorption capacity, environmentally friendly, and cost-effective for wastewater treatment [163]. Meanwhile, the physical separation of large particles of pollutants is a distinctive characteristic of filtration membranes [164].

Polymer nanocomposites as monitoring and detection devices: Polymer nanocomposites are also used as monitoring and detecting devices based on pH sensitivity, affinities for both organic and inorganic ions, and responses to microorganisms [165]. Polymer nanocomposites can sense and detect, which is derived by intrinsic properties of nanomaterials and polymer. Polymer nanocomposites are utilized for the detection of contaminants such as (a) heavy metals, (b) trace organic and inorganic contaminants, (c) persistent organic pollutants, and (d) pathogens in aqueous solution [166]. Additionally, some polymer nanocomposites are used for monitoring (a) pH [167], (b) dissolved oxygen [168], and (c) chemical oxygen demand [169] of water systems.

Polymer nanocomposites as antimicrobial agents: Eliminating microbial contaminants *Escherichia coli*, *Staphylococcus aureus*, etc., from water is one of the most challenging tasks during water treatment operations. In several studies, nanomaterials are used for their anti-microbial properties [170]. In recent years, the field of disinfection has received enormous attention due to the challenges associated with other disinfection methods. Apart from the nanomaterials, specific polymeric matrices contribute to the antimicrobial activity of polymer nanocomposites [171]. This procedure is expected to receive more attention in future as it is a viable alternative in the water treatment process. There is a need to investigate this technique more to eliminate the challenges encountered during the application.

5. **Biomedical:** Polymer nanocomposites are extensively used to heal lost and damaged organs or tissues [172]. Tissue engineering and the drug delivery system are among the most important fields using polymer nanocomposites [173]. A report suggests that polymer–clay nanocomposites are quite efficient for delivering antimicrobial drugs [174]. The films composed of semi-synthetic cellulose derivative (carmellose-sodium) and chlorhexidine diacetate like mucoadhesive for oral infectious treatment. Polymer nanocomposites offer promising mucoadhesive, mechanical, and chemical properties [175]. Three different fields of medicine are prevention, diagnosis, and therapy. Nanoscale

liposomes or micelles are used through a topical vaccine delivery system in the case of prevention as it provides an effective and easy way to generate cell-mediated immune response [176]. To detect or diagnose biomolecular signals at a very low concentration and detect diseases at an early stage, nanocantilevers, nanotubes, and nanowires are used to increase the sensitivity of detection devices [177]. The introduction of nanotechnology has benefited molecular imaging, computed tomography, and magnetic resonance imaging technology. Nanotechnology provides 3D images of tissues and organs with more information and higher resolution [178]. Nanocomposites can replace Lead-based products to provide light-weight and flexible radiation shields for diagnostic radiology and nuclear medicine. The utilization of nanoparticles as a drug carrier crosses the blood–brain barrier. Nanoparticles in the field of therapy can be used to destroy cancer cells. Scaffolds based on tissue growth can be produced using soft tissue engineering materials like (a) nanofibers, (b) nanotubes, and (c) peptide-based self-assembled nanostructure. Nanostructured materials, nanocomposites, and nano-coatings are extensively used for scaffolds and implants for bone and cartilage replacement in orthopaedics and dentistry. Nanocomposites also benefit vascular stents by providing nanoscale biocompatible or drug-eluting coatings. Nanotechnologies already made its impact in the field of pacemakers and hearing aids implantable devices. It is further developed and equipped with a smaller size and increased power provided by nanoscale electronics. Silver nanocrystals type of antibacterial nanoparticles has already been used in protective clothing, medical textiles, and wound dressings. Nano-enabled products in the health care field commercially available are surgical blades with nanoscale diamond coatings, medical tools, surgical threads with gold nano-coatings, and suture needles composed of stainless steel nanoparticles.

6. **Chemicals:** Chemical sector is one of the many fields which are benefited from nanotechnologies. Replacement of micro-fillers by nanoparticles as fillers in paints and other coatings, improves their swelling, scratch, radiation, abrasion, heat, and environmental ageing resistance [179]. Reduction in the formation of cracks and voids can be achieved by incorporating nanoparticles in the solution during the evaporation phase of the traditional sol–gel coating. Nanofillers can lead to antibacterial, antistatic, flame retardant, and transparent UV protective coatings. Improved performance of polymer composites can be achieved by using nanofillers [180]. Nanofillers, when added to polymer matrices, provide unique performance such as resistance to heat distortion. The addition of nano clay allows the improvement in heat distortion temperature, which is not possible in any other method. Nanoparticles found suitable for these applications should comprise of carbon allotropes and polymers.
7. **Construction:** Recently, polymer nanocomposite is introduced to structures to improve existing construction materials [181]. Nanomaterials are found in almost every house or building, specifically in three types of products like concrete, coatings and paints, and insulation. The addition of PVA and montmorillonite in polymer nanocomposite when added to concrete is responsible for increasing cement composites' properties without affecting the compression

strength [182]. A new approach is used to incorporate nanoparticle adhesives for building and civil engineering applications for retrofitting structures. An investigation is focussed on the properties of nano clay modified epoxy adhesive to strengthen concrete members with CFRP [183]. Identical research is carried on the preparation of PU-clay nanocomposite [184]. Another important issue in construction is the coating of concrete walls with polymer paint prone to weather damage. Polymer nanocomposites proved to be better than neat polymers for this purpose as it can cover the pores and crevices present on the concrete and other surfaces. It helps in resisting pollution and environmental attacks such as chloride ions and water seepage. The application of polymer nanocomposites to concrete surface demonstrated improvement in moisture penetration resistance [185]. Nanoporous structures like aerogels can be made out of silica or carbon to provide 2 to 8 times more efficient thermal and acoustical insulation than traditional insulation materials. The addition of nano clay to polymers in building materials provides flame resistance. It is also considered to be used as spraying or painting nanosensors to monitor stress and the temperature or air quality on the surface of building or structure.

8. **Electronics:** The three main areas of concern in electronics applications are displays, memory, and integrated circuits [186]. Nanowires, CNTs, and graphene are used for displaying like (a) organic light-emitting diodes, (b) organic light-emitting transistors, (c) electrophoretic paper, and (d) field emission display. Recent research is focussed on producing devices that are easier to manufacture, consume less energy, thinner and lighter, and can be flexed without being damaged. The memory chips are designed to increase memory and reduce power consumption. Recent advancements include the formation of p-n junctions with the help of graphene, integrated circuits fabrication by CNTs, and nanowires to create transistors without p-n junctions.

