Metal Particle Filled PVC Composites and Nanocomposites

Selcan Karakuş and Cemal Özeroğlu

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

Keywords PVC composite · Nanocomposite · Metal fillers

1 The Fabrication of Metal Particle Filled PVC Composites/Nanocomposites

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

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

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

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

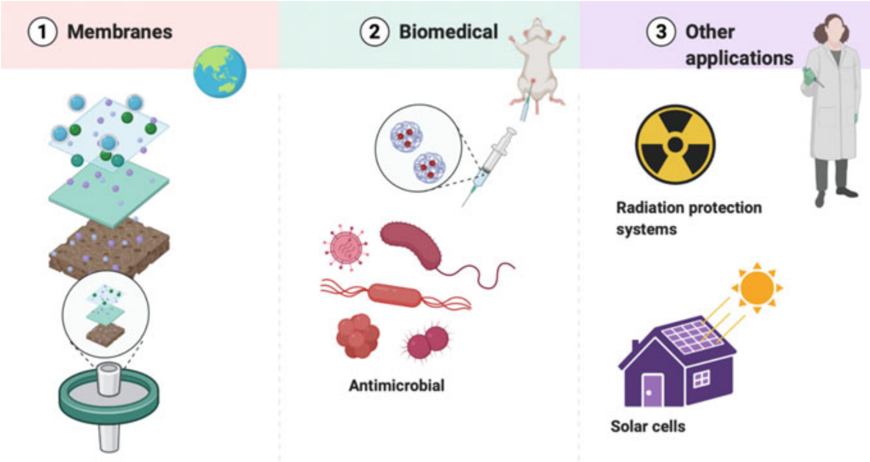

Fig. 1 The schematic diagram of classification and application of PVC composites. **Alt-text**: Different schematic diagrams of classification and application of PVC composites are presented. The shapes of three schematic diagrams of applications of PVC composites are shown. Different types of applications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

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

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

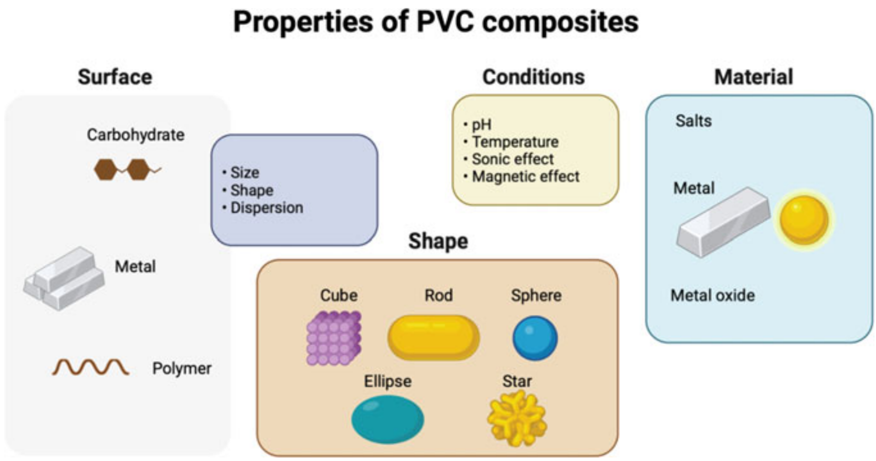

Fig. 2 The schematic diagram of properties of PVC composites. **Alt-text**: The schematic diagram of properties of PVC composites are presented. The shapes of four schematic diagrams of properties of PVC composites are shown. Different types of properties such as surface (carbonhydrate, metal additives,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

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

2 Iron/Iron Oxide Filled PVC Composites/Nanocomposites

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

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

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

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

3 Ag Filled PVC Composites/Nanocomposites

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

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

4 Cu/CuO Filled PVC Composites/Nanocomposites

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

5 ZnO Filled PVC Composites/Nanocomposites

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

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

6 ZrO_2 Filled PVC Composites/Nanocomposites

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

7 Al_2O_3 Filled PVC Composites/Nanocomposites

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

8 TiO_2 Filled PVC Composites/Nanocomposites

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

9 Other Metal Fillers Based PVC Composites/ Nanocomposites

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

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

10 Challenges and Future Research

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

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

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