Low filled conductive P(VDF-TrFE) composites: Influence of silver particles aspect ratio on percolation threshold from spheres to nanowires

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Polymer composites filled with silver nanowires enable the highest value of electrical conductivity known up to now in the case of conductive nanoparticle dispersion with a percolation threshold less than 1 vol%. Silver nanowires with high aspect ratio were elaborated by two types of synthesis: electrochemical deposition in a template and polyol synthesis. For the first time the influence of each kind of nanowires in composites was studied and compared to spherical nanoparticles as reference. The value of percolation threshold and conductivity level above the percolation threshold were measured and compared. These silver nanowires were introduced into poly(vinylidenedifluoride-trifluoroethylene) in comparison to spherical silver nanoparticles. The preparation method modified the effective aspect ratio of nanowires. The low percolation threshold and the microscopy observations confirmed the good dispersion of nanowires in composites. The lowest percolation threshold was determined in the case of the polyol synthesis nanowires (0.63 vol%) in comparison with electrochemical deposited nanowires (2.2 vol%). The level of conductivity above the percolation threshold obtained with each kind of particles is in the same range near 100 $S.m^{-1}$. The value of electrical conductivity obtained above the percolation threshold is unusual at this low content of conductive filler and is observed for the first time in a conductive polymer composite.

1. Introduction

Conductive polymer composites have attracted significant attention since the introduction of metal [1] or carbon [2] in polymer insulating matrix. Level of conductivity, conductive filler content and mechanical properties are the characteristics which define the composite application. Conventional spherical conductive particles or nanoparticles permit to reach high conductivity but for a large volume fraction (15 vol%). This parameter increases significantly the composite final weight and deteriorates mechanical properties. Obtaining low filled polymer composites (<5 vol%) is a new challenge for automotive or aeronautical applications. The studies of Balberg [3,4] have largely contributed to show the influence of the particles aspect ratio on the percolation threshold value. The ratio between the diameter and the length of a particle is crucial. In the group of conductive fillers of high aspect ratio, carbon nanoparticles such as CNTs [5] (1000–10000) and carbon nanofibers [6] can achieve low percolation thresholds of approximately 1% vol [7]. However, the maximum conductivity values obtained are close to 10^{-1} $S.m^{-1}$, this level enables composites for the charge transport. The metallic nanowires supply the highest electrical conductivity of the associated metal bulk [8]. Some results obtained with metallic nanowires showed extremely low percolation thresholds [9,10] for metal particles (<5% vol) and reached the highest conductivity values [11,12] in homogeneous dispersed low filled composites (10^2 $S.m^{-1}$).The mechanical behavior of the polymer matrix is maintained for a small amount of nanowires (5 vol%) [13]. The previous results [12] obtained with nickel nanowires have shown an oxidative surface layer which is incompatible with high conductivity level. A removing treatment was suggested successfully but induces a supplementary step in process. Silver nanowires have no oxidative layer on their surface. High conductive silver nanowires were easily realized by two kinds of methods. Electrochemical deposition using a template [14] produced regular nanowires but this technique provides a limited volume of nanowires. The polyol method [15] describes a technique more attractive for industrial applications where the volume of nanowires produced is proportional to the reactant quantities. They are excellent candidates to formulate high conductive composites polymer for multifunctional applications as structural conductive composites, flexible electrodes or EMI shielding.

In this study, different types of silver nanowires were elaborated by electrochemical deposition and by polyol process. These nanowires have been used to elaborate conductive composites with P(VDF-TrFE) as matrix. The percolation threshold and conductivity level were compared with spherical silver nanoparticles. The particle shape and the dispersion in composites were studied using scanning electron microscopy. The influences of preparation and particles aspect ratio on percolation threshold and level of conductivity were discussed.

