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Thermal, Mechanical and Electrical Properties of Ag Nanoparticle–Polymethyl Methacrylate Composites Under Different Service Temperatures

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Abstract: Ag-nanoparticle-reinforced polymethyl methacrylate (AgNP/PMMA) composites are widely used in healthcare, electronics, construction, transportation and many other fields. As the service temperature fluctuates easily, it is necessary to study the temperature effect on the properties of AgNP/PMMA composites. In this work, a preparation method of mixing and hot-pressing was used to fabricate multifunctional AgNP/PMMA composites that are suitable for large-scale industrial production. AgNPs are found to disperse homogeneously in the PMMA matrix. The thermal conductivity of the composite with 15 vol% AgNPs is 116.19% higher than that of PMMA and decreases as the temperature rises. Flexural strength increases first and then decreases with the rising of AgNP content and service temperature, while the flexural modulus decreases gradually. The minimum electrical resistivity of the composite achieves $1.37 \times 10^{-3} \, \Omega \cdot \text{m}$, with a low percolation threshold of 5 vol%, an improvement of nine orders of magnitude over PMMA. The results demonstrate that the service temperature has a significant effect on the comprehensive properties of AgNP/PMMA composites.

Keywords: nanoparticles; composites; thermal properties; mechanical properties; electrical properties

1. Introduction

Polymethyl methacrylate (PMMA) is an optically transparent thermoplastic polymer synthesized from methyl methacrylate monomer [1] and is widely used as a substitute for inorganic glass and polymer matrices of composites with outstanding weather resistance and scratch resistance [2–6]. Ag nanoparticles (AgNPs) with small particle size, large specific surface area and high surface energy have attracted great attention and are considered to be an ideal reinforcement material of nanocomposites with excellent optical, electrical and antibacterial properties [7–10]. Because of the outstanding thermal, mechanical and electrical properties, Ag-nanoparticle-reinforced polymethyl methacrylate (AgNP/PMMA) composites have rapidly developed in recent years and are widely used in healthcare, electronics, construction, transportation and many other fields [11–15]. When the AgNP/PMMA composites are used as dentures, antibacterial materials or other products, their ability to resist high temperatures has a significant impact on the service life and reliability of the products.

Much research has been conducted to improve the properties of AgNP/PMMA composites by modifying the polymer matrix, adding new fillers and improving the preparation process [16–18]. De Matteis et al. [19] added monodisperse citrate-covered AgNPs with an average diameter of 20 nm in PMMA composite and significantly reduced the adhesion and colonization ability of Candida albicans on PMMA dental prosthesis, attributed to the reduction in the surface roughness of PMMA by the addition of AgNPs. Philip et al. [20] synthesized PMMA nanofibers by the electrospinning method and AgNPs with an average diameter of 5–10 nm by the microwave-assisted biosynthesis method and found that the intensity of PMMA nanofibers was reinforced with redshift by the incorporation...
of AgNPs, which proved the capacity of PMMA nanofibers as a host matrix for AgNPs. Matamoros-Ambrocio et al. [21] synthesized AgNP/PMMA composites by an opal of PMMA microspheres with an average diameter of 298 nm and AgNPs with a 15 nm average diameter and found that the periodicity of the PMMA opals was slightly altered, and the photonic band gap maxima shifted toward longer wavelengths, decreased in intensity and broadened as the AgNP concentration was increased.

The service temperature of AgNP/PMMA composites can be easily affected by changes in ambient temperature, heating effect when current passes through the composites and heat transfer rate from high-temperature objects by the enhanced thermal conductivities. Sahputra et al. [22] found that the Young’s modulus and storage modulus of PMMA decreased significantly with the rise in temperature, while the volume increased with the rise in temperature. Because of the polymer matrix sensitivity to temperature, there is an urgent need to study the properties of Ag/PMMA composites under different service temperatures. In this work, multifunctional AgNP/PMMA composites with different AgNP contents were prepared by a mixing and hot-pressing method, which is suitable for large-scale industrial production. The microstructure analysis of AgNP/PMMA composites was conducted by SEM micrographs. The effects of service temperature and filler content on thermal conductivity, flexural strength, flexural modulus and electrical resistivity of AgNP/PMMA composites were measured and discussed according to the microstructures.

2. Materials and Methods

2.1. Materials

AgNPs were purchased from McLean Biochemical Co., Ltd. (Shanghai, China), with a purity of 99.5% and an average diameter of 50–75 nm measured by a particle analysis image-processing technique. PMMA particles were purchased from Zoomlion Plastics Technology Co., Ltd. (Jiangmen, China), with a purity of 99.5%. All other chemical reagents were of analytical grade and were used directly without purification.

