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High conductive Ag nanowire–polyimide composites: Charge transport mechanism in thermoplastic thermostable materials

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ABSTRACT

High conductive composites were elaborated by incorporating high aspect ratio (250) silver nanowires in polyimide matrix via solvent mixing way. Silver nanowires were synthesized in solution by polyol synthesis. The composite conductivity reaches the value of 10^2 S·m^{-1} above a very low percolation threshold (0.48 vol.% of silver nanowires). SEM-FEG images showed that metallic nanowires are well dispersed in PI matrix. They do not influence the physical structure of the polymer. Below the percolation threshold, γ, β and α relaxation modes were detected. γ relaxation mode was fitted to determinate the activation energy value (32.7 kJ·mol^{-1}) and the relaxation time (1.5×10^{-16} s). The mobility associated with the γ relaxation is considered to be localized and non-cooperative. According to the Mott theory, studies on composites below the percolation threshold showed that the conduction mechanism is ruled by tunneling at low temperatures. The transport mechanism led by hopping is activated at −50 °C.

1. Introduction

High aspect ratio particles have a great interest in conductive polymer matrix composite elaboration. They allow getting high performance composites at a very low content. A low concentration of fillers, homogeneously dispersed, enables to maintain the mechanical performance of polymer matrix and its processability. Polymers have been filled with different high aspect ratio particles (carbon nanotubes [1] and metallic wires [2]) to obtain conductive materials with a low percolation threshold. As far as we know, metallic wires are the best candidates to elaborate a composite with the highest conductivity above percolation threshold [3]. Polyimides present good chemical resistance, high thermal stability, and high mechanical strength. They are widely applied in aerospace as high performance engineering materials and in microelectronic industry as flexible substrates and dielectric layers [4–6]. For these applications it is desirable to use polyimides that are soluble in coating and casting processes [7]. The good dielectric properties of polyimides induce static charge accumulation problem. Their dissipation with preservation of mechanical properties is a great challenge. In order to increase the electrical conductivity, carbon black and carbon nanotubes have been already introduced in polyimides [4,5]. For polyimide/carbon nanotube composites, the electrical conductivity reached 10^{-5} S·m^{-1} for 3 wt.% [4] and 10^{-4} S·m^{-1} for 8 vol.% [8]. Carponcin et al. [9] obtained 10^{-1} S·m^{-1} in polyamide 11 for a loading of 0.96 wt.%. It was shown that elaboration of high electrical conductive polyimide is difficult. The highest values of conductivity reported in literature are for polymers filled with metallic particles [10]. The conductivity of a polymer matrix filled with metallic particles can be limited by the surface oxidation [3]. Ag nanowires are good candidates because they are preserved from surface oxidation layer. Recent studies showed that P(VDF-TrFE) matrix filled with Ag nanowires reaches 10^2 S·m^{-1} for a very low percolation threshold (0.63 vol.%) [11].

Ag NWs have been synthetized by the reduction of $AgNO_3$ in ethylene glycol solutions containing poly(vinyl pyrrolidone) (PVP) [12–14]. Literature reports several other methods: synthesis in aqueous solutions in the presence or absence of seeds and surfactants [15–18], hydrothermal synthesis using glucose as reducing agent [19], microwave assisted synthesis [20], and using template-directed synthesis in AAO [3]. But these elaboration techniques do not allow obtaining large quantities. In this work, Ag nanowires will be prepared by polyol process. They will be introduced in a polyimide matrix in order to reach a high electrical conductivity at a very low percolation threshold. Physical structure and electrical behavior of the matrix and of the composites will be studied.

2. Materials and methods

2.1. Materials

Polyimide (PI)/1-ethyl-2-pyrrolidone (NEP) solution (25 wt.%) was supplied by Evonik, Germany. Electroless Ag nanowires (Ag NWs) were synthesized by reducing $AgNO_3$ with ethylene glycol in the presence of poly(vinyl pyrrolidone). The reaction was carried out at 160 °C in a round-bottom balloon with magnetic stirring bar. This method and the solution concentrations were described by Sun et al. [13,14]. This method allows obtaining Ag NWs with a length distribution

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between 30 and 60 μm and a diameter around 200 to 300 nm. The Ag NWs morphology was characterized by SEM-FEG to estimate the mean aspect ratio ξ. The Ag NW suspension was rinsed in water and filtered through a polyamide (200 nm pore size) membrane. Filtered Ag NWs were stored in NEP and dispersed using a short pulse of sonication during 5 s, corresponding to a 25 W dissipated power.

2.2. Polyimide/Ag NW composite elaboration

A volume of Ag NW suspension was added to the PI/NEP solution under sonification. This suspension was film coated on a glass plate and placed in an oven at 80 °C during 30 min to evaporate the solvent. The film was removed from the glass plate and heated at 300 °C during 2 h in order to evaporate the residual traces of NEP. The formed composite was a film with a thickness around 50 μm. PI/Ag NW composites were elaborated with a volume fraction varying from 0 to 3 vol.%.

2.3. Scanning electron microscopy

The morphology of Ag NWs was observed by scanning electron microscopy (SEM) using a JEOL JSM 6700F instrument equipped with a field emission gun (SEM-FEG). The composites were fractured at the liquid nitrogen temperature to be observed by SEM-FEG.