6 Review Questions

- (1) What is a carbon nanotube? Explain why they are not as prevalent as other forms of carbon.
- (2) What is nanocomposite? Classify polymer-based nanocomposite.
- (3) What is the difference between top-down and bottom-up methods for creating nanostructures?
- (4) Describe the defects formed on the external layer of MWCNT structures and elucidate the importance of interlayer distance in overcoming above stated defects.
- (5) List out the factors which make nanocellulose as the most demanding and suitable material to fabricate composite material.
- (6) Which method is suitable for the fabrication of polymer nanocomposites out of melt compounding and solvent method? Justify the answer with practical reasons.

- (7) Explicate some new techniques used for the manufacturing of CNT-polymer nanocomposites.
- (8) State the purposes of adding nanomaterials in the fabrication of composite for the use of automobile and aerospace.
- (9) Elucidate the use of nanocomposite in the various fields of the biomedical.
- (10) Explain the role of interphase bonding between polymer and clay nanoparticles and its types in detail.

References

1. Thostenson, E.T., Li, C., Chou, T.W.: Nanocomposites in context. *Compos. Sci. Technol.* **65**(3–4), 491–516 (2005)
2. Thrower, P., Mason, T.W.: *Materials in Today's World*. McGraw-Hill, USA (2008)
3. <https://commons.wikimedia.org/w/index.php?curid=65688187>
4. Hussain, F., Hojjati, M., Okamoto, M., Gorga, R.E.: Polymer-matrix nanocomposites, processing, manufacturing, and application: an overview. *J. Compos. Mater.* **40**(17), 1511–1575 (2006)
5. Khezri, K., Mahdavi, H.: Polystyrene-silica aerogel nanocomposites by in situ simultaneous reverse and normal initiation technique for ATRP. *Microporous Mesoporous Mater.* **228**, 132–140 (2016)
6. Jordan, J., Jacob, K.I., Tannenbaum, R., Sharaf, M.A., Jasiuk, I.: Experimental trends in polymer nanocomposites—a review. *Mater. Sci. Eng. A* **393**(1–2), 1–11 (2005)
7. RTO Lecture Series.: EN-AVT-129. (May 2005)
8. Kojima, Y., Usuki, A., Kawasumi, M., Okada, A., Fukushima, Y., Kurauchi, T., Kamigaito, O.: Mechanical properties of nylon 6-clay hybrid. *J. Mater. Res.* **8**(5), 1185–1189 (1993)
9. Kojima, Y., Usuki, A., Kawasumi, M., Okada, A., Kurauchi, T., Kamigaito, O.: Sorption of water in nylon 6-clay hybrid. *J. Appl. Polym. Sci.* **49**(7), 1259–1264 (1993)
10. Sahoo, N.G., Rana, S., Cho, J.W., Li, L., Chan, S.H.: Polymer nanocomposites based on functionalized carbon nanotubes. *Prog. Polym. Sci.* **35**(7), 837–867 (2010)
11. Potts, J.R., Dreyer, D.R., Bielawski, C.W., Ruoff, R.S.: Graphene-based polymer nanocomposites. *Polym.* **52**(1), 5–25 (2011)
12. Schmidt, D., Shah, D., Giannelis, E.P.: New advances in polymer/layered silicate nanocomposites. *Curr. Opin. Solid State Mater. Sci.* **6**(3), 205–212 (2002)
13. Alexandre, M., Dubois, P.: Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Mater. Sci. Eng. R. Rep.* **28**(1–2), 1–63 (2000)
14. <https://www.marketsandmarkets.com/Market-Reports/polymer-nanocomposites-market-228956069.html>
15. Chung, D.D. *Composite Materials: Functional Materials for Modern Technologies*. Springer Science & Business Media (2013)
16. Khan, W.S., Hamadneh, N.N., Khan, W.A.: Polymer nanocomposites—synthesis techniques, classification and properties. *Science and Applications of Tailored Nanostructures*, pp. 50–67. (2016)
17. Pandey, N., Shukla, S.K., Singh, N.B.: Water purification by polymer nanocomposites: an overview. *Nanocomposites* **3**(2), 47–66 (2017)
18. Olad, A.: Polymer/clay nanocomposites. In: *Advances in Diverse Industrial Applications of Nanocomposites*. IntechOpen, pp. 113–138. (2011)
19. Mittal, V. (ed.): *Spherical and Fibrous Filler Composites*. Wiley (2016)
20. Akpan, E.I., Shen, X., Wetzal, B., Friedrich, K.: Design and synthesis of polymer nanocomposites. In: *Polymer Composites with Functionalized Nanoparticles* pp. 47–83. Elsevier (2019)