2.2. Preparation of AgNP/PMMA Composites

Figure 1 shows the preparation process of AgNP/PMMA composites. AgNPs of 0.247 g and PMMA particles of 2.753 g were mixed in ethanol solution and sonicated for 15 min for uniform mixing. Then, the brown turbid liquid was placed in an oven at 150 °C for 60 min to obtain a viscous mixture of AgNPs, PMMA and ethanol, which was placed in a tetrafluoroethylene mold and continued to be dried in an oven at 150 °C for 30 min until the mixture of AgNPs and PMMA was completely dried to a powder. Finally, the powder mixture was put into a hot-pressing mold and then hot-pressed several times at 150 °C for 30 s to obtain the AgNP/PMMA composite with a AgNP volume content of 1%. Similar processes were used to prepare PMMA and AgNP/PMMA composites with a AgNP volume content of 1%, 5% and 15%, corresponding to the sample names of PMMA, AgNPs1/PMMA, AgNPs5/PMMA and AgNPs15/PMMA. These content values are selected according to the related research results [7–12] and represent good properties and a high weight content of 61.48%.

Figure 1. Preparation process diagram of AgNP/PMMA composites.
2.3. Characterizations

The microstructure analysis of AgNP/PMMA composites was conducted by scanning electron microscopy (SEM) (S4800, Hitachi Co., Tokyo, Japan) with an accelerating electric voltage of 5 kV and an electric current of 10 µA. The thermal conductivities were measured by a xenon lamp thermal conductivity meter (DXF 500, TA Co., New Castle, PA, USA) following the standard test method of ASTM E1461 [23], with temperatures of 20 °C, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, 100 °C and 110 °C, in the range from room temperature to the glass transition temperature of PMMA. The three-point bending tests were conducted by an electronic universal testing machine (CMT6103, MTS Co., Minneapolis, MN, USA), according to the standard ISO 178 [24], with a loading rate of 1 mm/min and temperatures from 20 °C to 110 °C, controlled by a high-power infrared lamp. The electrical resistivities of AgNP/PMMA composites at different service temperatures were measured by a voltage–current method with composites samples, measuring electrodes and thermocouples placed in a heating oven, which controlled the temperature from 20 °C to 110 °C. Three electric meters, Keithley 2400 (Keithley Instruments Inc., Solon, OH, USA), AR907 and AR3125 (Smart Sensor Co., Dongguan, China), were used for different levels of electrical resistivity from insulators to conductors. The size of all the electrical test samples is the same with a diameter of 50 mm and a thickness of 1 mm.

3. Results and Discussion
3.1. Microstructure Analysis

The SEM micrographs of fracture surfaces of PMMA and AgNP/PMMA composites are shown in Figure 2. The fracture surface of PMMA is relatively flat, indicating a typical brittle fracture morphology. With the addition of AgNPs, AgNPs preferentially agglomerate into AgNP clusters, consistent with the results of other studies [25], while a small number of air bubbles is observed in SEM micrographs, which are difficult to visually observed during the preparation processing and cannot be avoided completely. The air bubbles are caused by the agglomeration of nanoparticles during the mixing process and are mainly observed in the AgNP clusters, as shown in Figure 2. The larger the AgNP cluster’s size, the greater the number of the air bubbles that are observed in the SEM micrographs. For the composite with 1 vol% AgNPs, the AgNP clusters with an average diameter of about 4 µm measured by the SEM micrographs are observed to homogenously dispersed in the PMMA matrix. Attributed to the small size and high surface energy, it is very difficult for Ag nanoparticles to be completely dispersed individually, and they tend to agglomerate as clusters. The homogeneous dispersion of AgNP clusters is also important for the properties of composites. At the AgNP content of 5 vol%, the AgNP clusters become smaller, with an average diameter about 2 µm, possibly due to the distances between AgNPs decreasing at higher content, while a small number of AgNPs without agglomeration are also observed to be homogenously dispersed in the PMMA matrix. When the content of AgNPs rises to 15 vol%, the diameter of AgNP clusters continually decreased to less than 1 µm, although the number of AgNP clusters and AgNPs uniformly dispersed in the PMMA matrix is increased significantly. This proves that the preparation method of mixing and hot-pressing is effective in obtaining the homogenous dispersion microstructure of AgNP/PMMA composites.
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Figure 2. SEM micrographs of (a) PMMA, (b) AgNPs1/PMMA, (c) AgNPs5/PMMA and (d) AgNPs15/PMMA.