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2. Experimental section

2.1. Materials and sample preparation

a. Silver nanowires by electrochemical deposition
Electrodeposited silver nanowires (Ag NWs) were synthesized by electrochemical deposition in an anodic aluminum oxide (AAO) porous template using free cyanide electrolyte. Direct current (dc) electrodeposition was carried out at 50 °C using a silver wire of 1.0 mm in diameter as anode. A porous AAO membrane with holes of 200 nm in diameter and 50 μm thickness was supplied by Whatman. One side of the AAO membrane was coated with a 35 nm thickness silver layer by using sputtering technique as cathode for electrodeposition. The AAO membrane was dissolved in NaOH 6 M for 30 min, releasing Ag NWs from the template. An ultrasonic treatment of short 5 s pulses corresponding to a dissipated power of 25 W permits to disperse all the aligned nanowires. High purity of Ag nanowires as fillers has a great interest in order to achieve high dc conductivity in composites. The Ag NWs morphology was characterized by scanning electron microscopy (SEM) to determine the aspect ratio ξ. Ag NWs exhibit a uniform length of 50 μm and a regular diameter of 200 nm. These AAO porous templates allow us to elaborate nanowires with a narrow distribution length and precise aspect ratio. The nanowire suspension was then filtered through a polyamide (200 nm pore size) membrane. Filtered nanowires were stored in acetone and dispersed using a short pulse of sonication for 5 s, corresponding to a dissipated power of 25 W. A droplet of this solution was deposited onto a SEM pin.

b. Silver nanowires by polyolelectroless process
Electroless silver nanowires were synthesized by reducing $AgNO_3$ with ethylene glycol in presence of poly(vinyl pyrrolidone) [16]. The reaction was carried out at 160 °C in a round-bottom balloon with magnetic stirring bar. This technique and the solution concentrations were described by Sun [15,16]. This technique allows us to obtain Ag NWs with a length distribution between 30 and 60 μm and a diameter around 200 to 300 nm. The Ag NWs morphology was characterized by SEM to estimate the mean aspect ratio ξ. The nanowire suspension was rinsed in water and then filtered through a polyamide (200 nm pore size) membrane. Filtered nanowires were dispersed using the same procedure that nanowires obtained by electrochemical deposition. A droplet of this solution was deposited onto a SEM pin.
For comparison, bulk Ag powder with 100 nm particle size, supplied by Aldrich, was chosen.

c. Composite preparation
Poly(vinylidene fluoride–trifluoroethylene) P(VDF-TrFE) (70/30) mol% copolymer was supplied by Piezotech S.A. (Hésingue, France). Melting temperature of 150 °C was determined by differential scanning calorimetry and the density was about 1.8 $g.cm^{-3}$.
The composites were prepared by using solvent casting method. P(VDF-TrFE) was dissolved in acetone. The nanowire acetone suspension was poured into the polymer solution and the mixture was subjected to 5 s short pulse of sonication, corresponding to a dissipated power of 25 W. Sonication parameters were optimized by the observation of Ag NWs dispersion using SEM [12]. The solvent was evaporated using a magnetic stirrer at 80 °C for 1 h. Pellets of randomly dispersed Ag NWs in P(VDF-TrFE) matrix were obtained. The pellets were cut and pressed into a steel mould with a piston to form a sample at 200 °C under 0.3 MPa. Sample geometry is a disk with 20 mm in diameter and 1 mm in thickness. No solvent residue was found in the thermogravimetric analysis, indicating a complete removal of acetone from samples. Ag NWs/P(VDF-TrFE) composites were elaborated with a volume fraction varying from 0 to 7.7 vol% with electrodeposited and polyol nanowires. Spherical Ag 100 nm/P(VDF-TrFE) composites were prepared with a volume fraction varying from 10 to 15 vol%.

2.2. Electron microscopy

The morphology of the nanoparticles was examined by scanning electron microscopy using a JEOL JSM 6700 F equipped with a field emission gun (SEM-FEG). Composite samples were fractured at the liquid nitrogen temperature for observation.

2.3. Electrical conductivity percolation

Bulk electrical conductivity of composites was measured by recording the complex conductivity $\sigma^*(\omega)$ using a Novocontrol broadband spectrometer. The measurements were carried out in the frequency range from 10^{-2} Hz to 10^6 Hz at room temperature. The real part $\sigma'(\omega)$, of the complex conductivity $\sigma*(\omega)$ was investigated. For all the composite samples considered in this study, the phase lag between the measured impedance and the applied ac voltage was negligible at low frequencies, so that the reported impedance at 0.01 Hz is equivalent to the dc resistance. The dc conductivity σ_{dc} of samples was determined from the independent frequency part of $\sigma'(\omega)$ [4]; i.e. the low frequency plateau. 1 mm thickness samples were introduced between two circular gold plated electrodes (20 mm in diameter). To reduce contact resistivity with the cell electrodes, a thin layer of gold (100 nm) was sputtered onto both sides of the films using a BOC Edwards scancoat sputter coater. The conductivity measurements were checked on Keithley 2420 source meter in a four-probe configuration.