2.4. Differential scanning calorimetry

Composite glass transition phenomenon was investigated by differential scanning calorimetry (DSC) using a TA Instrument 2920 DSC. Thermogravimetric analysis does not show degradation until 500 °C. DSC experiments were carried out in the temperature range 200–380 °C with a constant heating rate of 20 °C·min^{-1}. All the DSC measurements were performed under helium atmosphere. The DSC thermograms, reported in Fig. 3, represent the evolution of the heat capacity for neat PI and its composites filled with 0.5, 1, 1.5, 2, 2.5 and 3 vol.% of Ag NWs (Table 1).

2.5. Broadband dielectric spectrocopy

A BDS 4000 Novocontrol broadband dielectric spectrometer (BDS) system was used to obtain the dielectric relaxation map in a wide temperature and frequency range. The sample was inserted between two plan parallel electrodes. It was stimulated by a sinusoidal electrical field for an isothermal temperature and the complex impedance is recorded during frequency scan. The measurements were carried out in the frequency range 10^{-1}–10^{6} Hz from −150 to 250 °C by steps of 5 °C. This technique has been extensively described by Kremer and Schonhals [21]. In order to distinguish the influence of heating on the samples, two cycles of dielectric measurements were performed in this temperature range. The complex dielectric permittivity $\varepsilon^*_T(\omega)$ was recorded.

Relaxation modes were fitted with the Havriliak–Negami equation [22]:

$$\varepsilon^*_{T(\omega)} = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{(1 + (i\omega\tau_{HN})\alpha_{HN})\beta_{HN}} \quad (1)$$

where ε_∞ is the relative real permittivity at infinite frequency, ε_S is the relative real permittivity at zero frequency, τ_{HN} is the relaxation time, α_{HN} and β_{HN} are the Havriliak–Negami parameters and ω is the angular frequency.

Dipolar relaxations are often hidden by dissipative losses due to ohmic conduction. The Kramers–Kronig transform [23] offers an analytical tool to calculate ε''_{KK} from the real part $\varepsilon'_T(\omega)$:

$$\varepsilon''_{KK(\omega_0)} = \frac{\sigma_0}{\varepsilon_0\omega_0} + \frac{2}{\pi}\int_0^\infty \varepsilon'_{(\omega)} \frac{\omega_0}{\omega^2 + \omega_0^2} \cdot d\omega. \quad (2)$$

2.6. Electrical conductivity

The electrical conductivity of the PI/Ag NW composites was measured by a four wire sensing method using a Keithley 2420 when the sample resistance measured was below 100 Ω. When the value was above 100 Ω, electrical conductivity measurements were carried out by recording the complex conductivity $\sigma^*(\omega)$ using a Novocontrol broadband spectrometer. Measurements were done in the frequency range from 10^{-2} to 10^{6} Hz at room temperature. The real part, $\sigma'(\omega)$ of the complex conductivity $\sigma^*(\omega)$ was investigated. The value of $\sigma'(\omega)$ at 10^{-2} Hz was taken as dc conductivity σ_{dc} [1]. 50 μm thick film composites were placed between two circular gold platted electrodes (20 mm in diameter). To reduce contact resistivity with the cell electrodes, a thin silver lacquer layer was coated onto both sides of the films.

3. Results and discussion

3.1. Microscopic observation

The morphology and aspect ratio of Ag NWs were studied by SEM-FEG with secondary electron detection mode. Dispersed Ag NWs in NEP suspension are deposited on SEM pin. After NEP evaporation, Ag NWs are shown in Fig. 1. Individually nanowires are observed. They have no affinity with NEP, which allows a homogeneous dispersion in this solvent. They were not damaged after sonication treatment. Ag NW widths were ranged from 200 to 300 nm, and their lengths from 20 to 80 μm. However, we estimated that at least 70% of the nanowires were over 60 μm long which meant low size dispersion. The mean aspect ratio of silver nanowires was estimated around 250. Sun et al. [14] measured an intrinsic conductivity of 0.8×10^7 S·m^{-1} for a single Ag NW. Ag NWs observed indicate the interest of this method to obtain reproducible and large quantity of Ag NWs. PI/Ag NW composites were prepared with Ag NW volume fractions from 0.25 vol.% to 3 vol.%. Fig. 2 shows SEM-FEG cryocuts of the PI matrix filled with 0.5 and 3 vol.%. Films were fractured at liquid nitrogen temperature perpendicularly to the stretching direction. Bright domains show that the Ag NWs dispersed in the PI matrix. Ag NWs were uniformly distributed throughout the PI matrix and micron size aggregates were not observed. Indeed, NWs have no affinity in NEP and they kept their homogeneous dispersion in the polymer.

3.2. Physical structure

DSC thermograms of neat PI and its composites filled with 0.5, 1, 1.5, 2, 2.5 and 3 vol.% of Ag NWs are reported in Fig. 3. The second temperature scans are shown. Because of its amorphous nature, PI glass transition is studied. For the neat PI, the T_g is near 330 °C. The glass transition temperature exhibits a very slight modification with the filler content.

Table 1
Glass transition temperatures and heat capacity step at T_g of PI/Ag composites.

Volume fraction of Ag NWs (vol.%)	0	0.5	1.0	1.5	2.0	2.5	3
T_g (°C)	329 ± 2	331 ± 2	326 ± 2	327 ± 2	327 ± 2	327 ± 2	327 ± 2
ΔC_p (J·g^{-1}.°C^{-1})	0.30 ± 0.01	0.27 ± 0.01	0.26 ± 0.01	0.23 ± 0.01	0.20 ± 0.01	0.31 ± 0.01	0.21 ± 0.01