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Studies on Characteristics of Polymer/Ceramics Nanocomposites for Biomedical and Industrial Applications

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The nanocomposites of polymer doped with ceramic nanoparticles have many applications in biomedical and industrial sectors. The nanocomposites consisting of polymers like polyvinyl alcohol and polyacrylic acid with ceramic nanoparticles such as SrTiO₃ ones can be considered as promising materials for different modern fields. The present work includes review of recent publications on polymer/ceramic nanocomposites concerning their characterization and modern applications. From the previous studies, the polymer nanocomposites have huge applications in different fields like sensors, antibacterial agents, solar cells, transistors, etc.

Нанокompозити полімеру, легьованого керамічними наночастинками, мають багато застосувань у біомедичному та промисловому секторах. Нанокompозити, що складаються з полімерів, таких як полівініловий спирт і поліакрилова кислота з керамічними наночастинками, такими як SrTiO₃, можна розглядати як перспективні матеріали для різних сучасних областей. Ця робота включає огляд останніх публікацій з нанокompозитів полімер–кераміка щодо їхньої характеристики та сучасних застосувань. З попередніх досліджень полімерні нанокompозити мають величезні застосування в різних областях, таких як давачі, антибактеріальні засоби, сонячні елементи, транзистори тощо.

Key words: nanocomposites, polymers, SrTiO₃, antibacterial agents, sensors.

Ключові слова: нанокompозити, полімери, SrTiO₃, антибактеріальні засоби, давачі.

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1. INTRODUCTION

Nanotechnology is a field, in which applied technology and science deal with materials of wide surface areas in the nanoscale range. Most commonly, those nanoscale particles referred to as nanoparticles (NPs), they have potential to generate the micro- and macro-materials and atomic precision products. The development of processes for synthesis of NPs of various shapes, sizes and regulated disparity is an essential aspect of this research [1]. The sizes of NPs are ranged from 1 to 100 nm. The miniaturization of existing and new instruments, sensors and machines, which will significantly affect the environment, is an important feature of nanotechnology. Possible miniaturization examples include: computers with exponentially great strength of calculation algorithms to imitate human brains, biosensors, which alert us at the early stage of the onset of disease, targeting specific drugs, which attack diseased cells automatically *in situ*, and nanorobots, which can eliminate chemical toxins and repair internal damage in the human body. Nanotechnology research is developed and expands very quickly [2]. In the last decade, the synthesis of iron-oxide nanoparticles has been intensively developed to be produced for many technical and biomedical applications and not just for its fundamental scientific interest [3]. Other fields include biomaterials based on polymers, drugs delivery, fuel-cell electrodes, microemulsion particles, layer-by-layer self-assembling polymer films, polymer-bound catalysts, lithography, polymer blends, and nanocomposites. There are several different topics addressed by nanocomposites, such as: bactericidal properties, flame resistance, barrier properties, cosmetic applications, composite reinforcement, and electrooptical properties [4]. Nanotechnology is helping to change considerably many technology and business sectors, information technology, medicine, textiles, food, cosmetics, paints and coatings, glass, plastics, environmental science and many more [5]. Nanoscience and nanotechnology have great promise in the biologically diverse marine environment [6].

2. POLYMERS

Polymers may be synthetic or natural. There are a wide number of different kinds of man-made polymers: elastomers, adhesives, plastics, textile fibres, synthetic rubbers, *etc.* In each kind, there are subgroups; polymers of biological origin are enzymes, proteins and nucleic acids. Deoxyribose nucleic acid (DNA) is a customizable nu-

cleic acid polymer [7]. A polymer is a large molecule consisting of hundreds or thousands of atoms forming the combination in a chain or network structure of either one, two or, sometimes, more small molecule forms (monomers) [8]. The polymer special properties are due to its long-chain structure. The physical characteristics depend directly on the molecular weight and structures [9], which, in turn, are assembled from the original raw materials. Polymerization is the process by which covalent bonds join small molecules; usually, three phases are required for polymerization, *i.e.*, initiation, propagation, and termination. The number of repeating units in the polymer is called the degree of polymerization [10].

3. MOLECULAR COMPOSITION

The physical properties of polymeric materials not just depend on their form and molecular weight, but also on the structure of their molecules [11, 12].

(1) Linear polymers: there is Van der Waals bonding between chains, for examples, in nylon and polyethylene. **(2) Crosslinked polymers:** chains are connected by bonds, which are covalent; it is often achieved through the addition of atoms or molecules, which form covalent links between chains. **(3) Branched polymers:** the efficiency of chain packing is reduced compared to lower-density linear polymers; many rubbers have this structure. **(4) Network polymers:** 3D tri-function networks, for example, in epoxies.

