Silver Nanoparticle on Various Synthetic Polymer Matrices: Preparative Techniques, Characterizations, and Applications

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1 Introduction

Polymer nanocomposites achieved significant attention in recent years and also have become essential materials in modern nanotechnologies. This interest arises as a result of their outstanding performance, design flexibility, higher properties compared to constituent materials, low life cycle cost, and enormous applicability of nanocomposites in various engineering and industrial fields. The polymer nanocomposites are advanced functional materials that constitute nanoparticles/nanofillers dispersed inside the polymer matrix forming in a core-shell structure. The shape of these reinforcement varies (like fibers, platelets, spheroids) at least should have the dimension in the range of 1–50 nm. For manufacturing, nanocomposites follow strict requirements in each step, such as controlled/optimized mixing, stabilized dispersion, and orientation of the dispersed phase should be controlled for all multi-phase systems.

For particle, the transition from micro to nano is due to changes in their chemical and physical structure, which contributes to their unique properties. The smaller particle size enhances the surface area-to-volume ratio, which leads to the dominant behavior of atoms due to the higher surface area of nanoparticles. There is more possibility to have one-to-one interaction with other particles present inside. Therefore, the nano filled polymer composites pose enhanced thermal resistivity and mechanical strength by the inclusion of nanoscale filler. It is essential to maintain the uniform distribution of nanoparticles as it substantially improves the overall performance of the composites. Among nanoparticles, silver nanoparticles

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(AgNPs) merit special attention due to their efficient applicability in the biomedical field, especially as antimicrobial agents. AgNPs are commonly applied in various industrial applications such as the production of electronic circuits, inkjets, sensors, biomarkers, photography, etc. As mentioned, these properties of AgNPs are strongly influenced by their aspect ratio, shape, size, and distribution.

The synthesizes of AgNPs include various methods such as physical, chemical, photochemical, and biological routes (Natsuki 2015). Each of these methods has its advantages and disadvantages. Physical and photochemical methods for AgNPs synthesis need strict control over the reaction and expensive equipment, but it doesn't include the usage of toxic chemicals. However, the chemical synthesis of AgNPs is comparatively cheaper. The main drawback is the usage of very toxic chemicals. In recent years the AgNPs synthesized using plant-based non-toxic photochemical inclined to use a safer chemical process with an efficient transformation of desires products. The industrial production of AgNPs uses phytochemicals reducing agents and biocompatible polymer-based stabilizers. Thus, this method is considered more environmentally friendly. The microorganism based biological process for the synthesis of silver nanoparticles also recently developed. However, this method also has some disadvantages and is not preferred for the industrial production of silver nanoparticles.

It is well known that due to the size, shape, surface chemistry, and aspect ratio of AgNPs it characterizes quite different from bulk silver. The aforementioned properties of AgNPs give unique and desired properties to the nanocomposites while incorporating within different polymer matrices. The uniform dispersion and strong interfacial interaction of AgNPs with the polymer matrix create a huge nano-dimensional interface in the polymer nanocomposite. Thus, the polymer matrix is found to modify the surface chemistry of AgNPs and prevent the aggregation of nanoparticles. The interfacial interaction between the AgNPs and polymer matrix is responsible for the unique and desired properties, and thus suits many advanced applications. Many polymer matrices incorporated with AgNPs interestingly act themselves as the reductants for silver ions. The silver polymer nanocomposites utilized for wound healing applications can effectively eject silver ions which can act as an anti-microbial agent. The sliver-based nanocomposites can be used as a heterogeneous reusable catalyst and hence can be easily separated using the filtration method from the reaction medium. This chapter includes the elaborated discussions on AgNPs based polymer nanocomposites, synthesis, properties, and various applications.

2 Types of Polymer Matrices

To fabricate polymer nanocomposites almost all types of polymer matrices such as plastics, fibers, and elastomers are commonly used. This list of polymer matrix ranges from low molecular weight elastomers and high molecular weight resins are also utilized for manufacturing various thermosetting polymer nanocomposite. Both

thermoplastics and thermosetting polymers are used for manufacturing polymer nanocomposites. By the homogeneous dispersion of nanoparticles in the polymer matrix will improve its performance. The polymer matrix in which the nanofillers or nanoparticles uniformly dispersed is not only a continuous phase but also stabilizes and strongly interacts with nanoparticles.

Polymers are macromolecules (organic or inorganic molecules) constituents formed by the linkage of a large number of repeating units. The repeating units are called monomers which are formed of simple molecules. The process of linkage of simple monomers to giant polymer molecules is known as the polymerization process. The number of repeating units formed in a polymer chain is termed as a degree of polymerization and it is used for determining the molecular weight of polymer from the known molecular mass of repeating unit. The polymers are manufactured using different techniques such as addition, condensation, and rearrangement polymerization techniques. The addition polymerization includes the monomer bond together one after another by covalent bonding without elimination of any by-products. There are different types of addition polymerization, the first type is free radical polymerization that includes controlled radical polymerization such as atom transfer radical, group transfer, and chain transfer. The second type is ionic polymerization such as anionic and cationic polymerization, etc. The examples of polymers manufactured utilizing addition polymerization techniques are polyethylene, polystyrene, polyvinyl chloride, polymethyl methacrylate, polytetrafluoroethylene, polyisoprene, polybutadiene, polychloroprene, polyacrylonitrile, etc. are examples of homopolymers, that includes the combination of the same type of monomer. The different combinations of more than one type of monomers to form as co-polymers include polymers such as ethylene-propylene copolymer, polybutadiene-styrene poly acrylonitrile-butadiene, poly acrylonitrile-butadiene-styrene, poly-vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene), etc. All these polymers are manufactured utilizing the addition polymerization technique. The formation of co-polymers results in improved properties as compared to homopolymers and is also flexible polymers because of the internal plasticization effect. In the condensation polymerization technique, the mutually reactive reactants undergo polycondensation reactions in which the polymers are formed by the step-growth mechanism that involves the elimination of small molecules as byproducts. polyesters, polycarbonates, polyethers, poly(ester amide)s, polyamides polyimides, polysulfones, poly(ether ketone)s, etc. are examples of polymers manufactured utilizing condensation polymerization. On the other hand, if the polymers are formed by a step-growth mechanism without any elimination of byproducts, then the polymerization process is termed as a rearrangement polymerization process. The polymers formed by this process are polyurethanes, polyureas, polyurethanes, etc. All these aforementioned polymerization processes are conducted mainly by four polymerization techniques such as mass/bulk, solution, suspension, and emulsion polymerization. Moreover, these four techniques interfacial, template, electrochemical, and plasma polymerizations are employed depending on the requirements of the products.

The polymers process different structures that include linear chains with low branched, high-branched, and hyperbranched structures (dendrimers). The hyperbranched polymers possess three-dimensionally branched macromolecules with large surface free functional groups and these type polymers are highly compatible with others and highly soluble in a vast number of solvents. Compared to other types of polymers the hyperbranched polymers are easy to process, therefore these polymers are an ideal class of matrices for polymer nanocomposites. Generally, all the polymers mentioned above can be easily processed utilizing different techniques such as solution mixing, suspension mixing, emulsion mixing, melt mixing, and rubbery stage mixing, etc. The general classification of polymers includes thermoplastic polymers that can be processed repeatedly in a controlled manner without losing its property, other classification is thermosetting polymers as once they set or chemically cross-linked in the final stage of processing, they are not possible to process again. The overall properties of a polymer can be identified from its structure and molecular weight. The main drawbacks of polymers are its poor mechanical, thermal, flame retardant properties, and its biodegradability. However, polymers are superior over metals and ceramics because of their advantages like easy processing, versatility in structure, modification, and relatively low cost. Due to these advantages of polymers, they are chosen as superior material as matrices for manufacturing nanocomposites.

Based on the origin of polymers, they can be classified as natural polymers and synthetic polymers. All the polymers we mentioned above are synthetic polymers, natural polymers are the polymers that obtain naturally, including polysaccharides (starch, alginate, chitosan/chitin, hyaluronic acid derivatives) or proteins (collagen, soy, silk, fibrin gel), etc. There are many advantages and disadvantages that characterize these two different origins of polymers, as mentioned synthetic polymers have high mechanical strength and modifiable structure and properties compared to natural polymers. Natural polymers have their potential advantage of biologically reorganizations and, but they have poor mechanical properties compared to synthetic polymers. Natural polymers based nanocomposites where natural polymers act as matrix and nanoparticle act as nanofillers donates great potential to be utilized for various applications such as wound healing, food packaging, biomedical industry, etc.

3 Preparation of Polymer Silver Nanocomposites

Silver/polymer nanocomposites are fabricated using preformed AgNPs or either by introducing silver precursors to polymer matrix followed by the preparation of AgNPs. The other method includes the preparation of polymer in the presence of silver precursors or preformed AgNPs. The electrospinning technique for the fabrication of polymer/silver nanocomposites includes the homogeneous nanoscale dispersion of polymer-AgNPs in a polar solvent or solvent mixture such as methanol, ethanol, acetonitrile, etc. The AgNPs-polymer nanocomposites are

manufactured as silver-impregnated nanofibers utilizing an electrospinning technique. Generally, AgNPs- polymer nanocomposites are manufactured by the conventional techniques that are employed for the preparation of polymer nanocomposites. The main objective for the manufacturing of polymer nanocomposite is to fabricate them with a higher amount of interfacial interaction between polymer and nanoparticles, this could be attained by the uniform distribution of nanoparticle throughout the polymer matrix and maximum degree of nano dimensional interface should be achieved in the resultant polymer composite. The presence of an appropriate functional group in the polymer matrix and nanoparticle can increase interaction between nanoparticle and polymer matrix interface. The ultrasonic force and mechanical shearing are also employed commonly for the uniform distribution of nanoparticles inside the polymer matrix. Thus, it is very crucial for choosing the appropriate method for the manufacturing of polymer nanocomposite for exploring their maximum potential. A detailed description of the types of polymer matrices and preparative techniques for manufacturing nanocomposites are discussed below.

