



# High electrically conductive composites of Polyamide 11 filled with silver nanowires: Nanocomposites processing, mechanical and electrical analysis

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## ABSTRACT

Highly conductive composites of silver nanowires and semicrystalline polyamide 11 for different content were prepared. A new method was developed to introduce nanowires: a combination of solvent way and an extrusion process. This technic provides pellets of composites directly suitable for sample molding. The silver nanowires poured in polyamide 11 were obtained by polyol process to reach large volume of nanowires. The dispersion of nanowires was evaluated by scanning electron microscopy and confirmed by a very low percolation threshold around 0.59 vol.%. The level of conductivity above the percolation threshold is about  $10^2 \text{ S m}^{-1}$ . Differential scanning calorimetry and dynamic mechanical analyses have shown a stability of the composite physical structure and an optimization of the mechanical properties as a function of nanowires content until 3.6 vol.%. A simultaneous enhancement of the electrical conductivity of polyamide 11 was obtained.

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## 1. Introduction

A lot of works have been devoted to the elaboration of polymer conductive composites. Electrical conductivity is a crucial property for aeronautical composites polymer based. Conductive fillers are added to promote the increase of electrical conductivity. Metallic [1] or carbon micron particles [2,3] have been introduced and enable conductive composites at the expense of weight and mechanical properties. During the last decades new conductive particles have emerged such as carbon nanotube [4–6], carbon nanofibers [7], nanowires [8–10] with 1D geometry and submicrometer size. The interest of these new particles lies in their high aspect ratio. High values of aspect ratio enable the conductivity for lower rate of fillers. These low filled conductive polymer composites (<5 vol.%) generate a new class of multifunctional materials giving the conductivity of traditional conductive composite while preserving the mechanical properties [11] and limiting the overweight. To our knowledge, the best compromise to reach the higher electrical conductivity with the lower percolation threshold was obtained with metallic nanowires [10]. Silver nanowires elaborated by polyol process yields large volume of nanowires with high aspect ratio [12,13].

Polyamide 11 is a semi-crystalline thermoplastic with a low humidity permeability which allows a wide range of industrial applications like automotive, transportation and fluids industry. High electrically conductive composites of Polyamide 11 enable new conductive applications for these industries like protection of sensitive electrical systems.

The current method used for mixing particles with polyamide is the melt compounding. This technique requires a single or a twin screw extruder where the melt polymer and particles were poured. This technique gives pellets of composites. This technique provides generally interesting results for clays dispersion and for low aspect ratio particles [14]. Particles with high aspect ratio enhance largely the viscosity for very low rate of filler [15]. This phenomenon induces high shear stress during the mixing. It is hardly compatible with the preservation of the initial high aspect ratio of nanowires. The selective laser sintering is a different process currently used to elaborate three dimensional objects but rarely for composites [16]. The solvent dissolution of polyamide in the particles dispersion and precipitation reaches the best results for homogeneous dispersion. But the pellets obtained make it difficult to process in industrial conditions.

The aim of this study is to combine the advantages of processing methods. First, the solvent way was used to reach the lower percolation threshold with keeping the initial aspect ratio of nanowires. Then extrusion process was used to obtain composite pellets for sample elaboration. This study was particularly motivated by the

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desire to simultaneously enhance the electrical conductivity of polyamide 11 while preserving mechanical properties.

## 2. Experimental section

### 2.1. Materials and sample preparation

#### 2.1.1. Ag nanowires growth

Electroless silver nanowires were synthesized by reducing  $\text{AgNO}_3$  with ethylene glycol in presence of poly(vinyl pyrrolidone) [13]. 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 [12,13]. This technique allows us to obtain Ag nanowires (NWs) with a length distribution between 30 and 60  $\mu\text{m}$  and a diameter around 200 to 300 nm. The Ag NWs morphology was characterized by scanning electron microscopy (SEM) to estimate the mean aspect ratio ( $\xi = L/d$ ). The nanowire suspension was rinsed in water and then filtered through a polyamide (200 nm pore size) membrane. Filtered nanowires were stored in acetone and dispersed using a short sonication pulse for 5 s, corresponding to a dissipated power of 25 W. A droplet of this solution was deposited onto a SEM pin.