Figure 1 shows these four types of polymers [13].

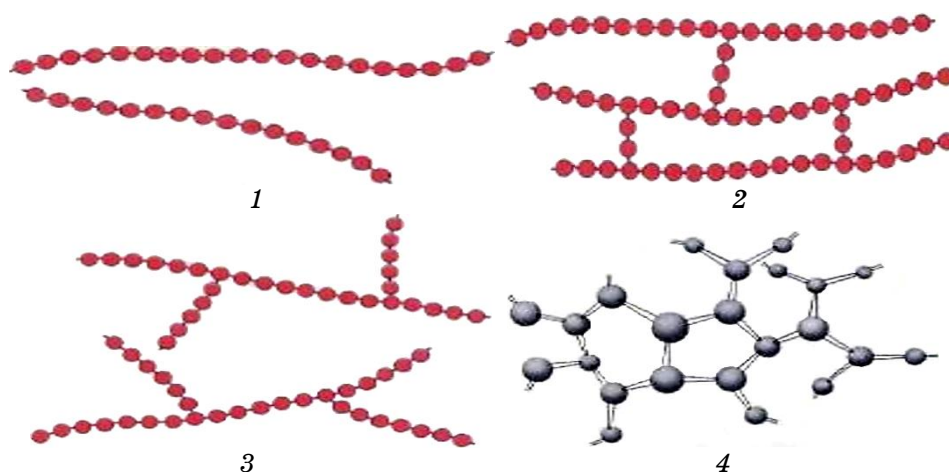


Fig. 1. Types of polymer: 1—linear; 2—branched; 3—crosslinked; 4—network [13].

4. POLYMER BLENDS

The fate of blends of polymers is derived from their components' compatibility and miscibility. The miscibility of two polymers depends on the particular relationships between the polymer chains.

The entropy component in the following equation, which describes Second law of thermodynamics, can explain this one:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}, \quad (1)$$

where ΔH_{mix} —change in enthalpy, ΔG_{mix} —change in free energy, T —absolute temperature, ΔS_{mix} —change in entropy; the Gibbs free mixing energy requires a negative value for a homogeneous miscible blend. The increase in entropy is negligible for high molecular-weight polymer blends. Consequently, the free mixing energy may be negative only if the mixing heat is negative. This implies that the blending should be exothermic, which involves typically distinct interactions between the components of the blend. These interactions, including bonding of hydrogen, ion–dipole, dipole–dipole, and donor–acceptor interactions, can range from strongly ionic to weak and non-bonding.

Three kinds of blends may be distinguished on the basis of miscibility: (i) absolutely miscible blends, (ii) partly miscible blends, (iii) totally immiscible blends. One of the homogeneous processes consists of mixtures, which are fully miscible. There is only one glass transition temperature, T_g , presented in this type of mixture, which lies between the magnitudes of T_g of each of the components of the mixture and has a close relationship to the composition of the mixture. Blends, which are partly miscible, in which a portion component of one of the blend is soluble in the other, typically show the good compatibility and morphology of the good process. Completely immiscible blends, however, have the morphology of a coarse phase with the sharp interface and the low adhesion between the two mixing stages. This is the explanation for the commonly weak properties for immiscible blend, which are observed and heavily dependent on the size and the distribution of the phase [14]. A common way to create new materials with improved properties is to shape polymer blends. Unfortunately, most polymer blends appear with phase separated because of the great unfavourable enthalpy, resulting in poor mechanical properties. The regulation of phase behaviour and morphology is, therefore, a key factor in determining the efficiency of polymer blends, which depend primarily on the interface between polymer components. In order to reinforce the interface and stabilize the morphology, block and graft copolymers are used traditionally. However, for systems with more than two components, they

are system-specific, relatively costly to engineer, and very difficult to produce [15].