3.1 Solution Technique

In this technique, a polymer solution and nanoparticle are well dispersed to a homogeneous mixture, this can be done by utilizing a mechanical shearing followed by ultrasonication. For making the homogenous mixture a polymer solution is prepared separately in a solvent, and the nanoparticle is dispersed in a liquid medium by proper homogenization. The liquid medium used for both polymer and nanoparticle should be miscible. Both the solution is mixed homogeneously, the unwanted solvent is removed from the prepared homogeneous mixture either by evaporating the solvent from the mixture or by precipitation of polymer/nanomaterial dispersion. The significant interaction between the polymer and nanomaterial must be greater than polymer-solvent and nanomaterial –solvent interactions. The strong interaction between the polymer and nanoparticle helps the polymer chains to penetrate inside the structure of nanoparticles, also the polymer chains are absorbed to the surface of nanoparticle while forming a polymer nanocomposite. In this manufacturing technique, both intercalated and exfoliated nanocomposites are formed. The state of intermixing between the polymer chain and nanoparticle depends on the thermodynamics of mixing, the prepared nanoparticle must be thermodynamically stable, which is governed by favorable enthalpy and entropic factors. The strong interaction between the polymer matrix and nanoparticle results in the higher enthalpy loss, and the Gibbs free energy becomes favorable, the strong interaction between the polymer and nanoparticles also results in a decrease of entropy factor due to the restriction of motions of the polymer chain. The solution technique is a simple process however, it is associated with various drawbacks, such as environmental and health hazards due to the usage of toxic organic solvents, higher cost, flammability, etc., (Xin and Li 2011)

decorated carbon nanotubes (CNT) with AgNPs for manufacturing advanced CNT/polymer nanocomposites utilizing solution technique. The polystyrene is dissolved in reductant followed by the addition of pre-prepared Ag-CNT filler, the mixture is ultrasonicated for 10 min, and the composite was dried in a vacuum oven at 50 °C for 6 h. The composite samples were molded using a hot-press molding machine.

3.2 Melt-Mixing Technique

This technique involves uniform mixing of nanoparticles in preformed polymer matrices utilizing the conventional melt processing equipment for manufacturing polymer nanocomposite with desired properties. The melt-mixing process is commonly preferred by industries because this process avoids the usage of toxic solvents, and is simple and economic. The industrial melt-mixing techniques involve the melting/softening of semicrystalline/amorphous polymers by heating in the mixing equipment such as an extruder, injection molding, Brabender mixer, etc. followed by the incorporation of nanoparticles. The homogenous dispersion of nanoparticle inside the polymer matrix is obtained from the applied mechanical shear force inside the mixing equipment. The environmental friendly processing is the main advantage of this technique, therefor the melt mixing technique for fabrication of polymer nanocomposites is well accepted by various industries. Pre-proofs et al. (2019) prepared AgNPs-polymer nanocomposite by melt-kneading of polymers and silver precursors in an internal mixer. Initially, the polymer was introduced to the mixing chamber, and then the silver precursors were added to the chamber after 2 min of processing of polymer. The polymer/silver precursor mixture was melt-kneaded for a specific duration. Molten silver/polymer nanocomposite was taken out from the chamber and kept at room temperature. The authors employed a one-step solvent less in situ reduction method to convert Ag-precursors to AgNPs during processing, which utilizes a mild reducing environment of thermoplastic polymer melts for reduction.

3.3 In Situ Polymerization Technique

In this technique, the nanoparticle is well dispersed in the low viscous monomer or prepolymer. The polymer is formed in the presence of dispersed nanoparticles and thereby forming the polymer nanocomposites. The dispersion of nanoparticles in the low viscous monomer or prepolymer allows it to adsorb on the surface of dispersed nanoparticle; during the polymerization, the polymer chains help in debundling or delamination or dispersion of nanoparticles. In the case of in situ technique, the viscosity of prepolymers or precursors of the monomer is lower than the respective preformed polymers compared to the solution polymerization technique. Thus the interaction of nanoparticle and the polymer matrix is relatively

stronger. The polymer composites formed by this technique are exfoliated polymer nanocomposites because of low viscosity of prepolymer, uniform dispersion of nanoparticles, and strong interfacial interaction between polymer matrix and nanoparticles. This technique is mainly preferable for manufacturing polymer nanocomposites from resin due to the minimum solvent used and lower energy requirement. In addition, it is notable that if the presence of an additional functional group in the nanomaterial can form a crosslinking reaction while processing thermosetting polymer nanocomposites. Eisa et al. (2012) prepared a well-dispersed AgNPs in polyvinyl alcohol (PVA)/polyvinyl pyrrolidone (PVP) blend films using in situ technique where PVP and PVA act as stabilizers and polyol as reductant. The authors used 0.6 ml of 0.05 M of $AgNO_3$ was added to the homogeneous solution of PVA/PVP blend prepared in different polymer ratios (100/0, 80/20 50/50, and 20/80). The polymer composite films obtained exhibit excellent anti-bacterial activities and are suitable for various biomedical applications.

3.4 Sol-Gel Method

In this method, nanoparticles are prepared in the polymer matrix. It involves the gel or aqueous solution containing the precursors, or building blocks of the nanoparticles polymer matrix is subjected to elevated temperature by heating. During the treatment, the polymer aids the nucleation and growth of nanoparticles and thus the nanoparticle formed are trapped inside the polymer matrix. The nanocomposites formed are in the colloidal form and polymer nanocomposites in the colloidal form are usually prepared using this technique. The main advantage of this technique involves the potential of promoting the uniform dispersion of nanoparticles inside the polymer matrix in a one-step process without applying any additional energy. However, this method possesses serious disadvantages like, in case of processing the nanoparticles that require high temperature may decompose polymer matrix. So, this technique is not suitable for manufacturing polymer nanocomposites with clay-based nanoparticle which requires high-temperature processing. Furthermore, the probability of aggregation of nanoparticles is higher due to the harsh processing conditions. Therefore, this technique is less common compared to the aforementioned techniques. synthesized silica silver nanocomposites utilizing the sol-gel process.

3.5 Electrospinning Technique

This is a standard technique for manufacturing polymer nanocomposite based nanofibers. The electrospinning technique involves an automatic hydraulic syringe with a micro-tip needle, a DC source with high voltage, and a collector connected with an electrical earthing. The process of electrospinning involves a polymer

solution in the form of a suitable polar polymer melt mixed with the required amount of nanoparticles. The homogeneous dispersion of polymer melt and nanoparticles are achieved utilizing mechanical shearing followed by ultrasonication similar to the solution technique. The high voltage electric field produces electrically charged jets from polymer solution or melt, which on drying of jets solidify through evaporation of solvent to produce nanofibers. The voltage used in this technique should be high enough so that the electrostatic must overcome the surface tension of polymer melt to come out from the needle tip. The highly charged nanofibers are directed towards an oppositely charged collector, which is in various shapes such as, flat, rotating drum, etc., to collect the fibers Subbiah et al. (2005). The uniformity, dimension, and morphology of manufactured nanofibers depend on the concentration, polarity, and viscosity of the polymer solution/melt, hydraulic pressure exerted from the syringe, flow rate, tip diameter, exerted electric field strength, tip to collector distance, etc. (Abdel-Mohsen et al. 2019) fabricated nanofiber mats by electrospinning of polyvinyl alcohol/hyaluronan solutions in the presence of uniformly dispersed AgNPs. Liu et al. (2017) developed PLA-based fibrous mats with graphene oxide-Ag nanoparticles utilizing electrospinning technique, it shows excellent anti-bacterial properties that are suitable for biomedical applications.

3.6 Template Method

In this method, nanoparticles are prepared from their precursor solution utilizing polymers as the template, the polymer nanocomposite is formed in situ. The main advantage of this process is the possibility of uniform distribution of nanoparticle in the polymer matrix in a single-step process. Even though the materials formed by the template method are of great interest because of the manufacturing of inorganic porous materials. This process is not a commonly used method for industrial manufacturing due to the poor quality of nanocomposites, and also this method does not hold good for the production of polymer nanocomposites.

4 Silver Nanoparticle in Different Synthetic Polymer Matrices

4.1 Polyethylene-Silver Nanocomposites

Polyethylene is a thermoplastic polymer with a crystalline structure. These plastics are classified into two types such as high-density polyethylene (HDPE) and low-density polyethylene (LDPE). The main advantages of polyethylene include high tensile strength, ductility, impact resistance, low moisture absorption.

The higher the density of polyethylene the material becomes more rigid and strong. The primary application of polyethylene includes containers and bottles, plastic bags, plastic films, and geomembranes.

The polyethylene used as a matrix polymer for AgNPs to form polyethylene/silver nanocomposites is widely used for several biomedical applications and food packaging industries due to its excellent anti-microbial activities. The LDPE is the most commonly used thermoplastics for the packaging application due to its high flexibility, easy processability, transparency, environment recyclability, thermal stability, and economic efficiency makes LDPE superior as a packing material. Dehnavi et al. (2013) proposed a novel method for the fabrication of antibacterial LDPE-AgNPs nanocomposite film for food packaging. The synthesis of nanocomposites involves three steps; the first step contains the preparation of AgNPs by the chemical reduction of silver salt using fructose as a reducing agent in a stable colloidal solution, the second step involves the corona air plasma treatment on LDEP film surface to increase the adhesion of AgNPs on the surface of LDPE, and the third step involves adhesion of AgNPs on the surface of LDPE by the immersion of pre-treated LDPE in the colloidal silver solution. The corona pre-treatment of LDPE films improved its adhesion of AgNPs on the polymer surface. This was proved by utilizing FTIR-ATR analysis of the untreated and corona treated LDPE films. The presence of polar groups such as C–O and C = O formed on the surface of LDPE by corona air plasma treatment helps the polymer to increase its hydrophilicity and reactivity of LDPE films; therefore, more AgNPs were coated on the surface of LDPE. The authors found the silver ion release rate of 0.00150 μg/mL cm^2 by immersing a nanocomposite sample of 6 × 10 mm^2 into 125 ml deionized water, and a 2 ml solution was taken at a defined period to identify the presence of silver ions utilizing atomic absorption spectroscopy. The manufactured AgNPs/LDPE nanocomposites exhibits excellent antibacterial properties and were evaluated by agar well diffusion and dynamic shake flask method. Olmos et al. (2018) manufactured homogeneous LDPE/AgNPs nanocomposites using a non-conventional processing method. The high energy ball-milling under cryogenic conditions was utilized to achieve a powder of well-mixed LDPE and AgNPs. The composite film was prepared by hot-pressing. The films possess excellent antibacterial properties against DH5a Escherichia coli cells according to the antimicrobial studies. The AgNPs incorporated with LDPE does not influence its physical, chemical, and thermal properties (Brito et al. 2020).

Several studies are reported on HDPE chosen as the matrix polymer for manufacturing nanocomposites as it has a wide range of biomedical application such as catheters, tubing, syringes, antimicrobial surfaces, device packaging, and several commodity applications such as pipes, water storage containers, kitchen storage plastics, etc. (Roy et al. 2020) manufactured HDPE/silver-clay hybrid nanocomposite by melt mixing technique utilizing a twin-screw extruder. The prepared nanocomposite shows excellent antimicrobial properties. The analysis of in vitro cytocompatible properties of HDPE/silver/clay nanocomposite represents complete compatibility and no viable cell count reduction to human dermal fibroblast and erythrocyte cell lines quantified in vitro in (3-(4,5-dimethylthiazol-2-yl)-

2,5-diphenyltetrazolium bromide (MTT) assay and RBC hemolysis protection assay. In the in vivo analysis, tissue section retrieved from rat skin was surgically stitched with HDPE/silver- clay nanocomposite showed no changes in the morphology after continuous exposure of 21 days.