21. Bower, C.A.: Studies on the form and availability of organic soil phosphorous. *IOWA Agric. Exp. Stat. Res. Bull.* **28**, 362 (1949)
22. Esteves, A.C.C., Barros-Timmons, A., Trindade, T.: Nanocompósitos de matriz polimérica: estratégias de síntese de materiais híbridos. *Quim. Nova* **27**(5), 798–806 (2004)
23. Kumar, A.P., Depan, D., Tomer, N.S., Singh, R.P.: Nanoscale particles for polymer degradation and stabilization—trends and future perspectives. *Prog. Polym. Sci.* **34**(6), 479–515 (2009)
24. Valapa, R.B., Loganathan, S., Pugazhenth, G., Thomas, S., Varghese, T.O.: An overview of polymer—clay nanocomposites. In: *Clay-Polymer Nanocomposites*, pp. 29–81. Elsevier (2017)
25. Raquez, J.M., Habibi, Y., Murariu, M., Dubois, P.: Polylactide (PLA)-based nanocomposites. *Prog. Polym. Sci.* **38**(10–11), 1504–1542 (2013)
26. Zaarei, D., Sarabi, A.A., Sharif, F., Kassiriha, S.M.: Structure, properties and corrosion resistivity of polymeric nanocomposite coatings based on layered silicates. *J. Coat. Technol. Res.* **5**(2), 241–249 (2008)
27. Dolez, P.I.: Nanomaterials definitions, classifications, and applications. In: *Nanoengineering*, pp. 3–40. Elsevier (2015)
28. Kroto, H.W., Heath, J.R., O'Brien, S.C., Curl, R.F., Smalley, R.E.: C₆₀: buckminsterfullerene. *Nature* **318**(6042), 162–163 (1985)
29. Iijima, S., Ajayan, P.M., Ichihashi, T.: Growth model for carbon nanotubes. *Phys. Rev. Lett.* **69**(21), 3100 (1992)
30. Thostenson, E.T., Ren, Z., Chou, T.W.: Advances in the science and technology of carbon nanotubes and their composites: a review. *Compos. Sci. Technol.* **61**(13), 1899–1912 (2001)
31. Salvétat, J.P., Bonard, J.M., Thomson, N.H., Kulik, A.J., Forro, L., Benoit, W., Zuppiroli, L.: Mechanical properties of carbon nanotubes. *Appl. Phys. A* **69**(3), 255–260 (1999)
32. Ma, P.C., Siddiqui, N.A., Marom, G., Kim, J.K.: Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review. *Compos. A Appl. Sci. Manuf.* **41**(10), 1345–1367 (2010)
33. Green, M.J., Behabtu, N., Pasquali, M., Adams, W.W.: Nanotubes as polymers. *Polymer* **50**(21), 4979–4997 (2009)
34. Yazid, M.N.A.W.M., Sidik, N.A.C., Mamat, R., Najafi, G.: A review of the impact of preparation on stability of carbon nanotube nanofluids. *Int. Commun. Heat Mass Trans.* **78**, 253–263 (2016)
35. Iijima, S.: Carbon nanotubes: past, present, and future. *Phys. B* **323**(1–4), 1–5 (2002)
36. Grady, B.P.: *Carbon Nanotube-Polymer Composites: Manufacture, Properties, and Applications*. Wiley (2011)
37. Yu, M.F., Lourie, O., Dyer, M.J., Moloni, K., Kelly, T.F., Ruoff, R.S.: Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. *Science* **287**(5453), 637–640 (2000)
38. Treacy, M.J., Ebbesen, T.W., Gibson, J.M.: Exceptionally high Young's modulus observed for individual carbon nanotubes. *Nature* **381**(6584), 678–680 (1996)
39. Zhou, H.W., Mishnaevsky, L., Jr., Yi, H.Y., Liu, Y.Q., Hu, X., Warriar, A., Dai, G.M.: Carbon fiber/carbon nanotube reinforced hierarchical composites: effect of CNT distribution on shearing strength. *Compos. B Eng.* **88**, 201–211 (2016)
40. Valentino, O., Sarno, M., Rainone, N.G., Nobile, M.R., Ciambelli, P., Neitzert, H.C., Simon, G.P.: Influence of the polymer structure and nanotube concentration on the conductivity and rheological properties of polyethylene/CNT composites. *Phys. E* **40**(7), 2440–2445 (2008)
41. De Volder, M.F., Tawfick, S.H., Baughman, R.H., Hart, A.J.: Carbon nanotubes: present and future commercial applications. *Science* **339**(6119), 535–539 (2013)
42. <https://www.transparencymarketresearch.com/carbon-nano-tubes-market.html>
43. Deplancke, T., Lame, O., Barrau, S., Ravi, K., Dalmas, F.: Impact of carbon nanotube prelocalization on the ultra-low electrical percolation threshold and on the mechanical behavior of sintered UHMWPE-based nanocomposites. *Polymer* **111**, 204–213 (2017)
44. Wang, H., Xie, G., Fang, M., Ying, Z., Tong, Y., Zeng, Y.: Mechanical reinforcement of graphene/poly (vinyl chloride) composites prepared by combining the in-situ suspension polymerization and melt-mixing methods. *Compos. B Eng.* **113**, 278–284 (2017)

45. Alian, A.R., Dewapriya, M.A.N., Meguid, S.A.: Molecular dynamics study of the reinforcement effect of graphene in multilayered polymer nanocomposites. *Mater. Des.* **124**, 47–57 (2017)
46. Arash, B., Wang, Q., Varadan, V.K.: Mechanical properties of carbon nanotube/polymer composites. *Sci. Rep.* **4**, 6479 (2014)
47. Li, Y., Wang, S., Wang, Q.: A molecular dynamics simulation study on enhancement of mechanical and tribological properties of polymer composites by introduction of graphene. *Carbon* **111**, 538–545 (2017)
48. Saito, R., Dresselhaus, G., Dresselhaus, M.S.: *Physical Properties of Carbon Nanotubes*. London, Imperial College Press, (1998)
49. Smalley, R.E.: *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*, vol. 80. Springer Science & Business Media (2003)
50. Zhang, R., Zhang, Y., Zhang, Q., Xie, H., Qian, W., Wei, F.: Growth of half-meter long carbon nanotubes based on Schulz-Flory distribution. *ACS Nano* **7**(7), 6156–6161 (2013)
51. Jasti, R., Bhattacharjee, J., Neaton, J.B., Bertozzi, C.R.: Synthesis, characterization, and theory of [9]-, [12]-, and [18] cycloparaphenylene: carbon nanohoop structures. *J. Am. Chem. Soc.* **130**(52), 17646–17647 (2008)
52. Zhao, X., Liu, Y., Inoue, S., Suzuki, T., Jones, R.O., Ando, Y.: Smallest carbon nanotube is 3 Å in diameter. *Phys. Rev. Lett.* **92**(12), 125502 (2004)
53. Sugime, H., Esconjauregui, S., Yang, J., D'Arسيé, L., Oliver, R.A., Bhardwaj, S., Cepek, C., Robertson, J.: Low temperature growth of ultra-high mass density carbon nanotube forests on conductive supports. *Appl. Phys. Lett.* **103**(7), 073116 (2013)
54. Hamada, N., Sawada, S.I., Oshiyama, A.: New one-dimensional conductors: graphitic microtubules. *Phys. Rev. Lett.* **68**(10), 1579 (1992)
55. Zhang, M., Li, J.: Carbon nanotube in different shapes. *Mater. Today* **12**(6), 12–18 (2009)
56. Hanemann, T., Szabó, D.V.: Polymer-nanoparticle composites: from synthesis to modern applications. *Materials* **3**(6), 3468–3517 (2010)
57. Dufresne, A.: Nanocellulose: a new ageless bionanomaterial. *Mater. Today* **16**(6), 220–227 (2013)
58. Moon, R.J., Martini, A., Nairn, J., Simonsen, J., Youngblood, J.: Cellulose nanomaterials review: structure, properties and nanocomposites. *Chem. Soc. Rev.* **40**(7), 3941–3994 (2011)
59. Fendler, J.H. (ed.): *Nanoparticles and Nanostructured Films: Preparation, Characterization, and Applications*. Wiley (2008)
60. Agwuncha, S.C., Anusionwu, C.G., Owonubi, S.J., Sadiku, E.R., Busuguma, U.A., Ibrahim, I.D.: Extraction of cellulose nanofibers and their eco/friendly polymer composites. In: *Sustainable polymer composites and nanocomposites*, pp. 37–64. Springer, Cham (2019)
61. Trache, D., Hussin, M.H., Haafiz, M.M., Thakur, V.K.: Recent progress in cellulose nanocrystals: sources and production. *Nanoscale* **9**(5), 1763–1786 (2017)
62. Phanthong, P., Reubroycharoen, P., Hao, X., Xu, G., Abudula, A., Guan, G.: Nanocellulose: extraction and application. *Carbon Resour. Convers.* **1**(1), 32–43 (2018)
63. Khalil, H.A., Bhat, A.H., Yusra, A.I.: Green composites from sustainable cellulose nanofibrils: a review. *Carbohydr. Polym.* **87**(2), 963–979 (2012)
64. Trache, D., Tarchoun, A.F., Derradji, M., Hamidon, T.S., Masruchin, N., Brosse, N., Hussin, M.H.: Nanocellulose: from fundamentals to advanced applications. *Front. Chem.* **8**, 392 (2020)
65. Ray, S.S.: A new possibility for microstructural investigation of clay-based polymer nanocomposite by focused ion beam tomography. *Polymer* **51**(17), 3966–3970 (2010)
66. Jiang, L., Lam, Y.C., Tam, K.C., Chua, T.H., Sim, G.W., Ang, L.S.: Strengthening acrylonitrile-butadiene-styrene (ABS) with nano-sized and micron-sized calcium carbonate. *Polymer* **46**(1), 243–252 (2005)
67. Tortora, M., Vittoria, V., Galli, G., Ritrovati, S., Chiellini, E.: Transport properties of modified montmorillonite-poly (ε-caprolactone) nanocomposites. *Macromol. Mater. Eng.* **287**(4), 243–249 (2002)
68. Gorrasi, G., Tortora, M., Vittoria, V., Pollet, E., Lepoittevin, B., Alexandre, M., Dubois, P.: Vapor barrier properties of polycaprolactone montmorillonite nanocomposites: effect of clay dispersion. *Polymer* **44**(8), 2271–2279 (2003)