3.2. Thermal Properties

The through-plane thermal conductivities of AgNP/PMMA composites as a function of AgNP content under different temperatures are shown in Figure 3. When the AgNP content increases from 0 to 1 vol%, the thermal conductivities of the composites decrease due to a small number of air bubbles produced during the preparation of the composites. Because of the larger size of AgNP clusters in composite of 1 vol% AgNPs, more air bubbles with ultra-low thermal conductivity are produced and cause a more serious effect on the reduction in thermal conductivity compared with composites of higher content. When the AgNP content rises from 1 vol% to 5 vol% and 15 vol%, the thermal conductivities of AgNP/PMMA composites increase significantly under all the different service temperatures, attributed to the positive influence of the high thermal conductivity of AgNPs gradually exceeding the negative influence of the air bubbles, which are obviously reduced when the size of AgNP clusters becomes smaller with the increasing of AgNP content. The thermal conductivity of AgNP/PMMA composite with a AgNP content of 15 vol% is 116.19% higher than that of PMMA. This is attributed to the thermal conduction networks composed by the connection of AgNPs with excellent thermal conductivity, making heat transfer faster and more efficiently [26].

The thermal conductivities of AgNP/PMMA composites at different AgNP contents as a function of temperatures are shown in Figure 4. The thermal conductivity of AgNP/PMMA composites decreases with the rise in temperature for all the composites. With the rise in temperature, the effect of temperature on the thermal conductivity of AgNP/PMMA composites is gradually decreased. The thermal conductivity of PMMA
 decreases with the temperature rising to its glass transition temperature of 110 °C, while AgNPs are less affected in this temperature period. The excellent thermal conduction ability of AgNPs causes a faster heat transfer ability and rise in temperature of composite samples with higher AgNP content. For example, the thermal conductivity of AgNP1/PMMA at 20 °C is 1.62 times that at 110 °C, while the thermal conductivity of AgNP15/PMMA at 20 °C is only 1.38 times that at 110 °C. This decrease in thermal conductivity with increasing temperature is mainly attributed to the reduction in phonon mean free path with the increase in collisions between phonons at higher temperatures [27] and the thermal conductivity of the PMMA matrix decreasing with the rise in temperature.

![Figure 3. Thermal conductivities of AgNP/PMMA composites at different AgNP contents.](image)

![Figure 4. Thermal conductivities of AgNP/PMMA composites under different temperatures.](image)

### 3.3. Mechanical Properties

The mechanical properties under different temperatures for AgNP/PMMA composites were measured by self-assembling equipment with a uniaxial testing machine, infrared lamp, thermocouple and digital thermocouple temperature control meter. The large fluctuation of flexural strengths of AgNP/PMMA composites is caused by the internal defects of composites, such as air bubbles and cracks, as shown in Figures 5 and 6. The flexural strength of composite is improved due to the strong interface between AgNP reinforcement and the PMMA matrix and excellent mechanical properties of AgNPs. When the AgNP content is lower than 5 vol%,
cracks are prevented by the homogenous dispersion of AgNPs in the PMMA matrix, achieving a maximum flexural strength of 45.63 MPa for the AgNPs5/PMMA composite. At a higher AgNP content of 15 vol%, the flexural strength of the composite is decreased, attributed to the fact that more AgNP clusters are formed by the agglomeration of AgNPs, causing more serious impacts on local stress concentration areas or initiation points of cracks [25].

![Figure 5](image-url)  
**Figure 5.** Flexural strengths of AgNP/PMMA composites at different AgNP contents.

![Figure 6](image-url)  
**Figure 6.** Flexural strengths of AgNP/PMMA composites under different temperatures.

The flexural strengths of AgNP/PMMA composites under different temperature are shown in Figure 6. Compared with the effect of AgNP content, the flexural strengths of composites are less affected by the service temperature. It is found that the flexural strengths of composites have different sensitivities to temperature, showing a positive correlation with the AgNP content. As the thermal conductivity of PMMA decreases with the temperature and AgNPs are less affected in this temperature period, AgNPs with high
thermal conductivity causes a faster heat transfer and rise in temperature of composite samples at a higher AgNP content. The flexural strengths show a similar trend of first increasing and then decreasing with the rise in temperature for all the composites. As the AgNPs are not connected to each other strongly, the breaking of composites is mainly dependent on the properties of the PMMA matrix. When the temperature rises from 30 °C to 80 °C, the flexural strength is improved by the increasing of molecular mobility in the polymer composite. When the temperature rises above the hot deformation temperature of 80 °C, the flexural strengths of the composites begin to decrease gradually.