The electrical optimization of filled polymer composite is strongly dependent on the volume fraction p and the aspect ratio ξ of the filler. In three-dimensional disordered systems, the insulator to conductor transition is marked by the percolation threshold. This phenomenon is driven by the percolation law [17].

$$\sigma = \sigma_0 (p - p_c)^t \tag{1}$$

Where σ_0 is a constant, p_c the percolation threshold and t is the critical exponent dependent on the lattice dimension.

In the case of spherical particles randomly dispersed, Scher [18] estimates the critical volume fraction $p_c = 15$ vol% of conductive spheres needed for the onset of conduction. In the meantime, some authors [2,19] observe a notable decrease of the measured percolation threshold compared with the theoretical value. Lower values of percolation threshold can occur with aggregated spherical particles. With nanosized particles, the nanofillers can create conductive aggregates with a secondary aspect ratio. These clusters have geometries similar to “grapes” described by Medalia [2] and forming secondary particles. An arrangement of these aggregates particles carrying percolative pathway and a discrepancy with the theoretical model. The phenomena can be also explained by segregation phenomenon [20]. However, the large presence of this kind of micronic aggregates is incompatible with the concept of homogeneous and isotropic dispersion, which guarantees the mechanical properties maintained.

Some models [3,4,21] described randomly dispersed composites with particles with high aspect ratio like the nanowires. In the case of the percolation model for cylindrical sticks system, proposed by Balberg and Binenbaum [4] looks to be adequate. It shows the dependence of the percolation threshold with the aspect ratio of conductive particles through their volume excluded. When the nanowires considered as randomly oriented sticks with $L/r >> 1$, their critical volume excluded expression derivative from the Balberg's equation is given by

$$V_{ex}^{cr} = \frac{L}{r} p_c = 1.6 \pm 0.2 \tag{2}$$

where p_c is the critical volume fraction for percolation.

3. Results

3.1. Conductive fillers

Fig. 1 shows the 100 nm particles provided by Sigma-Aldrich observed by SEM. At high magnification (B) the observation confirms the narrow distribution in diameter around 100 nm. The particles have a quasi spherical shape inducing an individual low aspect ratio. At low magnification (A) the particles have a tendency to agglomerate in grapes.

The silver nanowire morphology was studied by SEM to determine the aspect ratio. Fig. 2 shows the two types of nanowires. The silver nanowires produced by electrodeposition have the geometric features of the membrane pores with 200 nm in diameter and 50 microns in length (Fig. 2A).The dissolution process of the membrane in NaOH leads more ultrasonic solicitation of NWs. The silver NWs produced by this technique are more curved due to this ultrasonic treatment. The nanowires produced by growth in solution (Fig. 2B) have a diameter distribution range between 100 and 300 nm and have lengths between 20 and 80 microns in length. In both cases, the nanowires are well dispersed in acetone solution without dispersant agent and they do not aggregate.

3.2. Conductive composites

Fig. 3 shows the SEM images of the Ag NWs composite for 3 vol%. The individual NWs are clearly observed. NWs have no affinity in acetone and keep their homogeneous dispersion in the copolymer contrary to CNTs, metallic nanowires do not develop electrostatic interactions, and prevent them from aggregation. Fig. 3A shows the electrodeposited nanowires that have more pronounced curvature related to ultrasonic treatment during the elaboration. The nanowires obtained in solution (Fig. 3B) do not show curvature; a slight orientation associated with hot press is observed. P(VDF-TrFE) composites filled with silver spherical nanoparticles have been also elaborated. We can compare the percolation thresholds for the nanowires and spherical fillers.

The electrical conductivity of the insulating P(VDF-TrFE) copolymer is 10^{-12} S.m^{-1} at room temperature. The dc electrical conductivity σ_{dc} of the Ag/P(VDF-TrFE) samples at room temperature is plotted as function of the Ag volume fraction and Ag morphology (Fig. 4). These results highlight the major influence of the aspect ratio on the percolation threshold value.

4. Discussion

In each case, the electrical conductivity increases drastically and the data points are best fitted by a percolation scaling law according to Eq. (1) and reported in the table. The conductivity level above the percolation threshold has been systematically measured around 10^2 S.m^{-1}. The level of conductivity is independent from the aspect ratio and was coherent with literature. For metal particles, Alvarez [22] obtains maximum value of about 10^2 S.m^{-1} beyond 15 vol% of micronic copper particles in low-density polyethylene. Forster [23] gets the same value with gold nanoparticles.