69. Mrlik, M., AlMaadeed, M.A.S.: Fillers in advanced nanocomposites for energy harvesting. In: *Fillers and Reinforcements for Advanced Nanocomposites*, pp. 401–424. Woodhead Publishing (2015)
70. Okada, A., Usuki, A.: The chemistry of polymer-clay hybrids. *Mater. Sci. Eng. C* **3**(2), 109–115 (1995)
71. Christopher, O.O., Lerner, M.: *Nanocomposites and Intercalation Compound*. Academic Press, San Diego, *Encyclopedia of Physical Science and Technology* (2001)
72. Becker, O., Varley, R.J., Simon, G.P.: Thermal stability and water uptake of high performance epoxy layered silicate nanocomposites. *Eur. Polym. J.* **40**(1), 187–195 (2004)
73. Wang, S., Hu, Y., Song, L., Wang, Z., Chen, Z., Fan, W.: Preparation and thermal properties of ABS/montmorillonite nanocomposite. *Polym. Degrad. Stab.* **77**(3), 423–426 (2002)
74. Vyazovkin, S., Dranca, I., Fan, X., Advincula, R.: Kinetics of the thermal and thermo-oxidative degradation of a polystyrene–clay nanocomposite. *Macromol. Rapid Commun.* **25**(3), 498–503 (2004)
75. Yuen, S.M., Ma, C.C.M., Chiang, C.L., Chang, J.A., Huang, S.W., Chen, S.C., Chuang, C.Y., Yang, C.C., Wei, M.H.: Silane-modified MWCNT/PMMA composites—Preparation, electrical resistivity, thermal conductivity and thermal stability. *Compos. A Appl. Sci. Manuf.* **38**(12), 2527–2535 (2007)
76. Guthy, C., Du, F., Brand, S., Winey, K.I., Fischer, J.E.: Thermal conductivity of single-walled carbon nanotube/PMMA nanocomposites. *J. Heat Transfer* **129**(8), 1096–1099 (2007)
77. Choi, E.S., Brooks, J.S., Eaton, D.L., Al-Haik, M.S., Hussaini, M.Y., Garmestani, H., Li, D., Dahmen, K.: Enhancement of thermal and electrical properties of carbon nanotube polymer composites by magnetic field processing. *J. Appl. Phys.* **94**(9), 6034–6039 (2003)
78. Du, F., Guthy, C., Kashiwagi, T., Fischer, J.E., Winey, K.I.: An infiltration method for preparing single-wall nanotube/epoxy composites with improved thermal conductivity. *J. Polym. Sci., Part B: Polym. Phys.* **44**(10), 1513–1519 (2006)
79. Kiliaris, P., Papaspyrides, C.D.: Polymer/layered silicate (clay) nanocomposites: an overview of flame retardancy. *Prog. Polym. Sci.* **35**(7), 902–958 (2010)
80. Levchik, S.V.: Introduction to flame retardancy and polymer flammability. In: *Flame Retardant Polymer Nanocomposites*, pp. 1–29. (2007)
81. Koo, J.H., Pilato, L.A.: Polymer nanostructured materials for high temperature applications. *SAMPE J.* **41**(2), 7–19 (2005)
82. Pavlidou, S., Papaspyrides, C.D.: A review on polymer–layered silicate nanocomposites. *Prog. Polym. Sci.* **33**(12), 1119–1198 (2008)
83. Yano, K., Usuki, A., Okada, A., Kurauchi, T., Kamigaito, O.: Synthesis and properties of polyimide–clay hybrid. *J. Polym. Sci. Part A: Polym. Chem.* **31**(10), 2493–2498 (1993)
84. Lange, J., Wyser, Y.: Recent innovations in barrier technologies for plastic packaging—a review. *Packaging Technol. Sci. Int. J.* **16**(4), 149–158 (2003)
85. Koh, H.C., Park, J.S., Jeong, M.A., Hwang, H.Y., Hong, Y.T., Ha, S.Y., Nam, S.Y.: Preparation and gas permeation properties of biodegradable polymer/layered silicate nanocomposite membranes. *Desalination* **233**(1–3), 201–209 (2008)
86. Ranjan S, Dasgupta N, Lichtfouse E. (eds): *Nanoscience in Food and Agriculture*, 1st edn. Cham, Springer International Publishing (2016)
87. Adame, D., Beall, G.W.: Direct measurement of the constrained polymer region in polyamide/clay nanocomposites and the implications for gas diffusion. *Appl. Clay Sci.* **42**(3–4), 545–552 (2009)
88. Olad, A., Rashidzadeh, A.: Preparation and anticorrosive properties of PANI/Na-MMT and PANI/O-MMT nanocomposites. *Prog. Org. Coat.* **62**(3), 293–298 (2008)
89. Jeon, I.Y., Baek, J.B.: Nanocomposites derived from polymers and inorganic nanoparticles. *Materials* **3**(6), 3654–3674 (2010)
90. Ajayan, P.M., Schadler, L.S., Braun, P.V.: *Nanocomposite Science and Technology*. Wiley (2006)
91. Tanahashi, M.: Development of fabrication methods of filler/polymer nanocomposites: With focus on simple melt-compounding-based approach without surface modification of nanofillers. *Materials* **3**(3), 1593–1619 (2010)