4.2 Polystyrene-Silver Nanocomposites

Polystyrene (PS) is a hard and stiff thermoplastic polymer produced by the polymerization of its monomer called styrene. These are most commonly used in the food-service industry as containers, disposable eating utensils, and foamed plates, cups, and bowls. The polystyrene matrix for AgNPs could provide effective stabilization nanoparticles and enable the easy processibility for manufacturing AgNPs/PS nanocomposites for the desired application. These nanocomposites can be used in different applications such as surface-enhanced Raman scattering, molecular sensing, a digital memory device, biomedical applications, and antibacterial packaging. Vodnik et al. (2012) manufactured nanocomposites film with AgNPs incorporated in PS matrix in different quantities and its optical and thermal properties were studied as a function of silver content. The nanocomposites were prepared to utilize the solution mixing method. The nanocomposite films exhibited a plasma resonance peak at 470 nm, due to the collective oscillation of free electrons in AgNPs embedded in the PS matrix. The authors compared the experimental bands with theoretical absorption spectra calculated utilizing effective medium Maxwell-Garnett theory. The TGA analysis of the nanocomposite films reveals, the introduction of AgNPs to PS increased slightly the thermal stability of PS and a notable improvement in the thermal-oxidative stability of the nanocomposite films. The glass transition temperature of the nanocomposite film decreased due to the weak interfacial interaction between AgNPs and PS matrix. Ali et al. (2019) manufactured silver/PS-polyvinylpyrrolidone (PVP) nanocomposites utilizing polymerization by γ-ray irradiation. The mechanism of synthesis of silver/PS/PVP nanocomposite is represented in Fig. 1. The AgNPs was dispersed in PVP, the AgNPs was embedded in the PS matrix via subsequent reduction of Ag+ ions by γ-ray irradiation, as it is an effective method for the synthesis of the nanoparticle by the reduction of metal ions. The size of the nanoparticle is controlled by adjusting the values of the irradiation of samples. The PVP not only stabilized the polymer particles but also prevented the nanoparticle from agglomeration. The optical absorption spectra are characterized using UV visible absorption spectroscopy and confirm the redshift of peaks increased within the irradiation dose. As shown in Fig. 2, the absorption band appears at 295 nm is for the PS matrix, while increasing the irradiation dose the intensity peaks are shifted to longer wavelength ranges from ≈420 to 430 nm. This confirms the presence of a large number of nanoparticles with higher γ-irradiation doses. The TGA test reported the thermal stability of polystyrene enhanced with the increase in loaded AgNPs in the PS matrix. PS-methyl acrylic acid (MAA)/silver nanocomposites sphere with high

catalytic activity is prepared by (Liao et al. 2016). The PSMAA/silver nanocomposite spheres are prepared in the aqueous media where the silver precursor [Ag $(NH_3)_2$]+ ions are absorbed on to monodispersed PS-MMA spheres due to the strong electrostatic attraction between the electronegative carboxyl group and electropositive [Ag$(NH_3)_2$]+ ions. The [Ag$(NH_3)_2$]+ ions reduced to AgNPs are protected by PVP on the surface of PSMAA spheres. Krystosiak et al. (2017) proposed a novel approach for preparing PS/silver nanocomposites utilizing nitroxide mediated radical polymerization. This method involves the late injection of nitroxide-coated AgNPs into a TEMPOL mediated styrene polymerization system, the homogeneous PS/silver nanocomposites formed are with well-defined core-shell structure, high grafting density that varies from 2 to 5.9 chain/nm^2, and exhibits effective antibacterial activity.

4.3 Polycarbonate-Silver Nanocomposites

Polycarbonate (PC) are amorphous thermoplastic polymers, they are generally strong, tough, and some grades of this polymer are optically transparent. Unlike other thermoplastic polymers, the PC can undergo large deformations without breaks or cracking. The general application of PC includes digital disks like DVDs, automotive components, eyewear lenses, medical devices, etc. The incorporation of metal nanoparticles to the matrix of PC enhances its physical properties, the resultant nanocomposite obtained will be appropriate for several applications such as biotechnology, energy storage, packaging, optical devices and food stabilizing systems, etc. Several studies were reported on PC/silver nanocomposites. Nouh et al. (2017) manufactured Makrofol PC/silver nanocomposites films and analyze the effect of gamma irradiation on the structure and optical properties of nanocomposites. The PC/silver nanocomposites were prepared by casting technique, where Makrofol PC is dissolved in methylene chloride. The synthesized AgNPs (PVP reduction of silver nitrate in ethanol solution) is added to the PC solution under magnetic stirring. The aqueous mixture was cast into a petri dish and placed for 3 days in a closed box to evaporate the solvent. The PC/silver nanocomposite films are exposed to gamma radiation in the dose ranges from 20 to 300 kGy. The irradiation up to 150 kGy results in the increases of intermolecular interaction between PC chains and Ag that is attributed to the crosslinking that reduced the ordering structure, giving polymer more resilience. This reduces the optical energy gap and the increase in the refractive index. In another study conducted by (Nouh et al. 2020) synthesized PC/polybutylene terephthalate/silver nanocomposites and exposed to gamma irradiation ranges between 2 and 25 kGy. The resultant effect was characterized by utilizing the microscopic and spectroscopic technique. The authors found, the gamma irradiation causes proper spreading of AgNPs in the PC—polybutylene terephthalate matrix and thus resulted in the increase of amorphous phase with a decrease in the optical energy gap. Further, the nanocomposite exhibits a response to color change as intensity

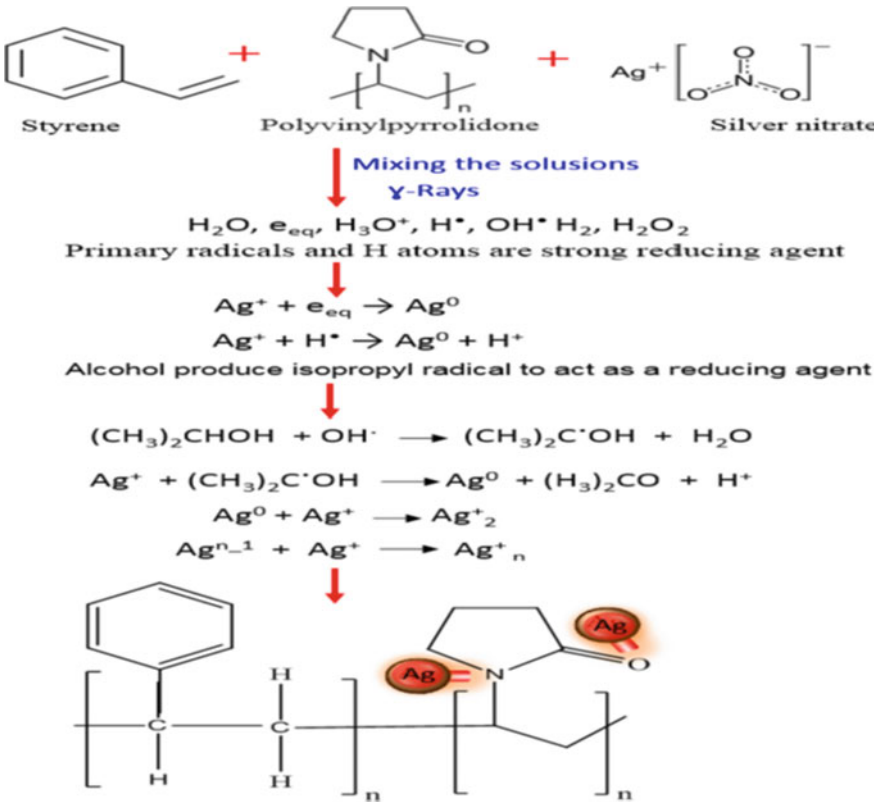

Fig. 1 Chemical structure and proposed mechanism of synthesis of silver/PS/PVP nanocomposites. Reproduced from References Ali et al. (2019) with permission

increases from 0.64 to 4.94. The association of PC matrix with conductive fillers such as Silver nanowires further extended the range of application of PC by the addition of electrical properties to PC/silver nanocomposites (Moreno et al. 2012).

4.4 Polypropylene-Silver Nanocomposites

Polypropylene (PP) is a very common thermoplastic polymer and has been compounded for a wide range of properties such as high resistance to stress and cracking, high melting point, excellent impact strength, biomedical field, etc. The common application of PP includes containers for food storage, household goods such as utensils, area rugs, athletic apparel, etc., automotive parts such as car batteries, etc. The modification of PP with inorganic nanoparticles such as AgNPs may provide additional functionality to the polymer. The presence of AgNPs in the

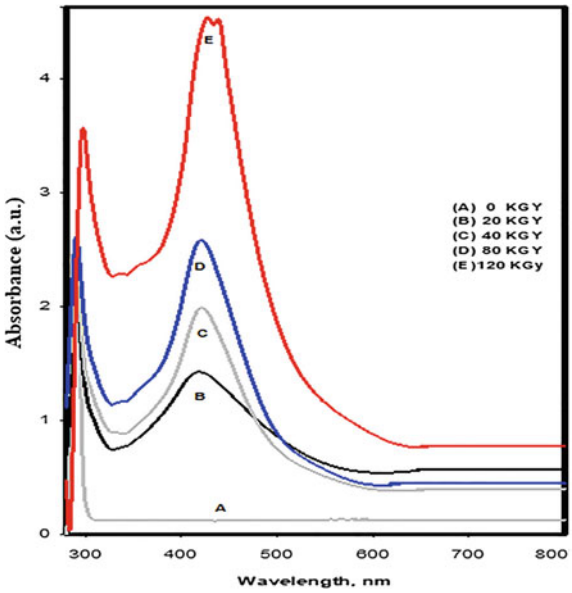

Fig. 2 Spectrum of UV/vis for silver/PS/PVP nanocomposite. Reproduced from Reference Ali et al. (2019) with permission

PP matrix increases the crystallization temperature of isostatic PP even at very low silver content, this represents a high efficiency of heterogeneous nucleation (Oliani et al. 2015). The investigation of the biocidal effect of gamma-irradiated PP/silver nanocomposites was studied by (Oliani et al. 2017). In this study, the PP was modified by gamma irradiation of isotactic PP in the presence of acetylene. The modified PP is with long-chain branching and distinct rheology. The authors blended 50/50 wt% of neat PP and modified PP and mixed using a twin-screw extruder then the AgNPs were infused into the polymer blend matrix at different concentrations of 0.1%, 0.25%, 0.5%, 1.0%, (1% PVP), 2% and 4% by wt%. The characterization of nanocomposite films utilizing Raman spectroscopy revealed the presence of a functional group associated with the stability of AgNps. Figure 3 shows the Raman spectrum of different concentrations of silver in the PP matrix. The band at 237 cm^{-1} represents stretching of Ag–O bond, band range between 397 cm^{-1} represents the Ag lattice vibration modes, intense peak at 1358 cm^{-1}, and 1589 cm^{-1} represents the enhancement of Raman lines by carbon polymeric segments absorbed on the silver oxide. The peak at 659 cm^{-1} represents the presence of PVP stabilized silver nanoparticles.

