Polypropylene and silver nanowires based nanocomposites as a part of nanocapacitors

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In this paper, the structure and dielectric properties of the nanocomposites based on polypropylene (PP) matrix and silver nanowire (AgNW) were investigated. Silver nanowires were prepared by a modified polyol method. The diameter range of the nanowires, according to atomic-force-microscopic investigation, is between 40 to 80 nm. PP/AgNW nanocomposites were synthesized by blending in the polymer solution. The thin films of PP/AgNW nanocomposites were prepared by the hot-pressing technique. The dielectric properties of the PP/AgNW nanocomposites depending on silver nanowires concentration were investigated at the 320-440 K temperature range.

(Received December 14, 2023; accepted August 1, 2024)

Keywords: Nanowire, Supercapacitor, Polypropylene, Nanocomposite

1. Introduction

Recently, polymer nanocomposites, in which the insulating polymer matrix contains metal or semiconductor nanoparticles, have attracted considerable interest [1-3]. The driving force behind the incorporation of metal and semiconductor nanoparticles into the polymer matrix is the possibility of improving certain features of polymers, such as electrical and thermal conductivity, and expanding the range of their applications.

Metal-polymer nanocomposites are considered one of the most promising advanced materials. Metal nano-additives play a vital role in polymer-based nanocomposite production with enhanced electro-physical features, particularly at low concentrations. The concentration of metal nano-additives also affects the polarization ability of the polymer-based nanocomposites [4-5]. At the filler concentration that closes to or is higher than the percolation threshold, the permittivity of the polymer significantly changes due to a tremendous amount of polarized dipoles in the interfacial region [6]. It is known that not only the concentration but also the size and shape of the nano-additives are very important for the formation of the targeted properties of polymer-based nanocomposites. Since nanowires have a larger surface area and a lower percolation threshold compared to nanoparticles, they can more effectively improve the electrophysical properties of a polymer medium [7-8]. In the scientific literature of recent years, there is a set of research works on the improvement of the dielectric properties of the polymer matrix at low concentrations of one-dimensional (1D) nanostructures [9–10]. Depending on the arrangement of these one-dimensional nanostructures in the polymer matrix, the formation of discrete regions with a high electrical energy storage capacity is possible. In such structures one-dimensional nanofiller and polymer matrix act as nanoelectrode and nanodielectric lier, respectively [11–12]. These polymer-based nanocapasitor structures have a great potential for storing electrical energy. Therefore, they have application areas, such as communication devices, actuators, charge storage devices, and capacitor systems [13-14].

Since silver nanowires possess high electrical and thermal conductivity, low surface resistance, high transparency, and good biocompatibility, they are widely used in catalysts, microelectronics equipment, thin-film solar cells, and biosensors. In addition, Ag nanowires (Ag NW), which have a large surface area and high electrical conductivity, are considered a promising material for charge storage devices, as well as for capacitor preparation [15-16]. However, the "Coherent market insight" research states that the expensive, multi-step process of producing silver nanowires prevents widespread commercial usage of them. Silver nanowires are thought to cost between $500 and $800 per gram.

Furthermore, the properties of nanocomposites based on Ag nanowires vary depending on the structure and properties of the filler. By the optimal synthesis techniques, it is possible to obtain nanocomposites with improved morphology, structure, and dielectric properties.

Taking into account all of the previously mentioned factors, the development of an affordable, simple-to-manufacture, and yet effective technique of regulating the Ag nanowires' characteristics is actual issue.

The polyol method is one of the main various synthesis methods for obtaining silver nanowires, with advantages such as lower cost and mass production [16].

The present study demonstrates the synthesis of PP/AgNW nanocomposites and the variation of the dielectric properties of the nanocomposites as a function of silver nanowires concentration in the framework of the nanocapacitor model.

2. Materials and methods

2.1. Materials

Silver nitrate ($AgNO_3$, 98%), sodium chloride (NaCl, 99.9%), potassium bromide (KBr, 99.0%), polyvinylpyrrolidone ((C_6H_9NO) n, MW≈130.000), ethylene glycol ($(CH_2OH)_2$, 99.8%), ethanol (C_2H_6O, 99.7%) were purchased from Karma Lab. (Izmir, Turkey). All chemicals were of analytical grade.