92. Velasco, J.I., Ardanuy, M., Antunes, M.: Layered double hydroxides (LDHs) as functional fillers in polymer nanocomposites. In: *Advances in Polymer Nanocomposites*, pp. 91–130. Woodhead Publishing (2012)
93. Rehab, A., Salahuddin, N.: Nanocomposite materials based on polyurethane intercalated into montmorillonite clay. *Mater. Sci. Eng. A* **399**(1–2), 368–376 (2005)
94. Song, W., Zheng, Z., Tang, W., Wang, X.: A facile approach to covalently functionalized carbon nanotubes with biocompatible polymer. *Polymer* **48**(13), 3658–3663 (2007)
95. Hlavatý, V., Oya, A.: Intercalation of methacrylamide into sodium, calcium and alkylammonium exchanged montmorillonites. *Appl. Clay Sci.* **9**(3), 199–210 (1994)
96. Jannapu Reddy, R.: Preparation, characterization and properties of injection molded graphene nanocomposites. Doctoral Dissertation, Wichita State University (2010)
97. Gojny, F.H., Wichmann, M.H.G., Köpke, U., Fiedler, B., Schulte, K.: Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content. *Compos. Sci. Technol.* **64**(15), 2363–2371 (2004)
98. Moiala, A., Li, Q., Kinloch, I.A., Windle, A.H.: Thermal and electrical conductivity of single- and multi-walled carbon nanotube-epoxy composites. *Compos. Sci. Technol.* **66**(10), 1285–1288 (2006)
99. Ma, P.C., Kim, J.K., Tang, B.Z.: Effects of silane functionalization on the properties of carbon nanotube/epoxy nanocomposites. *Compos. Sci. Technol.* **67**(14), 2965–2972 (2007)
100. Lee, H.S., Choi, M.Y., Srinivasan, A., Baek, D.H., Seo, S.W.: Microphase structure and physical properties of polyurethane/organoclay nanocomposites. In: *Abstracts of Papers of the American Chemical Society*, vol. 228, pp. U466-U466. 1155 16th ST, NW, Washington, USA (Aug, 2004)
101. Vaia, R.A., Ishii, H., Giannelis, E.P.: Synthesis and properties of two-dimensional nanostructures by direct intercalation of polymer melts in layered silicates. *Chem. Mater.* **5**(12), 1694–1696 (1993)
102. Yang, F., Ou, Y., Yu, Z.: Polyamide 6/silica nanocomposites prepared by in situ polymerization. *J. Appl. Polym. Sci.* **69**(2), 355–361 (1998)
103. Caseri, W.R.: Nanocomposites of polymers and inorganic particles: preparation, structure and properties. *Mater. Sci. Technol.* **22**(7), 807–817 (2006)
104. Althues, H., Henle, J., Kaskel, S.: Functional inorganic nanofillers for transparent polymers. *Chem. Soc. Rev.* **36**(9), 1454–1465 (2007)
105. Omanovic-Miklicanin, E., Badnjevic, A., Kazlagic, A., Hajlovac, M.: Nanocomposites: a brief review. *Heal. Technol.* **10**, 51–59 (2020)
106. Philip, P., Jose, E.T., Chacko, J.K., Philip, K.C., Thomas, P.C.: Preparation and characterisation of surface roughened PMMA electrospun nanofibers from PEO-PMMA polymer blend nanofibers. *Polym. Testing* **74**, 257–265 (2019)
107. Perea, O.K., Bode-Aluko, C., Ndayambaje, G., Fatoba, O., Petrik, L.F.: Electrospinning: polymer nanofibre adsorbent applications for metal ion removal. *J. Polym. Environ.* **25**(4), 1175–1189 (2017)
108. Wang, C., Fang, C.Y., Wang, C.Y.: Electrospun poly (butylene terephthalate) fibers: entanglement density effect on fiber diameter and fiber nucleating ability towards isotactic polypropylene. *Polymer* **72**, 21–29 (2015)
109. Raghavan, P., Lim, D.H., Ahn, J.H., Nah, C., Sherrington, D.C., Ryu, H.S., Ahn, H.J.: Electrospun polymer nanofibers: the booming cutting edge technology. *React. Funct. Polym.* **72**(12), 915–930 (2012)
110. Perea, O., Bode-Aluko, C., Laatikainen, K., Nechaev, A., Petrik, L.: Morphology, modification and characterisation of electrospun polymer nanofiber adsorbent material used in metal ion removal. *J. Polym. Environ.* **27**, 1843–1860 (2019)
111. Putz, K.W., Compton, O.C., Palmeri, M.J., Nguyen, S.T., Brinson, L.C.: High-nanofiller-content graphene oxide-polymer nanocomposites via vacuum-assisted self-assembly. *Adv. Func. Mater.* **20**(19), 3322–3329 (2010)
112. Wang, D., Kou, R., Choi, D., Yang, Z., Nie, Z., Li, J., Saraf, L.V., Hu, D., Zhang, J., Graff, G.L., Liu, J., Pope, M.A., Aksay, I.A.: Ternary self-assembly of ordered metal oxide-graphene nanocomposites for electrochemical energy storage. *ACS Nano* **4**(3), 1587–1595 (2010)