Using TEM analysis the authors verified the presence of AgNPs clusters with size ranges between 26 and 41 nm. The tensile strength of PP was found to decrease due to the addition of a higher concentration of AgNPs. The nanocomposite film with 1% AgNPs (PP/1.0% AgNPs-PVP) exhibits a comparatively excellent antibacterial effect. The manufactured nanocomposites prepared are

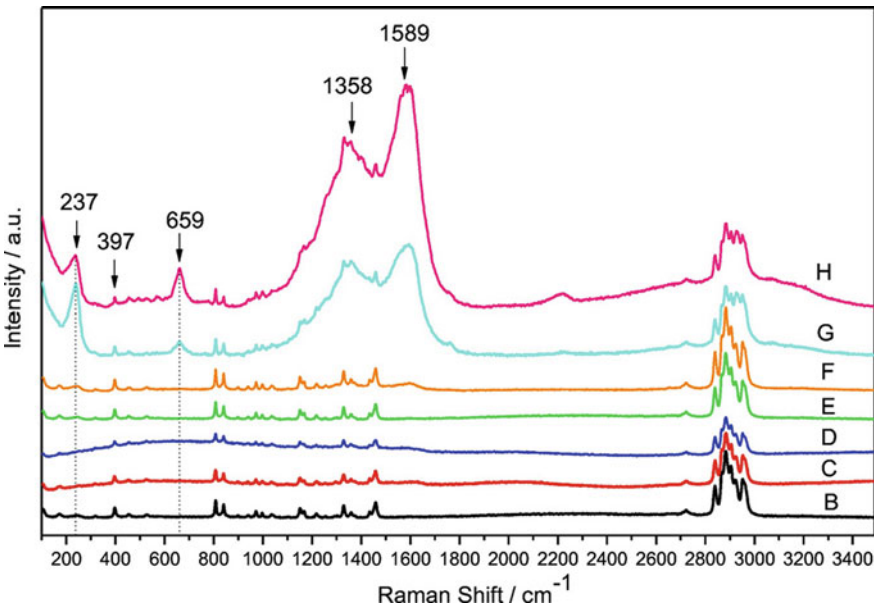

Fig. 3 Raman spectrum of PP films with AgNPs: B) PP/0.1%AgNPs; C) PP/0.25%AgNPs; D) PP/0.5%AgNPs; E) PP/1.0%AgNPs; F) PP/1.0%AgNPsPVP; G) PP/2.0%AgNPs; H) PP/4.0% AgNPs) Reproduced from reference (Oliani et al. 2017) with permission

noncytotoxic to human cells which are confirmed by a cell of a mouse. The authors also found the presence of surfactant-coated AgNPs allows antibacterial protection in contact-active without detectable biocide release. In another study conducted by (Ghorbani and Molaei 2017) the antibacterial properties of PP/silver nanocomposites were investigated. AgNPs were coated on the surface of PP films. For this purpose, the surface of the PP film was treated by corona discharge, and the modified PP films were then immersed in a colloidal solution of AgNPs. The AgNPs in the solution were synthesized by chemical reduction of silver salt using hydrazine hydrate (three silver nitrate solutions of 100 ml with various concentrations of 0.01, 0.005 and 0.001 M). The corona discharge treatment of PP/silver nanocomposite films was done to change the polarity of the nonpolar surface of PP and prepare it for coating. The corona discharge was applied to PP films for three different periods of 1, 3 and 5 min and the experiments were repeated for each time slot at three different powers of 100, 5000, and 10000 W. The SEM analysis of treated PP films confirms that the coating of the film enhances with an increase in time and power. The antibacterial activity of PP/silver nanocomposite films against gram-positive Staphylococcus aureus and Escherichia coli measured using the disk diffusion method reveals by increasing the time and power of corona discharge improves the quality of coating on the film. Ziabka and Dziadek (2019) prepared PP modified with AgNPs were manufactured utilizing injection molding and extrusion.

The authors studied to analyze whether AgNPs could influence the stability of the PP matrix during the 24 months of in vitro testing. It was found that the PP matrix with AgNPs displayed the significantly higher tensile strength and Young modulus during 12 and 24 months of investigation. The DSC analysis revealed that the incubation of composite material resulted in a slight reduction in the degree of crystallinity and melting temperature of PP. The overall performances of nanocomposite are observed stable even during 24 months, thus the authors concluded the material could be confidently applied as biomaterials.

4.5 Polyvinyl Chloride-Silver Nanocomposites

Polyvinyl chloride (PVC) is a lightweight, tough material that is rigid, durable, and is resistant to acids and bases. Most of the PVCs are used by construction industries as drainpipes, roofing sheets, gutters, and vinyl siding. The excellent antimicrobial properties of PVC/silver nanocomposite films are widely applied for food material packaging. Azlin-Hasim et al. (2016) manufactured antibacterial PVC/silver nanocomposite films utilizing the solvent casting method. From the mechanical characterization of nanocomposites film, the authors found that there is no significant difference between tensile strength and elongation at break of PVC films and PVC/silver nanocomposite films. From the thermal analysis, the Tg of PVC/silver nanocomposite decreased from 95 °C (PVC films) to 72 °C. The decrease in Tg may due to the van der Waals interaction between PVC chains and AgNPs. It is also suggested that the decrease in Tg of nanocomposites may due to repulsive force between nanoparticles and interfacial layer may lead to polymer chain mobility, thus yielding plasticizing effect by a reduction in the values of Tg. The antimicrobial activity of PVC/silver nanocomposite films for food packaging is confirmed significantly by extended shell-life of chicken breast fillets and reduced oxidation of chicken breast fillets compared to PVC wrapped equivalents. Afzal and Akhtar (2010) synthesized polyaniline-PVC/silver nanocomposites and analyzed the electrical properties of the nanocomposite. The dedecylbenzenesulfonic acid doped polyaniline (PANDR) has been produced by the doping method. AgNPs are then added to the PANDR solution and then mixed with PVC solution to prepare PANDS-PVC/silver nanocomposites. The incorporation of AgNPs has improved the mechanical properties of nanocomposite blends compared to pure polymer blends. It also reduces charge trapping centers and increases enhances the conducting channels. In another study Ismayil et al. (2020) silver doped polyaniline-PVC nanocomposite films were prepared by the non-solvent-induced phase inversion method. The AgNP's doped nanocomposites exhibit excellent photodegradation efficiency and excellent antibacterial efficiency.

4.6 Polymethyl Methacrylate (PMMA)-Silver Nanocomposites

PMMA is amorphous in nature, a linear polymer, rigid and transparent plastic material. PMMA is a strong and lightweight material with good impact strength. The environmental stability of PMMA is superior compared to other plastics such as PS and PE. PMMA is known for its various applications such as in automotive industries as car windows, car interior, and exterior panels, etc., in Electronic field such as LCD/LED TV screens, laptops/smartphone display, solar panels, etc. PMMA due to its high bio-compatibility it is also widely used in biomedical applications like dental cavity fillings and bone cement. Borse et al. (2016) studied the antibacterial efficiency and water treatment application of PMMA embedded AgNPs. One-pot synthesis by UV irradiation method was performed to synthesis PMMA/silver nanocomposites. The silver precursor was added in Milli-Q water. Low-pressure mercury lamps utilized as a UV source and the solution was irradiated for 24 h. After UV irradiation, the color of the solution changed from colorless to yellow that indicates the formation of PMMA embedded AgNPs. The nanocomposite shows excellent antibacterial properties against Gram-positive and Gram-negative bacteria. The authors also prepared PMMA/silver nanocomposite loaded membrane via the PMMA/AgNps solution through the membrane using a syringe. After passing the PMMA/silver nanocomposite solution through the membrane the color of the membrane changes from white to yellow. The antibacterial study of the treated membrane confirms the excellent antibacterial properties of the membrane. The water treatment was executed by passing sludge water through the treated membrane, and filter effluent water contains dead bacteria which, indicates that the treated membrane exhibits excellent antibacterial properties (Fig. 4).

In another study (Pullanchiyodan et al. 2017), AgNPs decorated boron nitride/PMMA nanosheets were manufactured for high thermal conductivity electronic substrates. The nanocomposites were prepared by considering the facile solution blending process. The dispersion of filler in the polymer matrix is characterized by using the elemental mapping of EDS coupled with SEM. The thermal conductivity analysis of nanocomposite reveals the high thermal conductivity is achieved by the hybrid AgNPs decorated boron nitride/PMMA (PMMA-BAX) nanocomposites than boron nitride/PMMA composites (PMMA-BX) and compared to prism PMMA. The experimentally measured thermal conductivity shows a good agreement with the theoretical model. The dielectric measurement performed at microwave frequencies and radio frequencies reveals that the nanocomposite shows a low dielectric constant (<5) and low alternating current conductivity. The authors concluded that the AgNPs decorated boron nitride/PMMA nanocomposites could efficiently be utilized for effective thermal management (Fig. 5).

Moreno et al. (2016) tuned the rate of silver release from the PMMA matrix to control the rate of release of silver ions, the nanocomposite is produced via the electrospinning technique. PMMA/silver nanocomposite fibers were then subjected

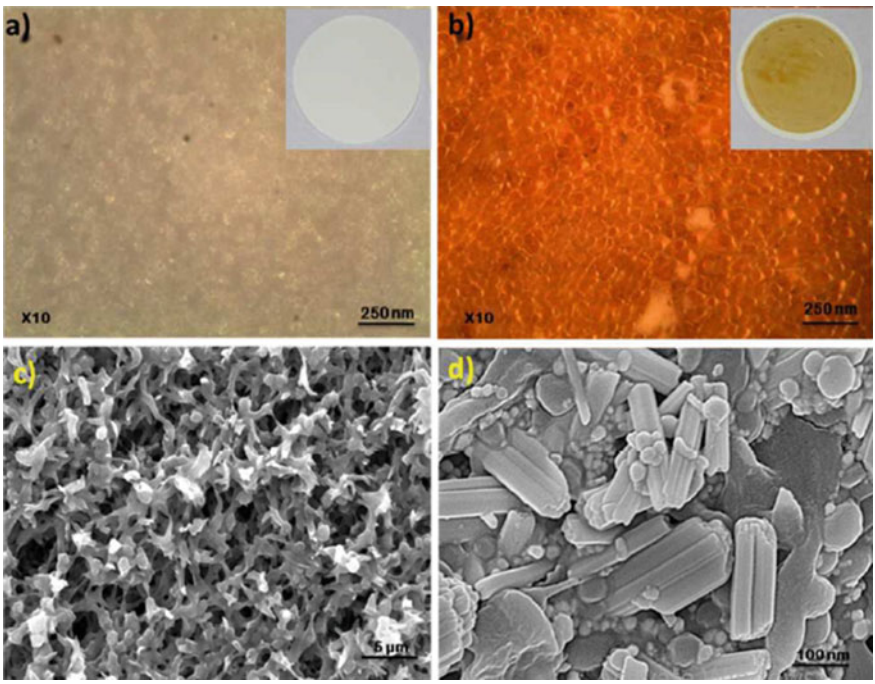

Fig. 4 Optical and FE–SEM images of untreated membranes (**a**, **c**) and treated membrane (**b**, **d**). The inset shows the photographic image of untreated and treated membrane (Borse et al. 2016)

to UV radiation in different levels of exposure to improve the gradual reduction of silver ions to AgNPs. The silver particle size increases from 2 to 5 nm under irradiation. The rate of Ag+ release found directly depends on the degree of exposure to UV. The fast release of Ag+ is observed for non-irradiated samples, in which the higher irradiation time is responsible for a slower release of Ag+, and the higher proportion of AgO and the increase in silver nanoparticle size is responsible for the slower release.