#### 2.1.2. Nanocomposite processing

Polyamide 11 (PA11) was supplied in granules by Arkema (France). The composites were prepared in two steps. In the first step, the mixing of nanowires and PA11 was prepared with using solvent casting method. PA11 was dissolved in a mixture of formic acid and dichloromethane (33.3–66.7 vol.%). The nanowires dichloromethane (DCM) suspension was poured into the polymer solution and the mixture was sonicated to 5 s short pulse. Sonication parameters were optimized by the observation of Ag NWs dispersion using SEM [9]. The solvent was evaporated using a magnetic stirrer at 110 °C for 1 h. Pellets of randomly dispersed Ag NWs in PA11 matrix were obtained and washed with distilled water to remove acid traces. In the second step, the pellets were melted at 200 °C and extruded with a die diameter of 1 mm. The composites extruded were cut in pellets and pressed into a steel mold with a piston to form a sample at 200 °C under 0.3 MPa. Sample geometry for conductivity measurement is a disc with 20 mm in diameter and 1 mm in thickness. For mechanical study, the sample geometry is a 40 mm length, 10 mm width and 1 mm in thickness parallelepiped. No solvent residue was found by thermogravimetric analysis, indicating a complete removal of solvent from samples. Ag NWs/PA11 composites were elaborated with a volume fraction varying from 0 to 3.6 vol.% with silver nanowires.

### 2.2. Scanning electron microscopy

The morphology of the silver nanowires was observed by scanning electron microscope using a JEOL JSM 6700F equipped with a field emission gun (SEM-FEG). Nanocomposite samples were cryocut at the liquid nitrogen temperature for observation by SEM.

### 2.3. Differential scanning calorimetry

Crystallization and melting phenomena were investigated using a TA Instruments 2920 differential scanning calorimeter (DSC). Before the heating and cooling runs, the samples were melted at 220 °C and maintained at this temperature for 5 min in order to erase the thermal history. The samples were then cooled from 200 to 45 °C at a rate of 20 °C  $\text{min}^{-1}$  and then maintained at 45 °C for 100 min. The aim of this annealing was to highlight the glass transition temperature ( $T_g$ ) with increasing the aging overshoot. Samples were then heated from –10 °C to 220 °C at a rate of 20 °C  $\text{min}^{-1}$  and then cooled back to –10 °C at the same rate. All the DSC measurements were performed under helium atmosphere. The glass transition was taken as the mid-point of the heat capacity step during the heating and the transition

temperatures were taken as the peak maximum or minimum in the DSC thermograms. The crystallinity ratio of the PA11 composites was calculated according to the weight fraction of polymer using the calculated value of the theoretical 100% crystalline enthalpy value of PA11,  $\Delta H_{0m} = 244 \text{ J g}^{-1}$ .

### 2.4. Electrical conductivity

To reduce contact resistivity with the cell electrodes, a thin gold layer (100 nm) was sputtered on the both samples sides using a BOC Edwards Scancoat Six sputter coater.

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

$$\sigma = \sigma_0(p - p_c)^t \quad (1)$$

where  $\sigma_0$  is a constant,  $p_c$  the percolation threshold and  $t$  is the critical exponent dependent on the lattice dimension. Some models [18–20] described randomly dispersed composites with high aspect ratio particles like the nanowires. In the case of the percolation model for cylindrical sticks system, proposed by Balberg and Binenbaum [19] looks to be adequate. It shows that the percolation threshold is dependent from the aspect ratio and the anisotropy of sticks through their excluded volume  $V_{\text{ex}}$ . At the percolation threshold,  $V_{\text{ex}}$  is found to be constant. When NWs are considered as randomly oriented sticks with  $L/r \gg 1$ , the critical excluded volume  $V_{\text{ex}}^{\text{cr}}$  is between 1.4 and 1.8 and is given by the expression derivative from the Balberg's equation:

$$V_{\text{ex}}^{\text{cr}} = \frac{L}{r} p_c = 1.6 \pm 0.2 \quad (2)$$

where  $p_c$  is the critical volume fraction for percolation.

#### 2.4.1. Low electrical conductivity values

Bulk electrical conductivity of nanocomposites was carried out by two independent methods. For conductive composites filled below the percolation threshold the Novocontrol broadband spectrometer was used to record the complex conductivity  $\sigma^*(\omega)$ . The measurements were done 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 nanocomposite 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  $\sigma_{\text{dc}}$  of samples was determined from the independent frequency part of  $\sigma'(\omega)$  [4]; i.e. the low frequency plateau. Cylinders of 1 mm thickness were introduced between two circular gold plated electrodes (20 mm in diameter).

#### 2.4.2. High electrical conductivity values

The conductivity value reach above the percolation threshold was measured by four point-probe technique. The conductivity of nanocomposites cylinders was obtained with a Keithley 2420 SourceMeter in a four-point-probe configuration.

### 2.5. Dynamic mechanical relaxation

The mechanical behavior of composites was evaluated through the measurement of the shear modulus. The mechanic relaxation mode has been determined using the constant frequency–constant amplitude temperature scan method. The real part of the modulus,  $G'(T)$ , and the imaginary part  $G''(T)$  of the matrix and NWs filled polyamide composites were measured as function of temperature. Dynamic

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