113. Moniruzzaman, M., Winey, K.I.: Polymer nanocomposites containing carbon nanotubes. *Macromolecules* **39**(16), 5194–5205 (2006)
114. Ma, P.X., Zhang, R.: Synthetic nano-scale fibrous extracellular matrix. *J. Biomed. Mater. Res.: Official J. Soc. Biomater. Jpn. Soc. Biomater. Aust. Soc. Biomater.* **46**(1), 60–72 (1999)
115. Grossiord, N., Loos, J., Regev, O., Koning, C.E.: Toolbox for dispersing carbon nanotubes into polymers to get conductive nanocomposites. *Chem. Mater.* **18**(5), 1089–1099 (2006)
116. Razzaz, A., Ghorban, S., Hosayni, L., Irani, M., Aliabadi, M.: Chitosan nanofibers functionalized by TiO₂ nanoparticles for the removal of heavy metal ions. *J. Taiwan Inst. Chem. Eng.* **58**, 333–343 (2016)
117. Zhang, Q., Du, Q., Hua, M., Jiao, T., Gao, F., Pan, B.: Sorption enhancement of lead ions from water by surface charged polystyrene-supported nano-zirconium oxide composites. *Environ. Sci. Technol.* **47**(12), 6536–6544 (2013)
118. Xia, H., Wang, Q., Li, K., Hu, G.H.: Preparation of polypropylene/carbon nanotube composite powder with a solid-state mechanochemical pulverization process. *J. Appl. Polym. Sci.* **93**(1), 378–386 (2004)
119. Masuda, J.I., Torkelson, J.M.: Dispersion and major property enhancements in polymer/multiwall carbon nanotube nanocomposites via solid-state shear pulverization followed by melt mixing. *Macromolecules* **41**(16), 5974–5977 (2008)
120. Vigolo, B., Penicaud, A., Coulon, C., Sauder, C., Pailler, R., Journet, C., Bernier, P., Poulin, P.: Macroscopic fibers and ribbons of oriented carbon nanotubes. *Science* **290**(5495), 1331–1334 (2000)
121. Mamedov, A.A., Kotov, N.A., Prato, M., Guldi, D.M., Wicksted, J.P., Hirsch, A.: Molecular design of strong single-wall carbon nanotube/polyelectrolyte multilayer composites. *Nat. Mater.* **1**(3), 190–194 (2002)
122. Wardle, B.L., Saito, D.S., Garcia, E.J., Hart, A.J., de Villoria, R.G., Verploegen, E.A.: Fabrication and characterization of ultrahigh-volume-fraction aligned carbon nanotube—polymer composites. *Adv. Mater.* **20**(14), 2707–2714 (2008)
123. Hristozov, D., Malsch, I.: Hazards and risks of engineered nanoparticles for the environment and human health. *Sustainability* **1**(4), 1161–1194 (2009)
124. Hedmer, M., Kåredal, M., Gustavsson, P., Rissler, J.: Carbon nanotubes. *Arbete och H€alsla. Occupational and Environmental Medicine at Sahlgrenska Academy*, p. 252. University of Gothenburg (2013)
125. Meador, M.: A future needs and opportunities in nanotechnology for aerospace applications: a NASA perspective. In: National Institute of Aerospace Nanotechnology Workshop Hampton, (Feb, 2014) VA
126. Gorinevsky, D., Hyde, T.T.: Adaptive membrane for large lightweight space telescopes. In: *Highly Innovative Space Telescope Concepts*, vol. 4849, pp. 330–338. International Society for Optics and Photonics (Dec, 2002)
127. Joshi, M., Chatterjee, U.: Polymer nanocomposite: an advanced material for aerospace applications. In: *Advanced Composite Materials for Aerospace Engineering*, pp. 241–264. Woodhead Publishing (2016)
128. Siegel, R.W., Chang, S.K., Ash, B.J., Stone, J.A.P.M., Ajayan, P.M.: Mechanical behavior of polymer and ceramic matrix nanocomposites. *Scripta Mater.* **44**(8–9), 2061–2064 (2001)
129. Poulin, P., Vigolo, B., Launois, P.: Films and fibers of oriented single wall nanotubes. *Carbon* **40**(10), 1741–1749 (2002)
130. Zhu, J., Wilkie, C.A.: Thermal and fire studies on polystyrene—clay nanocomposites. *Polym. Int.* **49**(10), 1158–1163 (2000)
131. Zhu, J., Start, P., Kenneth, A.: Mauritz. Thermal stability and flame retardancy of PMMA-clay nanocomposites. *Polym. Degrad. Stab.* **77**, 253–258 (2002)
132. Anadão, P.: Polymer/clay Nanocomposites: Concepts, Researches, Applications and Trends for the Future, pp. 1–16. *New Trends and Developments, Nanocomposites* (2012)
133. Kawasumi, M.: The discovery of polymer-clay hybrids. *J. Polym. Sci. Part A: Polym. Chem.* **42**(4), 819–824 (2004)