4.7 Polyvinyl Alcohol (PVA)-Silver Nanocomposites

PVA is a colorless water soluble thermoplastic polymer resin derived from the hydrolysis of polyvinyl acetate. PVA forms as a flexible water soluble material when the water evaporates. In general, PVA is resistant to solvents, oils, and fungi. The general application of PVA includes paper coatings, adhesives in packing, printing inks, thickeners, etc. Incorporating inorganic metal nanoparticles such as AgNPs to the PVA enhances its properties and could extend its application to various fields such as electronics, material packaging, biomedical applications, etc. Even as a synthetic polymer, due to the good biodegradability and water solubility

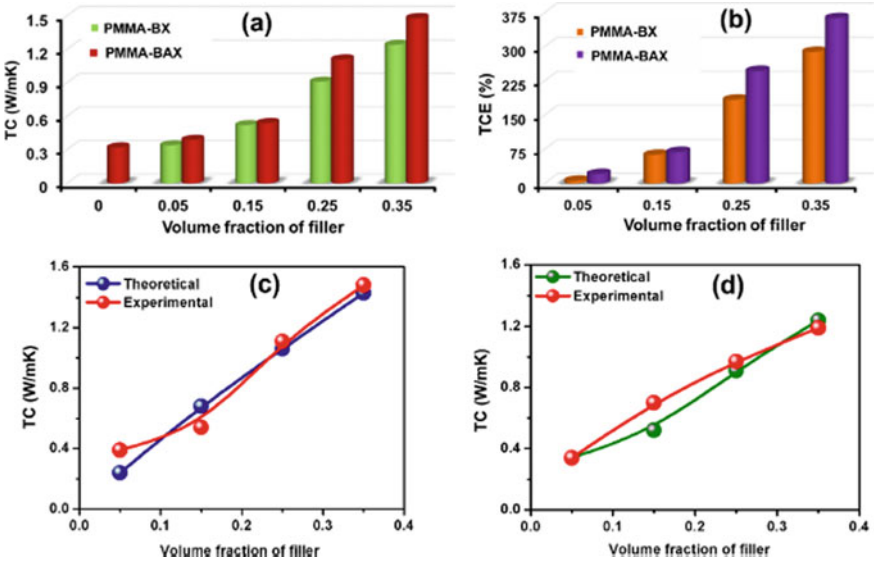

Fig. 5 (TC) Thermal conductivity (**a**), (TCE) thermal conductivity enhancement of nanocomposites (**b**). Measured and calculated thermal conductivity of PMMA−BAX and PMMA−BX nanocomposites respectively (**c**, **d**) (Pullanchiyodan et al. 2017)

of PVA, it is capable to replace conventional petroleum-based polymers from certain biomedical applications. Mukherjee et al. (2017) studied the conduction mechanism, dielectric relaxation, and current voltage of PVA/silver nanocomposites. The synthesis of silver nanotubes involves $AgNO_3$ as silver donor and PVP as a polymeric capping agent, ethylene glycol as the solvent and reducing agent. The preparation steps of PVA/silver nanocomposite involve dilution of PVA (1.2 gm) in deionized water under continuous magnetic stirring (at 353 K). Then AgNPs (2 wt%) dispersed in deionized water (10 ml) added dropwise to PVA solution at room temperature at continuous stirring. The obtained PVA/silver nanocomposite solution was poured to peptides and allowed to dry at room temperature for five days. The electrical properties were studied using a small portion of nanocomposite film the silver paste contact applied to the opposite phase, and it behaves like a capacitor. The DC conductivity of films checked utilizing Keithley 6514 electrometer reveals the conductivity increases with an increase in temperature that suggests the nanocomposite films exhibit semiconducting behavior. The two activation energies of nanocomposite films Ea = 0.73 eV within region (323–368 K) and Ea = 0.84 eV within the region (383–443 K) were determined using Arrhenius equation of conductivity, the variation of conductivity and Arrhenius fitted curve is shown in Fig. 6. The dielectric constant at room temperature and 10 kHz is observed as 8.02 which is higher than pure PVA (6.17). With the increase in temperature, the dielectric constant was observed steeper comparatively at a low frequency than high frequency due to space charge polarization and DC

conductivity contribution. The increase of dielectric properties of nanocomposite follows the modified Cole-Cole model, represented in Fig. 7. Mathew et al. (2019) fabricated PVA/chitosan/Ag nanocomposite membrane utilizing gamma irradiation technique with excellent antibacterial activity and for biomedical applications. The preparation of nanocomposite involves mixing PVA and chitosan with different copolymer compositions in the presence of $AgNO_3$ (silver donor) and glutaraldehyde (cross-linker), followed by in situ reductions with gamma irradiation in various doses. As the irradiation dose increases (25–75 kGy), the plasmon band shifted from 430 to 418 nm with high intensity, confirming the formation of smaller particles. The prepared nanocomposite films exhibit excellent antimicrobial and antifungal activities. Thrombogenicity and hemolytic potential studies reveal the weight of blood clotted on the PVA/chitosan/Ag nanocomposite membrane was very low; it confirms the manufactured membranes could be classified as non-thrombogenic and slightly hemolytic, suggesting the nanocomposite membranes are possible for biomedical applications. Mathew et al. (2019) synthesized PVA/AgNPs nanocomposite food packaging material utilizing the solvent casting method. The authors used ginger rhizome extract as a reducing agent, under the influence of direct sunlight. The prepared films show excellent antibacterial activity against foodborne pathogens such as Staphylococcus aureus and Salmonella Typhimurium.

4.8 Polyamides-Silver Nanocomposites

Polyamides are polymers in which monomers are linked together by amide linkage (also known as peptide bonds). Polyamides include synthetic polyamides or nylons and naturally occurring proteins (discussed in Chapter `Synthesis and Green Synthesis of Silver Nanoparticles'). Nylons are thermoplastic polymers that can be melt-processed into various forms such as films, fibers, or shapes. Nylons are produced diamines and dicarboxylic acid and are designated by two numbers, the first number is the number of carbon atoms in diamine and the second number is the number of carbon atoms in the dicarboxylic acid. The hydrogen bonds formed between the polymer chains give the polymer more strength and a high melting point. The nylons are used as textiles, carpets, ropes, also it can be cast into different shapes to manufacture things like bearings and cogs. By incorporating inorganic metal nanoparticle into polyamides can improve its mechanical, chemical, electrical, and optical properties. The AgNPs incorporated in the polyamides matrix is widely applied in many areas due to its unique mechanical, catalytic, electrical, chemical, and anti-bacterial properties. Especially AgNPs/nylon nanocomposites, which have various applications in different areas such as biomaterials, catalysis, electrical, protective clothing, etc. (Pant et al. 2011) synthesized AgNPs impregnated TiO_2/nylon-6 nanocomposite mats with excellent antimicrobial and photocatalytic properties. The nylon-6/TiO_2 nanocomposite mat was first prepared to utilize an electrospinning process. Then the silver photo deposition was done in

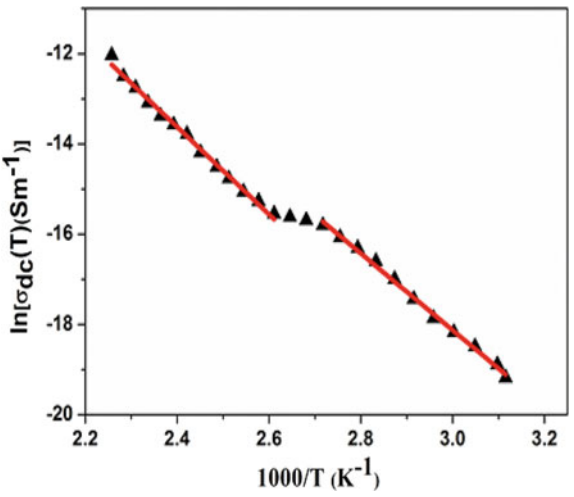

Fig. 6 Variation of DC conductivity with temperature of PVA/silver nanocomposite films, the solid lines represents the Arrhenius fitted curve (Mukherjee et al. 2017)

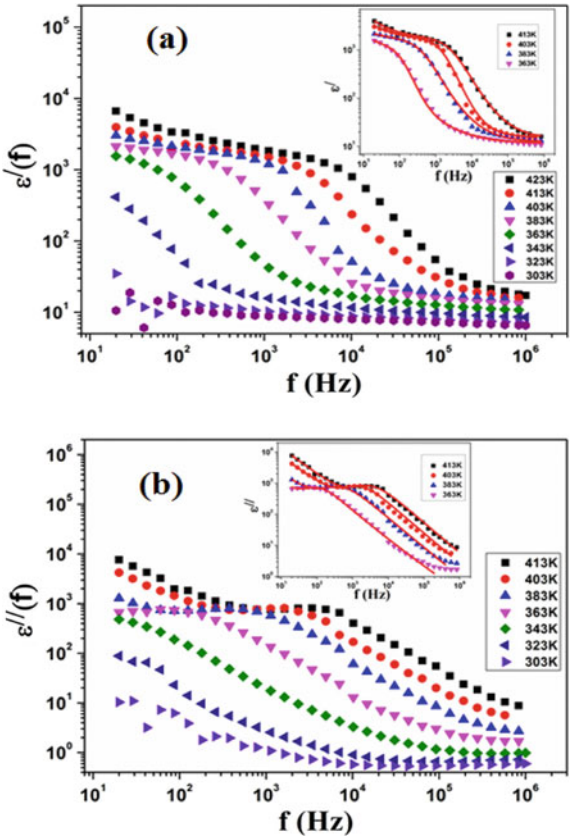

Fig. 7 The frequency variation of real part ($\varepsilon^{/}$) (**a**) and imaginary part ($\varepsilon^{//}$) (**b**) of PVA/Ag nanocomposite films. The inset plots represent the fit according to Cole-Cole equation (Mukherjee et al. 2017)