2.2. Preparation

A modified polyol method with two halides was used to produce Ag NWs [17]. Firstly, the ethylene glycol (EG) solutions of 0.01 M NaCl, and 0.005 M KBr were prepared. Further, 0.6 gr polyvinylpyrrolidone (PVP) dissolved in 20 ml EG under the 100 °C. Finally, $AgNO_3$ and the EG solutions of NaCl, and KBr were added to the PVP/EG system. The system was mixed for a minute. Then, the mixing process continued in a silicone oil bath heated to a temperature of 175 °C. At the end of the reaction, the mixture was diluted with ethanol and centrifuged several times to remove excess reagents until a transparent solution was obtained.

2.3. Preparation of PP/AgNW nanocomposites

Ag NW/PP nanocomposites were prepared by the following technique: polypropylene (PP) powder was solved in toluene under 100 °C for 20-30 minutes. In addition, Ag nanowires were dispersed in 10 ml toluene by ultrasonic cavitation. Further, dispersed Ag nanowires were added into the PP/toluene system and were mixed for 30 minutes. To remove the solvent from the system obtained nanocomposite solution was evaporated in the open Petri dishes for 24 hours. The nanocomposite system was compressed under 100 MPa pressure at 160 °C to a thin film was obtained. The thin films of polymer nanocomposite were produced with various mass concentrations of the filler, namely 1%, 3%, 5%, 7%, and 10%.

2.4. Characterization

Surface topography measurements were conducted using atomic force microscopy (AFM, INTEGRA PRIMA) and optical microscope (ZEISS Axio Imager. A2m). Special silicon cantilevers were used for the AFM scan. The scan size was 2 × 2 mm^2. The measurements were performed in the semicontact microscopy mode in the air lines of the image were, respectively, 256 and 1969 Hz.

The absorption spectra of AgNWs were obtained by ultraviolet visible (UV–vis) spectrophotometer (Specord 250).

X-ray diffraction (XRD) measurements were carried out in the reflection mode on a diffractometer (Rigaku Mini Flex 600). In all the cases, Cu Kα radiation from a Cu X-ray tube (run at 15 mA and 30 kV) was used. The samples were scanned in the Bragg angle 2 h range of 20–80 °C.

The dielectric properties of nanocomposites were investigated on the MINIPI E7-20 immitant device. By applying a broadband meter E7-20 immittance measured the frequency dependence of the dielectric permittivity and the dielectric loss at room temperature, in the frequency range f ¼ 100Hz–1MHz. Measurement of dielectric permittivity versus temperature was carried out at f = 1 kHz

The ultrasonification of the solutions was carried out by the Sonics Vibramobil VCX 500.

3. Results and discussion

3.1. The structural characterizations of Ag NW

The morphology and the size of synthesized Ag nanowires were investigated by optical (Fig. 1 a) and atomic force microscopies (Fig. 1 b and c). The average diameter and length of obtained Ag nanowires are 40-80 nm and 2-6 μm, respectively.