134. Gul, S., Kausar, A., Muhammad, B., Jabeen, S.: Research progress on properties and applications of polymer/clay nanocomposite. *Polym.-Plast. Technol. Eng.* **55**(7), 684–703 (2016)
135. Mueller, N.C., van der Bruggen, B., Keuter, V., Luis, P., Melin, T., Pronk, W., Reiszewitz, R., Rickerby, D., Rios, G.M., Wennekes, W., Nowack, B.: Nanofiltration and nanostructured membranes—should they be considered nanotechnology or not? *J. Hazard. Mater.* **211**, 275–280 (2012)
136. Pendergast, M.M., Ghosh, A.K., Hoek, E.M.V.: Separation performance and interfacial properties of nanocomposite reverse osmosis membranes. *Desalination* **308**, 180–185 (2013)
137. Humpalik, T., Lee, J., O’hern, S.C., Fellman, B.A., Baig, M.A., Hassan, S.F., Atieh, M.A., Rahman, F., Laoui, T., Karnik, R., Wang, E.N.: Nanostructured materials for water desalination. *Nanotechnology* **22**(29), 292001 (2011)
138. Das, R., Ali, M.E., Abd Hamid, S.B., Ramakrishna, S., Chowdhury, Z.Z.: Carbon nanotube membranes for water purification: a bright future in water desalination. *Desalination* **336**, 97–109 (2014)
139. Zhang, L., Shi, G.Z., Qiu, S., Cheng, L.H., Chen, H.L.: Preparation of high-flux thin film nanocomposite reverse osmosis membranes by incorporating functionalized multi-walled carbon nanotubes. *Desalin. Water Treat.* **34**(1–3), 19–24 (2011)
140. Ho, W., Sirkar, K.: *Membrane Handbook*. Springer Science & Business Media (2012)
141. Liang, C.Y., Uchytíl, P., Petrychkovych, R., Lai, Y.C., Friess, K., Sipek, M., Reddy, M.M., Suen, S.Y.: A comparison on gas separation between PES (polyethersulfone)/MMT (Nanmontmorillonite) and PES/TiO₂ mixed matrix membranes. *Sep. Purif. Technol.* **92**, 57–63 (2012)
142. Lua, A.C., Shen, Y.: Preparation and characterization of polyimide—silica composite membranes and their derived carbon—silica composite membranes for gas separation. *Chem. Eng. J.* **220**, 441–451 (2013)
143. Zornoza, B., Téllez, C., Coronas, J.: Mixed matrix membranes comprising glassy polymers and dispersed mesoporous silica spheres for gas separation. *J. Membr. Sci.* **368**(1–2), 100–109 (2011)
144. Zhao, Y., Jung, B.T., Ansaloni, L., Ho, W.W.: Multiwalled carbon nanotube mixed matrix membranes containing amines for high pressure CO₂/H₂ separation. *J. Membr. Sci.* **459**, 233–243 (2014)
145. Kim, H.W., Yoon, H.W., Yoon, S.M., Yoo, B.M., Ahn, B.K., Cho, Y.H., Shin, H.J., Yang, H., Paik, U., Kwon, S., Choi, J.Y., Park, H.B.: Selective gas transport through few-layered graphene and graphene oxide membranes. *Science* **342**(6154), 91–95 (2013)
146. Shen, J., Liu, G., Huang, K., Jin, W., Lee, K.R., Xu, N.: Membranes with fast and selective gas-transport channels of laminar graphene oxide for efficient CO₂ capture. *Angew. Chem.* **127**(2), 588–592 (2015)
147. Akharam, M.O., Oputu, O.U., Perea, O., Fagbayigbo, B.O., Razanamahandry, L.C., Opeolu, B.O., Fatoki, O.S.: Nanostructured Polymer Composites for Water Remediation. In: *Nanostructured Materials for Treating Aquatic Pollution*, pp. 275–306. Springer, Cham (2019)
148. Rekos, K., Kampouraki, Z.C., Sarafidis, C., Samanidou, V., Deliyanni, E.: Graphene oxide based magnetic nanocomposites with polymers as effective bisphenol-a nanoadsorbents. *Materials* **12**(12), 1987 (2019)
149. He, T., Wang, L., Fabregat-Santiago, F., Liu, G., Li, Y., Wang, C., Guan, R.: Electron trapping induced electrostatic adsorption of cations: a general factor leading to photoactivity decay of nanostructured TiO₂. *J. Mater. Chem. A* **5**(14), 6455–6464 (2017)
150. Wang, H., Wang, Y.N., Sun, Y., Pan, X., Zhang, D., Tsang, Y.F.: Differences in Sb (V) and As (V) adsorption onto a poorly crystalline phyllosilicate (d-MnO₂): adsorption kinetics, isotherms, and mechanisms. *Process Saf. Environ. Prot.* **113**, 40–47 (2018)
151. Oves, M., Ansari, M.O., Khan, M.Z., Shahadat, M., Ismail, I.M.: *Modern Age Waste Water Problems*. Springer International Publishing (2020)