nylon-6 and TiO_2/nylon-6 nanocomposite matrices by placing inside the $AgNO_3$ solution. The photo deposition of AgNPs in the polymer matrix was conducted under UV light at 254 nm for irradiation time 15, 30, 60 s, respectively. After the treatment, the mats were washed with distilled water and vacuum dried for 24 h at room temperature. During the electrospinning process, the TiO_2 inside the nylon-6 matrix was formed like a high aspect ratio spider-wave-like structure and facilitated the UV light photoreduction of $AgNO_3$ to Ag. The AgNPs were deposited selectively upon the TiO_2 nanoparticles of the prepared nanocomposite mat, represented in Fig. 8 TEM images and EDX spectra. The antibacterial properties of nanocomposites were evaluated by testing against Escherichia coli, and the photoactive properties of nanocomposite were tested by observing the degradation of methylene blue dye solution in a simple photochemical rector. The result shows the AgNPs loaded TiO_2/nylon nanocomposites are more effective than AgNPs/nylon-6 nanocomposite. The prepared nanocomposite has potential as an economically friendly photocatalyst and can be utilized as a potential water filter medium. Omar et al. (2016) also studied the anti-microbial properties of nylon 6, 10/AgNPs nanocomposite material. The anti-microbial activity of the synthesized nanocomposites is effective against Escherichia coli. Perkas et al. (2007) synthesized ultrasound-assisted coating of nylon 6,6 with AgNPs and the authors also studied its anti-bacterial activity. Maleknia et al. (2015) synthesized nylon 6/silver nanocomposite fibers for the permanent antibacterial activity to common synthetic textiles. The nanocomposites were prepared by a modular twin screw extruder. The anti-bacterial study of nanocomposite against staphylococcus aureus and Klebsiella pneumonia. The results obtained from the anti-bacterial study reveals the nylon 6/silver nanocomposites exhibit excellent anti-bacterial properties.

4.9 Polylactic Acid (PLA)-Silver Nanocomposites

PLA is a thermoplastic aliphatic polyester obtained by condensation of lactic acid or by the ring-opening of lactide, the cyclic dimer of the basic repeating unit. In 2010, PLA was ranked second in the world regarding its consumption volume. The most important specialty of PLA is its biocompatibility, and this makes PLA a perfect choice for medical implants intended to be absorbed by the body. PLA degrades in turn into lactic acid which, is non-toxic to the human body. Among nanocomposites, PLA/silver nanocomposites are widely used in biomedical applications due to the excellent antibacterial properties of AgNPs and the biocompatible behavior of PLA. PLA/silver nanocomposite is also applied in antibacterial packagings and electrical applications. Zhang et al. (2018) synthesized PLA/silver nanocomposites by coating silver on PLA microfibers and then molded via compression molding. The electromagnetic interference shielding effectiveness and electrical conductivity of the nanocomposites enhance due to the silver coating layers on PLA microfibers. Solution techniques are generally used for manufacturing PLA/silver nanocomposites. The electrical properties of the nanocomposite

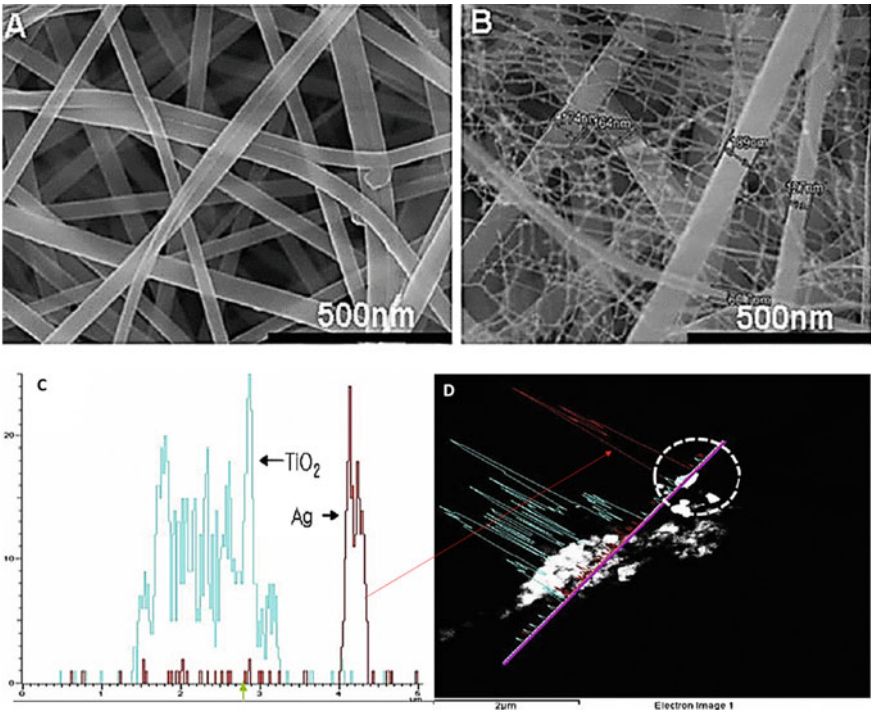

Fig. 8 FSEM images of neat nylon-6 mat (**a**) and TiO_2/nylon-6 mat (**b**), TEM-EDX of Ag–TiO_2/nylon-6 nanofibers: EDX spectra of TiO_2 and Ag NPs (**c**), TEM-EDX image of nanocomposite fibers (**d**) (Pant et al. 2011)

increased with the increase in the amount of silver coating which is controlled by adjusting the coating time. PLA/silver nanocomposite was prepared in a way of wet electroless deposition processing via controlling the deposition time, represented in Fig. 9. The preparation of PLA/silver nanocomposite involves two steps. First, PLA microfibers (3 g) were immersed in acidic $SnCl_2$ solution allowing the deposition of nuclei on the PLA fiber surface. The roughened PLA microfibers were extracted from the solution and washed with distilled water. Second, the roughened PLA fibers were exposed to Tollen's reagent prepared by dissolving $AgNO_3$ (2.0 g) in 100 ml distilled water and stirred well by adding NH_3OH until the solution turned clear. Sodium citrate was used as the reducing agent.

Liu et al. (2017) developed PLA based mats with graphene oxide (GO)-silver hybrid nanofillers. The PLA/GO-silver nanocomposites were prepared by the electrospinning technique. The manufactured nanocomposite exhibits excellent antibacterial properties against Escherichia coli and Staphylococcus aureus and enhanced thermal and tensile properties. These nanocomposite mats could be applied for biomedical applications due to efficient antibacterial properties. Busolo et al. (2010) synthesized silver-based layered silicate in PLA matrix antimicrobial

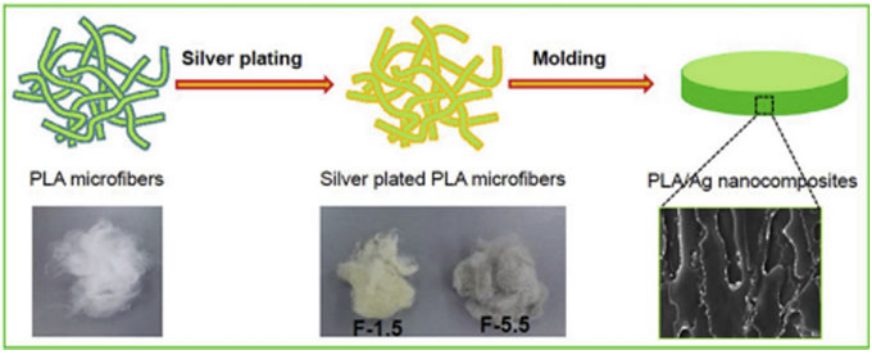

Fig. 9 Fabrication of PLA/silver nanocomposite with chain structures conductive network (Zhang et al. 2018) (sample named as F-x, where x denotes the deposition time in minutes)

food packaging coatings. The nanocomposite was prepared using the solvent casting method. The synthesized nanocomposite exhibits excellent antimicrobial activity against Gram-negative Salmonella spp.

4.10 Polylactic Glycolic Acid (PLGA)/Silver Nanocomposites

PLGA is an aliphatic polyester-based biodegradable polymer that comprises a copolymer of lactic acid (α-hydroxy propanoic acid) and glycolic acid (hydroxy acetic acid). PLGA due to its excellent biocompatible and biodegradable nature it has been used extensively used for several biomedical applications. PLGA is approved by the FDA and found to be both biocompatible and biodegradable for specific human clinical applications. PLGA in water media undergoes hydrolytic chain scission, the mechanism of degradation involves different steps such as penetration, chain scission, and diffusion of the degradation products. It is also possible to control the degradation rate with the influence of several factors such as the ratio of lactic and glycolic acid, molecular weight, length of lactic acid and glycolic blocks, porosity, structure, and morphology. The biodegradable PLGA nanocomposites based on inorganic metal nanocomposite such as gold, titanium, silver, etc. are used for various applications including sensors for diagnosis and antibacterial treatments. The AgNPs loaded on the PLGA matrix could effectively reduce the bacterial development through modification of their surface properties. Rinaldi et al. (2013) synthesized biodegradable PLGA/silver nanocomposite with controlled degradation rate and antibacterial properties. The AgNPs were synthesized using $AgNO_3$ as a silver donor in PVP/$CHCL_3$ solution under continuous stirring for 5 h at a constant temperature. PLGA/silver nanocomposite films were prepared by the solvent casting technique. The PLGA was dissolved in $CHCL_3$ under continuous stirring at room temperature. The nanocomposites were produced

by adding AgNPs (1–3 wt%) to PLGA/$CHCL_3$ suspensions with continuous stirring. The dispersion was cast in Teflon sheets and air-dried for 24 h and then 48 h in a vacuum at 37 °C. The effect of silver loading on the polymer matrix degradation was analyzed following the mass loss and morphology of the nanocomposite films at different stages of degradation. The release of Ag+ during the degradation of nanocomposite was analyzed through the diffusion model to have insight into the degradation kinetics. It was found that the release rate and the degradation rate was reduced at higher AgNPs loading. The nanocomposite shows excellent antibacterial properties. Scavone et al. (2016) manufactured and analyzed the antimicrobial properties and cytocompatibility of PLGA/silver nanocomposites. The nanocomposite was manufactured utilizing the solvent casting method. The nanocomposites exhibit excellent antibacterial properties against Escherichia coli and Staphylococcus aureus. The nanocomposite exhibits good cytocompatibility when assayed with L929 and SAOS-2 cells hence, the PLGA/ag nanocomposite is a promising candidate for tissue engineering applications.