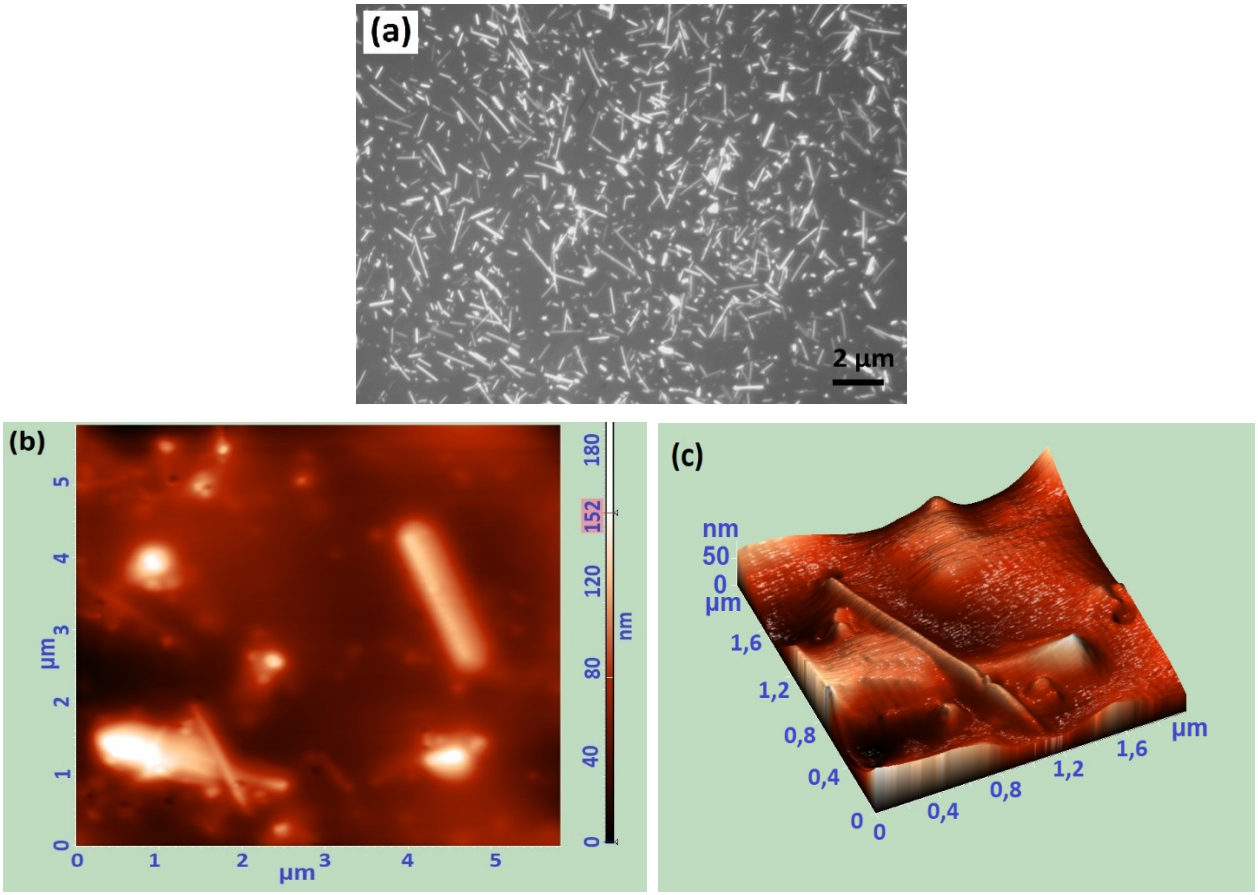

Fig. 1. Morphology of Ag NWs: (a) optical microscope image, (b) 2D AFM image, (c) 3D AFM image (color online)

3.2. The XRD measurement of the samples

The crystalline structures of the silver nanowires, pure PP, and PP/AgNW nanocomposites were studied by the X-ray diffraction method (Fig. 2). XRD pattern of the pure PP matched with the ICDD (PDF-2/Release 2011 RDB - 00-050-2397) date base perfectly and indicates α-PP with a monoclinic crystal structure [17]. The lines at the 38.67°, 44.73°, 64.79°, 77.77°, and 81.89° values of 2-theta corresponding to (111), (200), (220), (311), (222) indexes belong to silver nanowires and shows good agreement with card number 00-004-0783 (ICDD database) [18].