5. POLYMER NANOCOMPOSITES

Nanocomposites (NC) are multiphase materials where nanoscale additives are used in one of the components. Nanocomposites could be categorized as nanocomposites of polymer matrix, according to matrix materials (PMNC), ceramic-matrix nanocomposites (CMNC) and metal-matrix nanocomposites (MMNC) [16, 17]. Nanocomposites have been developed with enhanced electrical, optical and thermal properties and other unique characteristics through the variety and progress of studies, and this is why nanocomposites are used in many fields. It can be produced using simple and cheap technologies. Due to their dielectric properties and high resistivity, polymers were used as insulators in early operations. Polymer insulator uses include the electronic devices for corrosion protection, the printed circuit boards, and materials for the sheathing of cables. There are various other applications such as biological implants, automotive or aircraft components. There are many benefits of polymers, for example, low cost, fast treatment, durability, strong high strength and mechanical properties. They are used in the photolithography process in the microelectronic fabrication industry [18–20]. Polymeric nanocomposites consisting of inorganic nanoparticles and organic polymers constitute a class of materials, which, in recent years, have created considerable interest [21]. Nanocomposites have other promising applications such as sensors, drug delivery, optical integrated circuits, consumer goods, *etc.* [22]. Nanocomposites and composite materials have huge applications in the different biomedical, environmental and industrial fields like energy storage and release [23–26], antibacterial agents [27–35], humidity sensors [36–39], bioenvironmental and radiation shielding [40–46]. The adding of micro- or nanoparticles of biomaterial to polymer or polymer blend can improve the properties of polymer matrix like electronic properties [47–52], optical properties [53–75], electrical and dielectric properties [76–89]. Bionanocomposites are a fascinating interdisciplinary field of materials science, biology, and nanotechnology. BioNC consist of a polymer matrix and a nanoscale organic/inorganic filler with at least one dimension [90].

6. POLYVINYL ALCOHOL (PVA)

One of the most common polymers available in the form of powders, fibres and films is polyvinyl alcohol (PVA). Intensive research has

recently been the focus of research since it has many industrial applications and relatively low levels of production costs. The polyvinyl alcohol is a soluble in water, non-toxic, and a synthetic polymer that, because of its strong physical properties, is widely used in the polymer nanocomposite [91]. Polyvinyl alcohol is a semi-crystalline at 230°C, and a temperature of glass transition, T_g , is of 85°C. Polyvinyl alcohol is colourless and odourless as a film, resistant to solvents, oils and greases, with excellent cellulose and other hydrophilic surface adhesion [92, 93]. When it is pure, the polyvinyl alcohol (PVA) is a white, light, powdery solid polymer. A light PVA dust during processing can be a fire and explosion threat due to oxidation during preparation; PVA specimens are often off-white or even light yellow [94]. It is possible to combine PVA with other material in order to obtain a stronger composite according to its utility [95]. The precipitate of this reaction is known as the polyvinyl alcohol.

Figure 2 [96, 97] shows the PVA structure.

PVA has unique characteristics: excellent chemical stability, eco-friendly one, optical and electrical characteristics. Semi-crystalline nature of PVA, namely, amorphous and crystalline regions, causes interfacial effects, which increase physical features [98].

The key physical and chemical properties of PVA are described in Table 1.

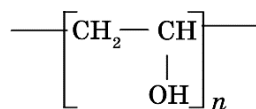


Fig. 2. The chemical structure of polyvinyl alcohol [97].

TABLE 1. Physical and chemical properties of PVA [99].

Property	Description
Appearance	White to ivory white granular powder
Molecular formula	$(\text{C}_2\text{H}_4\text{O})_n$
Density, g/cm^{-3}	1.19–1.31
Solution pH	5–6.5
Refractive index	1.55
Decomposition	above 200°C
Glass transition temperature (T_g), °C	75–85
Melting temperature (T_m), °C	230

7. POLYACRYLIC ACID (PAA)

In 1843, the term 'acrylic' was coined for a chemical derivative of acrolein, which is oil derived from glycerol. Polyacrylic acid (PAA; trade name 'Carbomer') is a polymer with high molecular synthetic weight.

Dry PAA sold powders are white, fluffy and often used in personal care and cosmetic items as gels. In the cosmetics, their function is to suspend solids in fluids, to prevent separation of emulsions, and to monitor the consistency of cosmetic flow.

Polyacrylic acid (PAA) is a type of commercial polymer that is widely used in a variety of industries, agriculture, and medicine [100].

PAA and related compounds are increasingly being used as polymeric carriers for proteins, enzymes, drugs, and other biologically active materials. In the above case, PAA can be used to solve problems relating to biopolymer chemistry and technology for medical applications.

Polyacrylic acid is a common term for acrylic acid polymers with a high molecular weight. PAA is an anionic polymer in a neutral pH water solution, meaning that many of its side chains lose their protons and gain a negative charge [101]. Polyacrylic acid (PAA) is a valuable medical and pharmaceutical material that can play a role in the delivery and defence mechanism of drugs. Unfortunately, the use of PAA as a mucoidhesive drug carrier is critically restricted by high water solubility [102].

And for biomedical uses of different polymers and polymer-based materials, including polyacrylic acid (PAA) and the derivatives of it, they are used in the development of the medical probes for examination, the portable filters for water, the surface coatings and the fibre disinfectants [103].