4.11 Epoxy/Silver Nanocomposites

Epoxy resins are categorized as thermosetting polymers. Epoxy resins refer to a broad group of reactive compounds that are characterized by the presence of an epoxy ring, which is represented by a three-member ring containing one oxygen atom bonded with two carbon atoms. The molecules with the presence of this functional group define as epoxide, where this molecular base can vary widely resulting in different classes of epoxy resins. Epoxy resins may be cross-linked either with themselves via catalytic homopolymerization, or with co-reactants including acids, amines, alcohols, thiols, and phenols. The co-reactants are referred to as hardeners and the process of cross-linking as curing. The epoxy resins are utilized in a wide range of applications such as electronic components, adhesives, laminates, coatings, aerospace, and marine applications, etc., owing to its high tensile strength and young's modulus, solvent resistance, and good thermal stability (Uthaman et al. 2020). Recently epoxy nanocomposites due to their unique physicochemical properties have gained great interest. In particular silver nanoparticle incorporated in the epoxy matrix gives excellent electrical, mechanical, and antibacterial properties to the resultant nanocomposites. Yagci et al. (2008) synthesized epoxy/silver nanocomposites by simultaneous polymerization-reduction approach. The visible light photoinitiator (camphorquinone) was utilized to generate electron-donating radicals. The oxidation of these radicals to the corresponding cations in the presence of $AgSbF_6$ (hexafluoroantimonate) leads to the formation of AgNPs. These cations formed are capable of initiating cationic ring-opening polymerization of the epoxides. So, the stable AgNPs were formed in the polymerizing medium, the rather formation of AgNPs depends on the radical concentration. Boumedienne and Maaroufi (2020) studied the structural and optical-electronic properties of epoxy/silver nanocomposite films (0.01–0.1 vol.fr

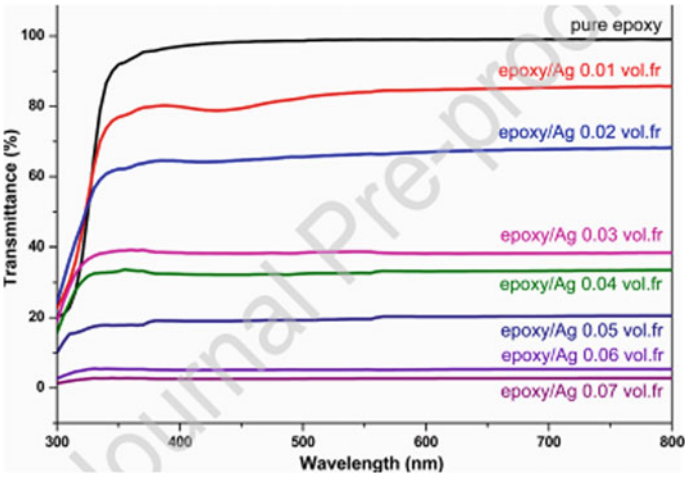

Fig. 10 UV–Vis spectra/Transmittance of epoxy/Ag nanocomposite films (Boumedienne and Maaroufi 2020)

of Ag) prepared to use the extrusion technique. The spectroscopic and microscopic analysis of the nanocomposite reveals good dispersion of AgNPs in the epoxy matrix. The water absorption study of the nanocomposites reveals negligible absorption of water. The electrical properties of the epoxy/silver nanocomposites depend on the filler conductivity, geometry, filler fraction, and interaction with matrix, the electrical conductivity increases with the increase in the amount of silver. The optical properties also depend on the number of silver particles in the epoxy matrix. The transmittance in the wavelength range significantly reduced with the increment in filler content, represented in Fig. 10. The optical band gap for pure epoxy is observed higher due to its optical transparency. However, the optical band gap shifts three times towards a lower value with the increase in AgNPs loading. The authors demanded the synthesized epoxy/silver nanocomposites could vary the bandgap by varying the filler concentration owing to its good chemical stability, electrical conductivity, and optical properties, the prepared nanocomposite could be safely applied as a demanding material in thermoelectricity, optoelectronics, and solar cells.

4.12 Polyurethenes (PU)-Silver Nanocomposites

Polyurethane polymers are composed of urethane linkages in their repeating unit. The PU is formed by the polyaddition reaction between diisocyanate with polyols. PU is generally used in manufacturing high-resilience foam seatings, seals, gaskets, high-performance adhesives, surface coatings, and sealants, etc. PU has been also widely used for manufacturing medical equipment due to its good

hemocompatibility and excellent mechanical properties. PU is generally classified as a thermosetting polymer even though thermoplastic PU (TPU) is also available. TPUs are widely applied in the biomedical field and for manufacturing medical devices. The unique chemistry of PU gives them versatility with a wide range of behaviors that ranges from rigid plastics to soft and flexible plastics. Silver nanoparticle as an excellent antibacterial agent while incorporated within the PU matrix enhances the antibacterial properties of the resultant nanocomposites and is widely applied in different biomedical fields. One of the first applications of polymer/silver composites in medicine was the "Erlanger Silberkatether" that was developed in the 1990s by incorporating silver powder with the TPU matrix. Triebel et al. (2011) prepared TPU/silver nanocomposites utilizing two different routes. The first is in situ preparation, AgNPs were produced by thermal reduction of silver acetate during the melt mixing process. The second route involved an ex situ preparation, AgNPs produced in an invertible polyester resulting in smaller particle size. The AgNPs obtained from this method surrounded by a polyester cage that helps to stabilize the nanoparticles and prevent agglomeration. The incorporation of AgNPs in the polymer matrix was done by utilizing the extrusion technique. The silver ion release from the polymer matrix was analyzed using anodic stripping voltammetry. The Ag ions release of various PU/silver nanocomposites as a function of immersion time is evaluated. The amount of silver ions released during a particular immersion time increases with the higher concentration of AgNPs in the PU matrix. At a constant weight percentage of AgNPs in the PU matrix, the composite with ex situ AgNPs exhibits a release of silver ions which is about two orders of magnitude greater than the release from the nanocomposite with in situ AgNPs. Zhao et al. (2019) fabricated waterborne PU/silver nanocomposite foam with enhanced mechanical, thermal, and antibacterial properties. The nanocomposite foams were prepared for the mechanical foaming method. The uniform distribution of AgNPs in the PU matrix facilitated cell growth, leading to an enhanced average pore size, air permeability, thermal stability, etc. The incorporation of AgNPs in the PU matrix also increased the mechanical stability of the PU/silver nanocomposite. The nanocomposite exhibits excellent antibacterial properties against Escherichia coli and Staphylococcus aureus.

5 Conclusions

Polymer nanocomposites based on AgNPs are essential materials in the field of nanoscience and technology because of their excellent properties and capability for applications in various areas. This chapter discussed the preparative techniques of polymer nanocomposites and the synthetic polymer nanocomposites based on silver nanoparticles. The excellent antimicrobial activities, the inhibiting effect of infection, and the microbial proliferation of AgNPs lead the polymer nanocomposites based on silver nanoparticles to apply widely in the various biomedical field. The design of bio-nano composites with specific requirements involves using a wide

range of polymer matrices. In this chapter, we discussed the incorporation of silver nanoparticles in various synthetic polymer matrices. Much research are still ongoing, and there is yet to be a definite conclusion on the behavior of nanoparticles on different polymer systems.

References

Abdel-Mohsen, A.M., Pavliňák, D., Čileková, M., Lepcio, P., Abdel-Rahman, R.M., Jančář, J.: Electrospinning of hyaluronan/polyvinyl alcohol in presence of in-situ silver nanoparticles: preparation and characterization. Int. J. Biol. Macromol. **139**, 730–739 (2019). https://doi.org/10.1016/j.ijbiomac.2019.07.205

Afzal, A.B., Akhtar, J.J.: Effect of inorganic silver nanoparticles on structural and electrical properties of polyaniline/PVC blends. J. Inorg. Organomet. Polym Mater. **20**(4), 783–792 (2010). https://doi.org/10.1007/s10904-010-9405-2

Ali, I., Meligi, G.A., Akl, M.R., Saleh, T.A.: Influence of γ-ray irradiation doses on physicochemical properties of silver polystyrene polyvinyl pyrrolidone nanocomposites. Mater. Chem. Phys. **226**(December 2017), 250–256 (2019). https://doi.org/10.1016/j.matchemphys.2018.12.084

Aryal, S., Park, H., Leary, J.F.: Top-Down Fabrication-Based Nano/Microparticles For Molecular Imaging and Drug Delivery. Int. J. Nanomed. **14**, 6631–6644 (2019). https://doi.org/10.2147/IJN.S212037

Azlin-Hasim, S., Cruz-Romero, M.C., Morris, M.A., Padmanabhan, S.C., Cummins, E., Kerry, J. P.: The potential application of antimicrobial silver polyvinyl chloride nanocomposite films to extend the shelf-life of chicken breast fillets. Food Bioprocess Technol. **9**(10), 1661–1673 (2016). https://doi.org/10.1007/s11947-016-1745-7

Borse, S., Temgire, M., Khan, A., Joshi, S.: Photochemically assisted one–pot synthesis of PMMA embedded silver nanoparticles: antibacterial efficacy and water treatment. Royal Soc. Chem. **1**, 1–10 (2016). https://doi.org/10.1039/C6RA08397H

Boumedienne, N., Maaroufi, A.: Structural and opto-electronic properties of epoxy/silver nanocomposite films. In: Physica B: Condensed Matter, vol. 578. Elsevier B.V. (2020) https://doi.org/10.1016/j.physb.2019.411853

da Brito, S.C., Bresolin, J.D., Sivieri, K., Ferreira, M.D.: Low-density polyethylene films incorporated with silver nanoparticles to promote antimicrobial efficiency in food packaging. Food Sci. Technol. Int. **26**(4), 353–366 (2020). https://doi.org/10.1177/1082013219894202

Busolo, M.A., Fernandez, P., Ocio, M.J., Lagaron, J.M.: Novel silver-based nanoclay as an antimicrobial in polylactic acid food packaging coatings. Food Additives Contaminants—Part A Chemistry, Analysis, Control, Exposure and Risk Assessment **27**(11), 1617–1626 (2010). https://doi.org/10.1080/19440049.2010.506601

Dehnavi, A.S., Aroujalian, A., Raisi, A., Fazel, S.: Preparation and characterization of polyethylene/silver nanocomposite films with antibacterial activity. J. Appl. Polym. Sci. **127** (2), 1180–1190 (2013). https://doi.org/10.1002/app.37594

Eisa, W.H., Abdel-Moneam, Y.K., Shabaka, A.A., Hosam, A.E.M.: In situ approach induced growth of highly monodispersed Ag nanoparticles within free standing PVA/PVP films. Spectrochimica Acta—Part A: Mol. Biomol. Spectr. **95**, 341–346 (2012). https://doi.org/10.1016/j.saa.2012.03.085

Ghorbani, H.R., Molaei, M.: Antibacterial nanocomposite preparation of polypropylene-Silver using Corona discharge. Prog. Org. Coat. **112**(July), 187–190 (2017). https://doi.org/10.1016/j.porgcoat.2017.07.020