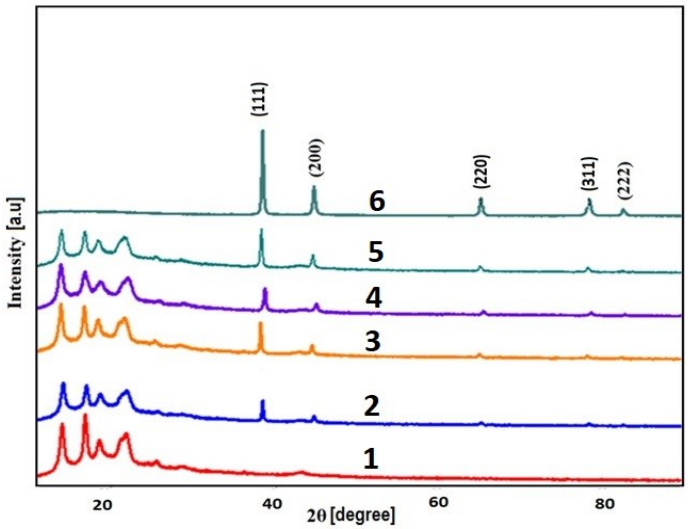

Fig. 2. X-ray diffraction pattern of the silver nanowires, pure PP and PP/AgNW nanocomposite with different filler concentration: 1-Pure PP, 2- PP/AgNW_1%, 3- PP/AgNW_5%, 4- PP/AgNW_7%, 5- PP/AgNW_10%, 6-Ag NWs (color online)

Ag nanowires possess face-centered cubic unit cell structure, and lattice parameters are a=b=c=4.086 A° and a=b=g=90°, respectively. Uniform nanowires were obtained through the slow release of Ag^+ ions and the fast growth rate of the (111) plane. The X-ray diffraction image of PP/AgNW nanocomposite possesses the characteristic lines of both components. An increase in the filler concentration in the polymer matrix leads to the intensity enhancement of the silver nanowires' characteristic X-rays.

3.3. The dielectrical measurement of the samples

Fig. 3 demonstrates the temperature dependence of the resistivity of PP and PP/AgNW nanocomposites. According to the figure, it became clear that the addition of the AgNW leads to a decrease in the resistivity of the pure polymer, which can be explained by the conductive nature of the Ag nanowires. At low filler concentrations, the distance between conductive wires in the polymer matrix is big. So the nanowires cannot form a conductive network in the matrix. As the amount of filler increases, the probability of bonding of the nanowires increases, so the contact resistance becomes dominant. In this case, the filler wires bond together to form a conductive network throughout the system, leading to a high conductivity of the composite [19].

The resistivity of the pure polymer and nanocomposite increased up to 360 K, which is explained by the temperature-induced polymer expansion. An increase in temperature causes thermal expansion and attenuation of material conductivity [20]. It is known that the orientation and anisotropy of filler in the polymer matrix affects the expansion ratio of the polymer [20]. Accordingly, a sharp change of the resistivity versus temperature was observed for the nanocomposite with a high concentration of the filler (Fig. 3; 4th curve).

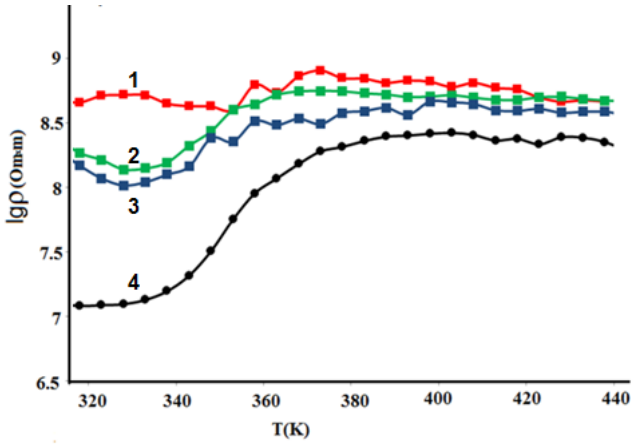

Fig. 3. Temperature dependence of the resistivity of PP and PP/AgNW nanocomposites: 1- Pure PP, 2- PP/AgNW_5%, 3- PP/AgNW_7% , 4- PP/AgNW_10% (color online)

Since PP withstands temperatures up to 363 °K, starting from this point structure of nanocomposite changes, and nanowires play the role of the carcass for nanocomposite. The resistivity of nanocomposite depends mainly on the number of nanowires and stands stable between 263-440 °K [21].