The critical exponent value t is in the range of the universal value for three-dimensional percolation systems which is equal to 1.9. This value confirms the 3D nature of the percolation pattern. From the scaling law, $\sigma_{(p=100\%)}$ is an extrapolation at 100 vol% of conductive

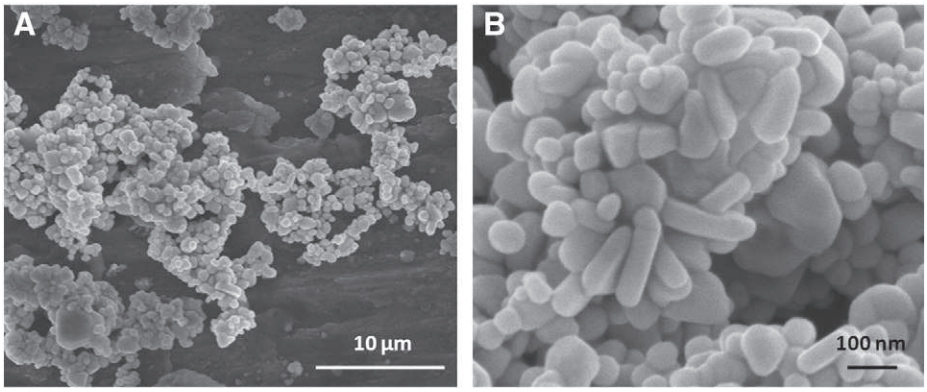

Fig. 1. SEM Image, at two magnifications, of silver particles supplied by Sigma-Aldrich.

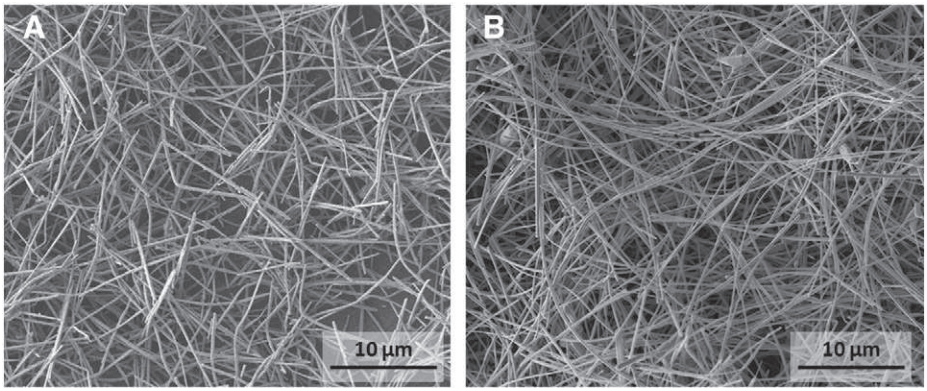

Fig. 2. SEM Images of silver nanowires obtained by electrochemical deposition (A) and polyol reduction process (B).

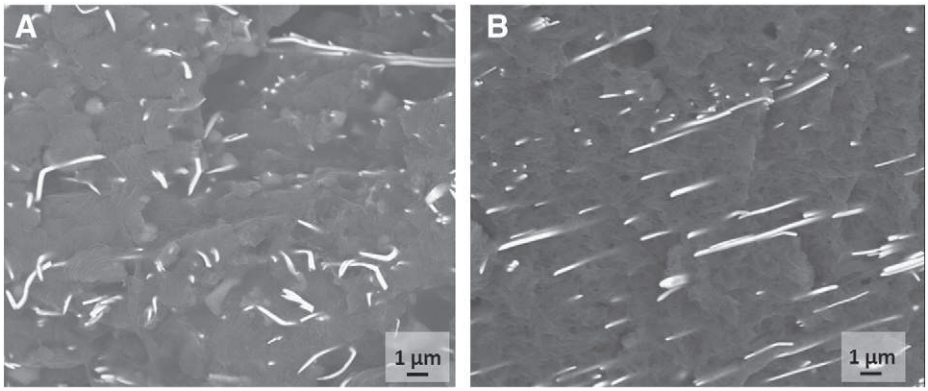

Fig. 3. SEM Images of the fracture surface of silver nanowire/P(VDF-TrFE) copolymer composites filled at 3 vol%. (A) Electrochemical deposition nanowires, (B) Polyol reduction nanowires.

particles, which corresponds to the electrical conductivity of bundles of Ag NWs or nanospheres. The dc conductivity of Ag nanowires pressed in a sheet form was measured at 1×10^5 S.m^{-1}. Hence, $\sigma_{(p=100\%)}$ value is in a good agreement with the conductivity of pressed Ag NWs.