Gubarev, A.S., Lezov, A.A., Mikhailova, M.E., Senchukova, A.S., Ubyivovk, E.V., Nekrasova, T. N., Girbasova, N.V., Bilibin, A.Y., Tsvetkov, N.V.: Ag(0) nanoparticles stabilized with Poly (Ethylene Glycol)s modified with amino groups: formation and properties in solutions. Colloid J. **81**(3), 226–234 (2019). https://doi.org/10.1134/S1061933X19030062

Hamdy, S., Elamanchili, P., Alshamsan, A., Molavi, O., Satou, T., Samuel, J.: Responses by codelivery of ovalbumin and toll-like receptor ligand monophosphoryl lipid A in poly (D, L - lactic-co-glycolic acid) nanoparticles. J. Biomed. Mater. Res. Part A. (2006). https://doi.org/10.1002/jbm.a

Ismayil, K.M., Varghese, A., Antony, R.: Silver-doped polyaniline–polyvinyl chloride nanocomposite films for photocatalytic and antibacterial applications. J. Elastomers Plast. **52**(2), 103–116 (2020). https://doi.org/10.1177/0095244318819238

Krystosiak, P., Tomaszewski, W., Megiel, E.: High-density polystyrene-grafted silver nanoparticles and their use in the preparation of nanocomposites with antibacterial properties. J. Colloid Interface Sci. **498**, 9–21 (2017). https://doi.org/10.1016/j.jcis.2017.03.041

Liao, G., Chen, J., Zeng, W., Yu, C., Yi, C., Xu, Z.: Facile preparation of uniform nanocomposite spheres with loading silver nanoparticles on polystyrene-methyl acrylic acid spheres for catalytic reduction of 4-nitrophenol. J. Phys. Chem. C **120**(45), 25935–25944 (2016). https://doi.org/10.1021/acs.jpcc.6b09356

Liu, C., Shen, J., Yeung, K.W.K., Tjong, S.C.: Development and antibacterial performance of novel polylactic acid-graphene oxide-silver nanoparticle hybrid nanocomposite mats prepared by electrospinning. ACS Biomater. Sci. Engg. **3**(3), 471–486 (2017). https://doi.org/10.1021/acsbiomaterials.6b00766

Maleknia, L., Rashidi, A.S., Ghamsari, N.A.: Preparation and characterization of nylon 6/silver nanocomposite fibers for permanent antibacterial effect. Oriental J. Chem. **31**(1), 257–262 (2015). https://doi.org/10.13005/ojc/310128

Mathew, S., Mathew, J., Radhakrishnan, E.K.: Polyvinyl alcohol/silver nanocomposite films fabricated under the influence of solar radiation as effective antimicrobial food packaging material. J. Polym. Res. **26**(9), 1–10 (2019). https://doi.org/10.1007/s10965-019-1888-0

Moreno, I., Navascues, N., Irusta, S., Santamaria, J.: Modulation of bactericidal action in polymer nanocomposites: Light-tuned Ag + release from electrospun PMMA fibers. RSC Advances **6** (81), 78036–78042 (2016). https://doi.org/10.1039/c6ra16876k

Moreno, I., Navascues, N., Irusta, S., Santamaría, J.: Silver nanowires/polycarbonate composites for conductive films. IOP Conf. Series: Mater. Sci. Engg. **40**(1) (2012). https://doi.org/10.1088/1757-899X/40/1/012001

Mukherjee, P.S., Das, A.K., Dutta, B., Meikap, A.K.: Role of silver nanotube on conductivity, dielectric permittivity and current voltage characteristics of polyvinyl alcohol-silver nanocomposite film. J. Phys. Chem. Solids **111**(July), 266–273 (2017). https://doi.org/10.1016/j.jpcs.2017.07.032

Natsuki, J.: A Review of Silver Nanoparticles: Synthesis Methods, Properties and Applications. Int. J. Mater. Sci. Appl. **4**(5), 325 (2015). https://doi.org/10.11648/j.ijmsa.20150405.17

Nouh, S.A., Abou Elfadl, A., Benthami, K.: Gamma-induced changes in some of the structural and optical properties of Makrofol polycarbonate/silver nanocomposites films. Radiat. Eff. Defects Solids **172**(1–2), 48–60 (2017). https://doi.org/10.1080/10420150.2017.1286656

Nouh, S.A., Benthami, K., Samy, R.M., El-Hagg, A.A.: Effect of gamma radiation on the structure and optical properties of polycarbonate-polybutylene terephthalate/silver nanocomposite films. Chem. Phys. Lett. **741**, 137123 (2020). https://doi.org/10.1016/j.cplett.2020.137123

Oliani, W.L., De Lima, L.F.C.P., Rogero, S.O., Riella, H.G., Lugao, A.B., Parra, D.F.: AgNPs polypropylene gel films-thermal study and antibacterial activity. J. Therm. Anal. Calorim. **119** (3), 1963–1970 (2015). https://doi.org/10.1007/s10973-014-4353-7

Oliani, W.L., Parra, D.F., Komatsu, L.G.H., Lincopan, N., Rangari, V.K., Lugao, A.B.: Fabrication of polypropylene/silver nanocomposites for biocidal applications. Mater. Sci. Eng., C **75**, 845–853 (2017). https://doi.org/10.1016/j.msec.2017.02.109

Olmos, D., Pontes-Quero, G.M., Corral, A., González-Gaitano, G., González-Benito, J.: Preparation and characterization of antimicrobial films based on LDPE/Ag nanoparticles with potential uses in food and health industries. Nanomaterials **8**(2) (2018). https://doi.org/10.3390/nano8020060

Omar, R.A., Smail, A.K., Omar, K.A. Study on the activity of Ag/Nylon 6, 10 Nanocomposite Against Escherichia coli. Int. J. Curr. Microbiol. Appl. Sci. **5**(4), 935–941 (2016). https://doi.org/10.20546/ijcmas.2016.504.106

Pant, H.R., Pandeya, D.R., Nam, K.T., Baek il, W., Hong, S.T., Kim, H.Y.: Photocatalytic and antibacterial properties of a TiO_2/nylon-6 electrospun nanocomposite mat containing silver nanoparticles. J. Hazard. Mater. **189**(1–2), 465–471 (2011). https://doi.org/10.1016/j.jhazmat.2011.02.062

Perkas, N., Amirian, G., Dubinsky, S., Gedanken, A.: Ultrasound-assisted coating of nylon 6,6 with silver nanoparticles and its antibacterial activity. J. Appl. Polym. Sci. **104**, 1423–1430 (2007). https://doi.org/10.1002/app.24728

Pre-proofs, J., Arroyo, Y., Balogh-michels, Z., Caseri, W., Ren, Q.: Polymer-assisted in-situ thermal reduction of silver precursors : a solventless route for silver nanoparticles-polymer composites. Chem. Engg. J. 123983 (2019). https://doi.org/10.1016/j.cej.2019.123983

Pullanchiyodan, A., Nair, K.S., Surendran, K.P.: Silver-Decorated boron nitride nanosheets as an effective hybrid filler in pmma for high-thermal-conductivity electronic substrates. ACS Omega **2**(12), 8825–8835 (2017). https://doi.org/10.1021/acsomega.7b01436

Rinaldi, S., Fortunati, E., Taddei, M., Kenny, J.M., Armentano, I., Latterini, L.: Integrated PLGA-Ag nanocomposite systems to control the degradation rate and antibacterial properties. J. Appl. Polym. Sci. **130**(2), 1185–1193 (2013). https://doi.org/10.1002/app.39255

Roy, A., Joshi, M., Butola, B.S., Ghosh, S.: Evaluation of biological and cytocompatible properties in nano silver-clay based polyethylene nanocomposites. J. Hazard. Mater.. **384**(May 2019), 121309 (2020). https://doi.org/10.1016/j.jhazmat.2019.121309

Scavone, M., Armentano, I., Fortunati, E., Cristofaro, F., Mattioli, S., Torre, L., Kenny, J.M., Imbriani, M., Arciola, C.R., Visai, L.: Antimicrobial properties and cytocompatibility of PLGA/Ag nanocomposites. Materials **9**(1), 1–15 (2016). https://doi.org/10.3390/ma9010037

Subbiah, T., Bhat, G.S., Tock, R.W., Parameswaran, S., Ramkumar, S.S.: Electrospinning of nanofibers. J. Appl. Polym. Sci. **96**(2), 557–569 (2005). https://doi.org/10.1002/app.21481

Triebel, C., Vasylyev, S., Damm, C., Stara, H., Özpinar, C., Hausmann, S., Peukert, W., Münstedt, H.: Polyurethane/silver-nanocomposites with enhanced silver ion release using multifunctional invertible polyesters. J. Mater. Chem. **21**(12), 4377–4383 (2011). https://doi.org/10.1039/c0jm03487h

Uthaman, A., Xian, G., Thomas, S., Wang, Y., Zheng, Q., Liu, X.: Durability of an epoxy resin and its carbon fiber-reinforced polymer composite upon immersion in water, acidic, and alkaline solutions. Polym. **12**(3) (2020). https://doi.org/10.3390/polym12030614

Vodnik, V., Božanić, D.K., Džunuzović, J.V., Vukoje, I., Nedeljković, J.: Silver/polystyrene nanocomposites: optical and thermal properties. Polym. Compos. **33**(5), 782–788 (2012). https://doi.org/10.1002/pc.22207

Xin, F., Li, L.: Decoration of carbon nanotubes with silver nanoparticles for advanced CNT/polymer nanocomposites. Compos. A Appl. Sci. Manuf. **42**(8), 961–967 (2011). https://doi.org/10.1016/j.compositesa.2011.03.024

Yagci, Y., Sangermano, M., Rizza, G.: A visible light photochemical route to silver–epoxy nanocomposites by simultaneous polymerization–reduction approach. Polymer **49**(24), 5195–5198 (2008). https://doi.org/10.1016/j.polymer.2008.09.068

Zhang, K., Yu, H.O., Yu, K.X., Gao, Y., Wang, M., Li, J., Guo, S.: A facile approach to constructing efficiently segregated conductive networks in poly(lactic acid)/silver nanocomposites via silver plating on microfibers for electromagnetic interference shielding. Compos Sci. Technol. **156**, 136–143 (2018). https://doi.org/10.1016/j.compscitech.2017.12.037

Zhao, B., Qian, Y., Qian, X., Fan, J., Feng, Y.: Fabrication and characterization of waterborne polyurethane/silver nanocomposite foams. Polym. Compos. **40**(4), 1492–1498 (2019). https://doi.org/10.1002/pc.24888

Ziabka, M., Dziadek, M.:Long-Lasting examinations of surface and structural properties of medical polypropylene modified with silver nanoparticles. Polym. **11**(12) (2019). https://doi.org/10.3390/polym11122018

Zielińska, A., Skwarek, E., Zaleska, A., Gazda, M., Hupka, J.: Preparation of silver nanoparticles with controlled particle size. Procedia Chem. **1**(2), 1560–1566 (2009). https://doi.org/10.1016/j.proche.2009.11.004