Figure 7 shows the flexural moduli of AgNP/PMMA composites under different service temperatures and illustrates a similar trend of first decreasing and then increasing with the increase in AgNP content, achieving a maximum value of 3028.71 MPa for the AgNPs15/PMMA composite. This is attributed to the fact that the air bubbles produced during the preparation of AgNP/PMMA composites have more significant influence on the mechanical properties of composites when the AgNP content is lower than 5 vol%. For the composites with higher AgNP contents and strong interface between AgNPs and PMMA, the networks composed by the connection of AgNPs with excellent flexural modulus become the main influencing factor and reinforce the ability to resist deformation. The flexural modulus is also reinforced by the high stiffness of AgNPs [28].

As shown in Figure 8, with the rise in temperature, the flexural moduli decrease significantly for PMMA and all the AgNP/PMMA composites. This is attributed to the softening of the PMMA polymer matrix with rising temperature. With the increase in molecular motion and molecular energy caused by the rising temperature, the interaction between molecules is weakened, leading to changes in structure and property. Compared with PMMA, the flexural moduli of composites are more sensitive to temperature and decrease more severely with the rise in temperature, due to the photothermal effect of AgNP/PMMA composites, which makes the composites easier to self-heat and more sensitive to temperature at a higher AgNP content.
3.4. Electrical Properties

Figure 9 shows the electrical resistivities of AgNP/PMMA composites at different contents of AgNPs. The resistance values of PMMA, AgNPs1/PMMA and AgNPs5/PMMA samples are obtained after being broken down by high voltages, 2500 v, 5000 v and 500 v, respectively, while the resistance values of AgNPs15/PMMA are obtained without being broken down. This illustrates that the AgNP/PMMA composites transform from an insulator to a conductor within the content range from 5 vol% to 15 vol%, where the volume electric resistivity is rapidly decreased by five orders of magnitude. This means the content of 5 vol% is the electric percolation threshold of AgNP/PMMA composites and is crucial for applications in electronics fields such as sensors and devices. The percolation threshold is higher than that of the composite with a specific orientation microstructure or three-dimensional reinforcement due to the homogeneous dispersion of particles delaying the conduction network at a specific loading fraction. When the content of conducting fillers is larger than the percolation threshold, the fillers contact each other and start to form networks with more and more conducting paths and change the insulation property immediately [29].
The electrical resistivities of PMMA and AgNP/PMMA composites as a function of temperature are shown in Figure 10. The electrical resistivities of AgNP/PMMA composites are not sensitive to temperature, which is possibly because of the significant difference in electrical conductivity between AgNPs and the PMMA matrix. In the temperature range of 20–110 °C, the thermal, mechanical and electrical properties of AgNPs are less affected than those of the polymer matrix. The AgNPs15/PMMA composite shows the best electrical property as a good conductor and achieves a minimum electrical resistivity of $1.37 \times 10^{-3} \, \text{Ω} \cdot \text{m}$, which is equal to a maximum electrical conductivity of $0.137 \, \text{s} \cdot \text{m}^{-1}$ and is an improvement of nine orders of magnitude over that of PMMA, which has better electrical conductivity than other similar composites and great potential applications in electronics fields such as detection and sensing [12,30,31].

![Figure 10. Electrical resistivities of AgNP/PMMA composites under different temperatures.](image)

### 4. Conclusions
AgNP/PMMA composites with homogeneously dispersed AgNPs were successfully prepared by a fast method of mixing and hot-pressing. The thermal conductivities of AgNP/PMMA composites first decrease and then increase with the increase in AgNP content, while continuously decreasing with the rise in service temperature. The AgNP/PMMA composite with a AgNP content of 15 vol% achieves the maximum thermal conductivity and 116.19% higher than that of PMMA. The flexural strength shows a trend of first increasing and then decreasing with the increase in AgNP content and temperature, while the flexural modulus shows a similar trend to flexural strength with the increase in AgNP content and decreases gradually with the rise in temperature. The resistivities of composites continuously decrease with the increase in AgNP content and achieve the electric percolation threshold of 5 vol%. The minimum electrical resistivity of AgNPs15/PMMA composite decreases by nine orders of magnitude compared to that of PMMA. This work proves that the service temperature has significant influence on the thermal and mechanical and electrical properties of AgNP/PMMA composites.

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