In the case of electrodeposited Ag NWs, the geometry is well known and displays a narrow distribution of their aspect ratio centered on an average aspect ratio of $\zeta\approx250$. According to Balberg, assuming that the stick is an Ag nanowire, we can calculate the theoretical percolation threshold near 0.64 ± 0.08 vol% using Eq. (2). This value is lower than the experimental one of 2.2 vol% reported in Table 1. This difference can be explained by the curvature of Ag NWs as shown in Fig. 3 due to the supplementary sonication treatment required to disperse them after the AAO release. Their apparent aspect ratio has been estimated to 74. The nanowires grown in solution exhibit a lower experimental percolation threshold around 0.6 vol%. We can extrapolate the apparent aspect ratio to 254.

The percolation threshold with spherical particles was determined for 12 vol%. This value is slightly lower than the theoretical value of 15 vol% calculated by the spherical particles model. Literature data confirmed this value for PVDF filled with different kind of spherical particles [24,25]. When we observe our silver spherical particles by SEM, we note an ability to form grape structures. These clusters create aggregated conductive particles with a higher secondary aspect ratio shown on Fig. 1. These grape structures may explain the discrepancy observed with the theoretical model.

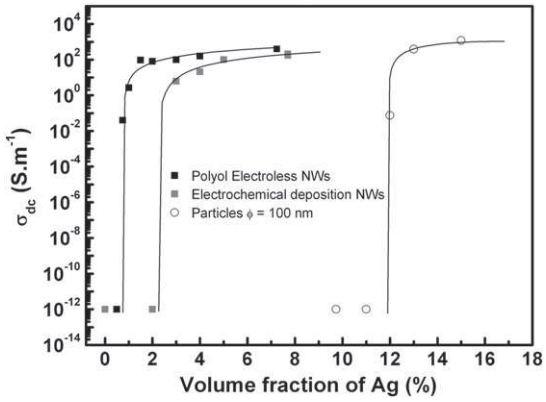

Fig. 4. Dependence of the dc conductivity (σ_{dc})on the silver volume fraction in P(VDF-TrFE) matrix at 25 °C as function of particles geometry: Polyol reduction process nanowires (■), Electrochemical deposited nanowires (■),100 nm particles (○).

5. Conclusion

Conductive polymer/silver nanowires composites reach the highest value known up to now in the case of conductive nanoparticle dispersion with a percolation threshold less than 1 vol%. These low percolation thresholds are observed with silver nanowires elaborated by template electrochemical deposition and by polyol process. Conductive composites with different types of particles were successfully prepared. These results contrast with the value obtained for spherical silver nanoparticles for the same matrix. The values of percolation threshold and conductivity of spherical silver filled polymer correspond to literature [22–24]. Therefore, the very low percolation threshold reached in P(VDF-TrFE) is only due to the high aspect ratio of nanowires as described in Balberg model. The SEM observations have shown a similar geometry of nanowires in spite of the synthesis method. An excess of ultrasonic treatment like in electrochemical deposition leads to a curvature of nanowires and results in a shape modification of the nanowires. This geometric deformation decreases drastically the effective aspect ratio of silver nanowires. Nanowires prepared by polyol process and introduced in P(VDF-TrFE) are less subjected to ultrason and keep an high effective aspect ratio. The percolation threshold obtained with silver nanowires elaborated by solution is the lowest measured with metallic conductive nanoparticles filled in non-segregated system despite the slight orientation due to the hot press process. The level of conductivity above the percolation threshold corresponds to highly conductive composites filled with various nanowires (Ni, Au) or spherical metallic particles. Such a level of conductivity is unusual at this low content of conductive filler and is observed for the first time to our knowledge in a conductive polymer composite.

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Table 1
Percolation law values obtained as function of the nanoparticles shape obtained by fitting in coordinates Log $\sigma=f$ [Log$(p-p_c)$] and $\sigma_{(p=100\%)}$ extrapolated value using Eq. (1).

Silver filler	p_c	$\sigma_{(p=100\%)}$	t
Particles Ø = 100 nm	12 vol%	6.1×10^5	1.7
NWs by electrodeposition	2.2 vol%	0.5×10^5	1.9
NWs by solution growth	0.6 vol%	0.5×10^5	2.2

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