Table 2 shows the properties of PAA.

TABLE 2. The properties of PAA [104].

Property	Value
Chemical formula	$(C_3H_4O_2)_n$
Molar mass, g/mole	72.1
Surface tension, mN/m	29–35
Density (ρ), g/cm ³	1.48
Glass transition temperature (T_g), °C	106
Refractive index	1.527
Molar heat capacity (C_p), J/(mol·K) ⁻¹	92
Viscosity coefficient, cm ³ ·mol ^{1/2} ·g ^{-3/2}	0.076–0.165

8. STRONTIUM TITANATE (SrTiO₃)

Let us explore strontium titanate nanoparticles (SrTiO₃ NPs) in order to contribute to the development of applications sensitive to electrochemical enzyme. SrTiO₃ NPs have a large surface area, which enhances this apparently direct electron transmission [105]. Strontium titanate (SrTiO₃) is a technologically important electric ceramic material; its properties depend strongly on the crystal structure, shape, crystallinity, and size [106]. SrTiO₃ is used for sensors, photoelectrodes, *etc.* [107].

Table 3 shows the physical properties of SrTiO₃.

Nanocomposites have many uses for medical and industrial purposes. In previous studies, the optical and electrical characteristics were investigated for their applications with respect to various composites and nanocomposites. In 2010, I. Ivieva *et al.* [109] studied the optical properties of PVA films with diamond and titania nanoparticles; they found that the refractive index increases as the concentration of titania and diamond inclusions in the PVA matrix are increasing. In 2012, H. Ahmad *et al.* [110] examined the electrical and optical properties of PVA/LiI polymer electrolyte films. They found that dielectric loss and dielectric constant are increased with the rise of LiI concentration. The optical energy gap decreases with increasing LiI concentration.

In 2013, R. Tomar and C. R. Sharma [111] examined the effect of doping alumina nanoparticles in ion-conducting polymer and found that the nanocomposite conductivity increases with increasing of alumina nanoparticles' concentration. In 2014, H. Chandrakala *et al.* [112] studied the electrical, optical and structural properties of polyvinyl alcohol/zinc oxide–cerium oxide nanocomposites. They found that dielectric constant and dielectric loss increase with increasing nanoparticles' concentration, but decrease with increasing frequency. A.C. conductivity of PVA–ZnO–Ce₂O₃ nanocompo-

TABLE 3. The physical properties of SrTiO₃ [108].

Property	Value
Lattice parameter at RT, nm	0.3905
Atomic density, g/cm ³	5.12
Melting point, °C	2080
Mohs hardness	6
Dielectric constant	300
Thermal conductivity, W/(m·K)	12
Coefficient of thermal expansion, Å/°C	9.4·10 ⁻⁶
Refractive index	2.31–2.38

sites was increased with increasing frequency. Optical properties show the formation of charge-transfer complexes between hydroxyl groups of PVA and nanoparticles. In 2015, B. Chatterjee *et al.* [113] studied the electrical properties of a starch–PVA polymer blend with add KCl. They found that conductivity and dielectric constant of starch–PVA polymer blend raise with rising of the concentration ratio of salt. In 2018, R. M. Tripathi *et al.* [114] studied the antibacterial activity of nanocomposite film (polyvinyl alcohol–silver) for food-packaging materials. The results show that the disk diffusion method was used to investigate the antibacterial activity of the nanocomposite film against *Salmonella typhimurium*. The antibacterial efficacy of a polyvinyl alcohol–silver nanocomposite film against *Salmonella typhimurium* is excellent. In 2019, F. M. Ali *et al.* [115] investigated the optical characteristics of the PVA films, which are doped with methyl violet-6B (MV-6B), which is obtained *via* the casting process. They found that the addition of MV-6B to PVA leads to increase in absorbance, and the value of energy gap is decreasing with raising concentration of MV-6B (0, 0.01, 0.04, 0.08 and 0.1) mol.% to become of 5.01, 4.91, 4.76, 4.66 and 4.59 eV, respectively.

9. CONCLUSIONS

In the present work, review on characterization and modern applications of polymer–ceramic nanocomposites was investigated. The previous studies showed that the polymer nanocomposites have huge applications in different fields like sensors, antibacterial agents, solar cells, transistors, and others applications. The nanocomposites of polymer doped with ceramic nanoparticles have many applications in biomedical and industrial sectors. The nanocomposites consisting of polymers like polyvinyl alcohol and polyacrylic acid with ceramic nanoparticles such as SrTiO₃ nanoparticles can be considered as promising materials for different modern fields.

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