Fig. 4 shows the frequency dependence of the dielectric loss tangent of PP/AgNW nanocomposites. As can be seen from the figure, with an increase in the number of electrically conductive silver nanowires in the polymer matrix, a slight increase in the value of the dielectric loss tangent is observed. However, the dielectric loss tangent of all samples decreases with the increasing frequency. This decrease can be related to eliminating the Ohmic and polarization losses [22]. Furthermore, a relaxation peak of the pure polypropylene in the range of 10 kHs-100 kHs was lost after the inclusion of AgNWs. It can be assumed that the internal local field of the polymer matrix changes after the incorporation of the conductive nanowires, which, in turn, leads to change in energy dissipation nature of matrix.

The dielectric loss tangent values of PP/Ag NW nanocomposite show good agreement with resistivity measurement data.

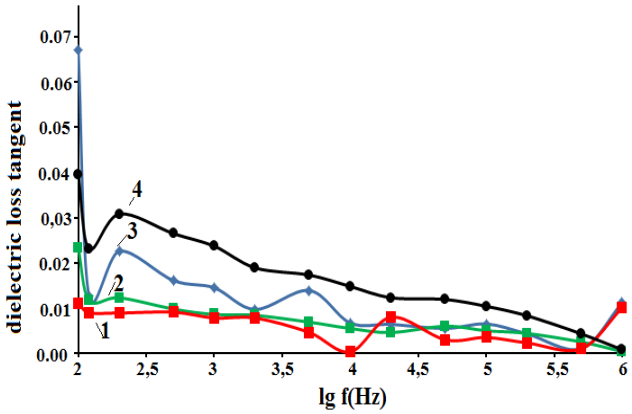

Fig. 4. Dependence of the dielectric loss tangent of PP and PP/AgNW nanocomposites on logarithmic value of the frequency 1- Pure PP, 2- PP/AgNW_5% , 3- PP/AgNW_7% , 4- PP/AgNW_10% (color online)

The dielectric constant of the PP/AgNW composite depending on silver nanowires concentrations was investigated at the 300-400 K temperature range (Fig. 5). It is known that the mobility of the polymer chain dramatically depends on the temperature. The temperature increase leads to the free movement of the dipole and easy polarization of the sample under the external electric field. It is clear from Fig. 5 that the permittivity of PP/AgNW nanocomposites remained stable under the influence of temperature at all filler concentrations. This fact indicates no significant change in the polarization of polymer layers happening in the considered temperature interval [23].

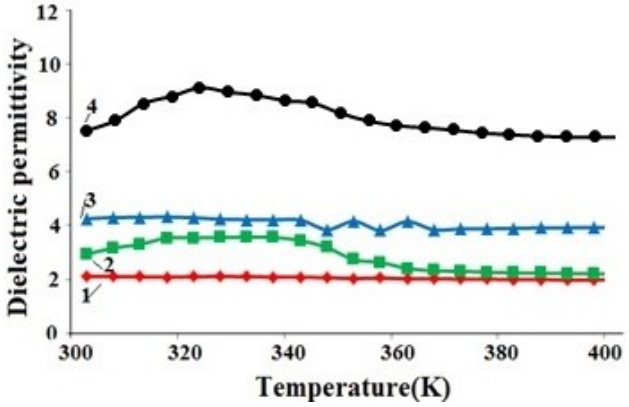

Fig. 5. Temperature dependence of the dielectric permittivity of the pure PP and PP/AgNW nanocomposites: 1- Pure PP, 2-PP/AgNW_5%, 3- PP/AgNW_7%, 4- PP/AgNW_10% (color online)

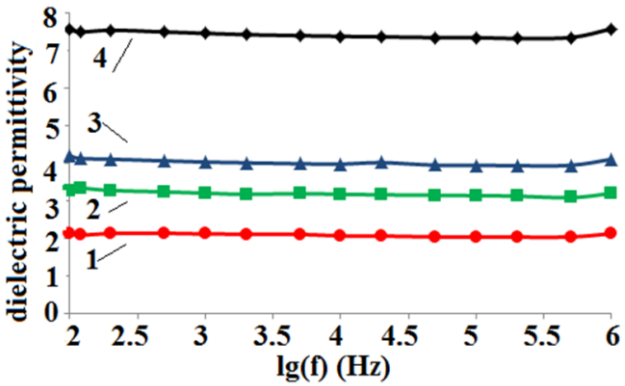

Fig. 6. Dependence of the dielectric permittivity of PP and PP/AgNW nanocomposites on logarithmic value of the frequency 1- Pure PP, 2- PP/AgNW_5%, 3- PP/AgNW_7%, 4- PP/AgNW_10% (color online)