152. Ahmad, J., Deshmukh, K., Hägg, M.B.: Influence of TiO₂ on the chemical, mechanical, and gas separation properties of polyvinyl alcohol-titanium dioxide (PVA-TiO₂) nanocomposite membranes. *Int. J. Polym. Anal. Charact.* **18**(4), 287–296 (2013)
153. Šupová, M., Martynková, G.S., Barabaszová, K.: Effect of nanofillers dispersion in polymer matrices: a review. *Sci. Adv. Mater.* **3**(1), 1–25 (2011)
154. Yan, L., Hong, S., Li, M.L., Li, Y.S.: Application of the Al₂O₃–PVDF nanocomposite tubular ultrafiltration (UF) membrane for oily wastewater treatment and its antifouling research. *Sep. Purif. Technol.* **66**(2), 347–352 (2009)
155. Liang, B., Zhang, P., Wang, J., Qu, J., Wang, L., Wang, X., Guan, C., Pan, K.: Membranes with selective laminar nanochannels of modified reduced graphene oxide for water purification. *Carbon* **103**, 94–100 (2016)
156. Yin, J., Zhu, G., Deng, B.: Graphene oxide (GO) enhanced polyamide (PA) thin-film nanocomposite (TFN) membrane for water purification. *Desalination* **379**, 93–101 (2016)
157. Abdullah, N., Gohari, R.J., Yusof, N., Ismail, A.F., Juhana, J., Lau, W.J., Matsuura, T.: Poly-sulfone/hydrous ferric oxide ultrafiltration mixed matrix membrane: preparation, characterization and its adsorptive removal of lead (II) from aqueous solution. *Chem. Eng. J.* **289**, 28–37 (2016)
158. Ghaemi, N.: A new approach to copper ion removal from water by polymeric nanocomposite membrane embedded with γ -alumina nanoparticles. *Appl. Surf. Sci.* **364**, 221–228 (2016)
159. Jo, Y.J., Choi, E.Y., Choi, N.W., Kim, C.K.: Antibacterial and hydrophilic characteristics of poly (ether sulfone) composite membranes containing zinc oxide nanoparticles grafted with hydrophilic polymers. *Ind. Eng. Chem. Res.* **55**(28), 7801–7809 (2016)
160. Huang, P., Ye, L.: In situ polymerization of cationic polyacrylamide/montmorillonite composites and its flocculation characteristics. *J. Thermoplast. Compos. Mater.* **29**(1), 58–73 (2016)
161. Xie, P., de Lannoy, C.F., Ma, J., Wang, Z., Wang, S., Li, J., Wiesner, M.R.: Improved chlorine tolerance of a polyvinyl pyrrolidone-polysulfone membrane enabled by carboxylated carbon nanotubes. *Water Res.* **104**, 497–506 (2016)
162. Lee, J., Ye, Y., Ward, A.J., Zhou, C., Chen, V., Minett, A.I., Lee, S., Liu, Z., Chae, S.R., Shi, J.: High flux and high selectivity carbon nanotube composite membranes for natural organic matter removal. *Sep. Purif. Technol.* **163**, 109–119 (2016)
163. Thomas, S., Mishra, R.K., Asiri, A.M. (eds.): *Sustainable Polymer Composites and Nanocomposites*. Springer (2019)
164. Akhrame, M.O., Fatoki, O.S., Opeolu, B.O., Olorunfemi, D.I., Oputu, O.U.: Polymeric nanocomposites (PNCs) for wastewater remediation: an overview. *Polym.-Plast. Technol. Eng.* **57**(17), 1801–1827 (2018)
165. Palit, S.: *Nanomaterials for Industrial Wastewater Treatment and Water Purification*. Handbook of Ecomaterials, Springer, Cham (2017)
166. Goei, R., Dong, Z., Lim, T.T.: High-permeability pluronic-based TiO₂ hybrid photocatalytic membrane with hierarchical porosity: fabrication, characterizations and performances. *Chem. Eng. J.* **228**, 1030–1039 (2013)
167. Raoufi, N., Surre, F., Rajarajan, M., Sun, T., Grattan, K.T.: Optical sensor for pH monitoring using a layer-by-layer deposition technique emphasizing enhanced stability and re-usability. *Sens. Actuators, B Chem.* **195**, 692–701 (2014)
168. Hsu, L., Selvaganapathy, P.R., Brash, J., Fang, Q., Xu, C.Q., Deen, M.J., Chen, H.: Development of a low-cost hemin-based dissolved oxygen sensor with anti-biofouling coating for water monitoring. *IEEE Sens. J.* **14**(10), 3400–3407 (2014)
169. Gutiérrez-Capitán, M., Baldi, A., Gómez, R., García, V., Jimenez-Jorquera, C., Fernández-Sánchez, C.: Electrochemical nanocomposite-derived sensor for the analysis of chemical oxygen demand in urban wastewaters. *Anal. Chem.* **87**(4), 2152–2160 (2015)
170. Pelaez, M., Nolan, N.T., Pillai, S.C., Seery, M.K., Falaras, P., Kontos, A.G., Dunlop, P.S.M., Hamilton, J.W.J., Byrne, J.A., O’Shea, K., Entezari, M.H., Dionysiou, D.D.: A review on the visible light active titanium dioxide photocatalysts for environmental applications. *Appl. Catal. B* **125**, 331–349 (2012)

171. Yuan, Y., Liu, F., Xue, L., Wang, H., Pan, J., Cui, Y., Chen, H., Yuan, L.: Recyclable escherichia coli-specific-killing AuNP–polymer (ESKAP) nanocomposites. *ACS Appl. Mater. Interfaces*. **8**(18), 11309–11317 (2016)
172. Ma, P.X.: Scaffolds for tissue fabrication. *Mater. Today* **7**(5), 30–40 (2004)
173. Feldman, D.: Polymer nanocomposites in building, construction. *J. Macromol Sci, Part A* **51**(3), 203–209 (2014)
174. Carretero, M.I., Pozo, M.: Clay and non-clay minerals in the pharmaceutical industry: part I. Excipients and medical applications. *Appl. Clay Sci.* **46**(1):73–80 (2009)
175. Gajdziok, J., Holešová, S., Štembírek, J., Pazdziora, E., Landová, H., Doležel, P., Vetchý, D.: Carmellose Mucoadhesive Oral Films Containing Vermiculite/Chlorhexidine Nanocomposites as Innovative Biomaterials for Treatment of Oral Infections, p. 580146. *BioMed Research International*, Article ID (2015)
176. Saraceno, R., Chiricozzi, A., Gabellini, M., Chimenti, S.: Emerging applications of nanomedicine in dermatology. *Skin Res. Technol.* **19**(1), e13–e19 (2013)
177. Roszek, B., De Jong, W.H., Geertsma, R.E.: Nanotechnology in Medical Applications: State-of-the-Art in Materials and Devices. RIVM report 265001001/2005 (2005)
178. Meaney, J.F., Goyen, M.: Recent advances in contrast-enhanced magnetic resonance angiography. *Eur. Radiol.* **17**:B2–B6 (2007)
179. Mathiazhagan, A., Joseph, R.: Nanotechnology-a new prospective in organic coating-review. *Int. J. Chem. Eng. Appl.* **2**(4), 225–237 (2011)
180. Gacitua, W., Ballerini, A., Zhang, J.: Polymer nanocomposites: synthetic and natural fillers a review. *Maderas. Ciencia Y Tecnología* **7**(3), 159–178 (2005)
181. Majeed, K., Jawaid, M., Hassan, A.A.B.A.A., Bakar, A.A., Khalil, H.A., Salema, A.A., Inuwa, I.: Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. *Mater. Des.* **46**, 391–410 (2013)
182. Pourjavadi, A., Fakoopoor, S.M., Hosseini, P., Khaloo, A.: Interactions between superabsorbent polymers and cement-based composites incorporating colloidal silica nanoparticles. *Cement Concr. Compos.* **37**, 196–204 (2013)
183. Al-Safy, R., Al-Mahaidi, R., Simon, G.P., Habsuda, J.: Experimental investigation on the thermal and mechanical properties of nanoclay-modified adhesives used for bonding CFRP to concrete substrates. *Constr. Build. Mater.* **28**(1), 769–778 (2012)
184. Amini, R.S., Tirri, T., Wilen, C.E.: Synthesis and characterization of polyurethane (PU)/clay nanocomposite adhesives. *J. Appl. Polym. Sci.* **129**, 1678–1685 (2013)
185. Scarfato, P., Di Maio, L., Fariello, M.L., Russo, P., Incarnato, L.: Preparation and evaluation of polymer/clay nanocomposite surface treatments for concrete durability enhancement. *Cement Concr. Compos.* **34**(3), 297–305 (2012)
186. Korkin, A., Rosei, F. (eds.): *Nanoelectronics and Photonics: from Atoms to Materials, Devices, and Architectures*. Springer Science & Business Media (2008)