In Fig. 6 the dependence of the dielectric permittivity of pure PP and PP/AgNW nanocomposites on frequency at room temperature is shown. According to Fig. 6 the nature of frequency-dependence of pure polymer dielectric constant is unchangeable with the introduction of silver nanowire. However, it became clear that the value of dielectric permittivity increases with the incorporation of silver nanowires.

This increase can be associated with the formation of the nanocapacitor structure in the polymer matrix. It is assumed that two silver nanowires, located close to each other, act as electrodes of capacitors, separated by a thin polymer layer. The intensity of the local electric field created by the silver nanowires around them increases sharply, which in turn causes the electronic polarization of the polymer layer.

It is clear that since the nanowires are randomly distributed, in a polymer matrix, the probability of the nano-capacitor formation is less when the concentration of the silver nanowires is low. While the number of Ag nanowires rises in the polymer matrix, the number of pairs that can be considered nanocapacitors increases, and this leads to an increase in the composite dielectric permeability [24]. Analogigal nano-capasitors on the bases of 1D nanomaterials were presented by several researchers [25-26]. A schematic representation of the nano-capacitor, formed by the orderly arrangement of the Ag nanowires in PP/AgNW nanocomposites is given in Fig. 7.

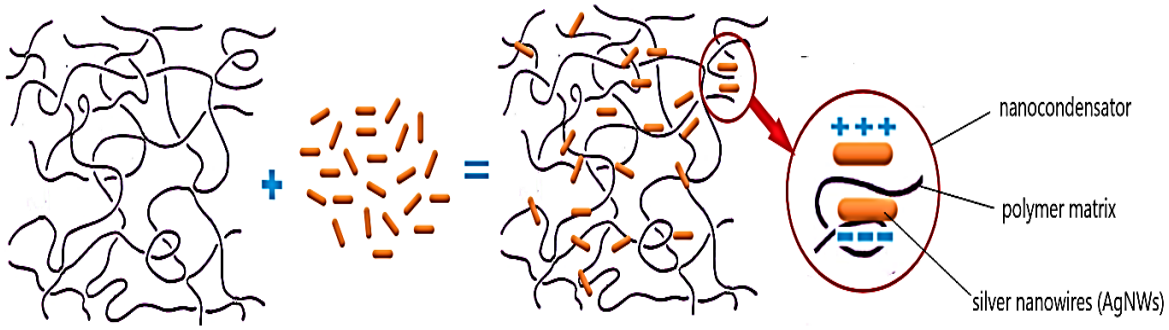

Fig. 7. A schematic representation of the nano-capacitor formed by the orderly arrangement of the Ag nanowires in PP/AgNW nanocomposites (color online)

4. Conclusion

AgNW with a diameter of 40-80 nm and a length of 2-6 μm was synthesized by a modified polyol method. XRD pattern of the Ag NW shows that nanowires possess a face-centered cubic unit cell structure. Uniform nanowires were obtained through the slow release of Ag^+ ions and the fast growth rate of the (111) plane. The dielectric properties of PP/AgNW nanocomposites were investigated. It was clear that the permittivity of PP/AgNW nanocomposites remained stable under the influence of temperature at all filler concentrations. This fact indicates that in the considered temperature interval, no significant change in the polarization of polymer layers occurs.

Furthermore, it became clear that the addition of the AgNW leads to a decrease in the resistivity of the pure polymer, which can be explained by the conductive nature of the Ag nanowires. It was also investigated that the value of dielectric permittivity increases with the incorporation of silver nanowires. The rise of dielectric permittivity of nanocomposite was explained by the formation of the nano-capacitor structure in the nanocomposite.

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