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High-performance thermoplastic composites poly(ether ketone ketone)/silver nanowires: Morphological, mechanical and electrical properties

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ABSTRACT

High-performance conductive thermoplastic composites poly(ether ketone ketone) (PEKK)/silver nanowires were elaborated by melt blending. Silver nanowires (AgNWs) with high aspect ratio (ξ~220) were elaborated through the polyol process in presence of poly(vinyl pyrrolidone) (PVP) and ethylene glycol. Scanning electron microscopy observations of nanowires were performed after an adapted cleaning process. The dispersion of NWs in the polymeric matrix was evaluated. A very low percolation threshold of 0.6 vol% was obtained. Electrical conductivity values obtained above the percolation threshold were among the highest measured for low-filled conductive polymer composites. The influence of AgNWs on the PEKK matrix has been investigated by differential scanning calorimetry and dynamic mechanical analyses. It is important to note that thermal and dynamic mechanical performances of the polymeric matrix were preserved in composites.

1. Introduction

Polymer composites increased their popularity in aerospace industry for their remarkable mechanical properties and low weight. Carbon fibers have a good electrical conductivity but the epoxy matrix is an insulator and reduces drastically the final electrical conductivity of the composite material. The lightning can strike statistically once or twice a year a commercial plane and consequences could be hazardous for composite structures and on-board electronics [1,2]. It is necessary for composite structures to mitigate the effects of lightning strikes and electrostatic accumulation. Some technological solutions have been proposed to enhance the electrical conductivity of epoxy based composites parts as metal mesh placed on composites surface parts [3]. The introduction of conductive particles sounds a promising route to improve the electrical conductivity of composite structures [1,4–7]. Nowadays, there is a great interest in thermoplastic polymer matrix due to high mechanical strength, high resilience and processability. The high-performance thermoplastic poly(aryl ether ketone) (PAEK) and in particular poly(ether ketone ketone) (PEKK), provides appropriate mechanical, chemical and thermal properties for aeronautical applications [8–12]. The rate of filler necessary to obtain conductive composites is directly linked to the aspect ratio ξ (ratio between length to width) of conductive particles [13,14]. The filler fraction required to generate infinite continuous conductive path through a material is called the percolation threshold. Low values of percolation threshold ensure the preservation of mechanical properties of the matrix with minimal weight increase. Previous works of conductive composites filled with CNTs exhibit a percolation threshold values near to 0.1–1 wt% with an electrical conductivity around 10^{-1}–10^{-2} $S \cdot m^{-1}$ [15–17] above the percolation threshold. This level of conductivity is relatively close to carbon fiber based composites and too low for aeronautical applications. In order to increase electrical conductivity, filler particles need to have higher intrinsic conductivity. Metallic nanowires with high aspect ratio are an excellent candidate to obtain conductive polymer composites [18–20]. Thermoplastic/metallic nanowires composites provide materials with high conductivity values (10^2 $S \cdot m^{-1}$) for a low content of filler (≤5 vol%) [6,19,21,22]. Lonjon et al. have shown the importance to introduce nanowires without oxidative layer on their surface. Conductive polymer composites realized with silver nanowires [18,22,23] provide the best compromise to prevent oxidative surface layer and exhibit higher conductivity with an acceptable weight increasing. Xia [24] and Sun [25] have described a polyol process where AgWs with high aspect ratio can be elaborated in large scale by using $AgNO_3$ as precursor and PVP as capping agent in ethylene glycol.

PEKK is a high-performance thermoplastic from the PAEK family. It is a semi-crystalline aromatic polymer with high temperature stability, good chemical resistance and excellent mechanical properties. Its high glass transition temperature T_g (~160 °C) and high melting point T_m (~330 °C to 360 °C) are compatible with aeronautical specifications of the PAEK group [8–10]. PEKK KEPSTAN 6003 has a lower melting temperature (~303 °C) while keeping a high value of T_g. This slight lower T_m may facilitate composites processing. Some works of PEKK reinforced composites had studied crystallization behavior and mechanical properties of PEKK/CF and PEKK/mica composites [8,11,26–28]. The composites properties strongly depend

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on the quality of dispersion of nanowires. This work exposes a new reliable method to elaborate low-filled conductive PEKK nanocomposites with good dispersion quality. Several methods have been developed to prepare metallic nanowires/polymer composites in order to enhance dispersion. Solvent way provides the best dispersion of high aspect ratio particles. Unfortunately, it cannot be used with PEKK due to his high solvent resistance. The melt blending method was chosen in this study. However, in twin-screw extrusion, the nanowires with high aspect ratio may be damaged by the shear stress as presented by Lin [20] and Lonjon et al. [22]. The aim of this study is to obtain a new high-performance thermoplastic conductive composites with a low rate of filler. The best way to achieve a low rate of filler is to preserve the aspect ratio of the nanowires in homogenous dispersion using a mixing process at high temperature.

We have prepared the nanocomposites by simple melt compounding method without mechanical melt mixing. We report our results about the dependencies of electrical conductivity and percolation threshold on the Ag NWs. The influence on the thermal and dynamic mechanical properties of metallic nanowires on PEKK polymer matrix was studied by differential scanning calorimetry (DSC) and dynamical mechanical analysis (DMA).

2. Experimental section

2.1. Nanowires and nanocomposites elaboration

Silver nanowires were synthesized by reducing $AgNO_3$ with ethylene glycol in the presence of poly(vinyl pyrrolidone) ($M_w = 55\,000$) through the polyol process. All chemical solutions were purchased from Sigma Aldrich. They were used without further purification. The reaction was carried out at 160 °C in a round-bottom balloon for 1 h. Stirring rate was 400 rpm. This technique and the involved chemical reactants were described by Sun et al. [25]. Only few variations in solution concentrations were made. PVP/$AgNO_3$ initial ratio was increased to 3.51 compared with previous work [22]. Sun et al. [29] and Wiley et al. [30] have established hypotheses of Ag NWs growing through this process. Growing process implies a favored reaction between [100] planes of silver multiply twined-particles and PVP. After the process reaction, silver nanowires were cleaned and separated of Ag particles by centrifugation during 2 min at 2000 rpm several times. Clean silver nanowires were stored in ethanol and dispersed using an ultrasonic bath for short time. The polyol process allows silver nanowires gram scale synthesis required to prepare conductive polymer composites. After the cleaning process, the yield reaction was evaluated at 70 %.

PEKK KEPSTAN 6003 was supplied by Arkema France in powder form (20 μm) ($M_w = 25000$). Composites were processed by melt blending without mechanical mixing. PEKK powder was mixed with clean silver nanowires previously dispersed in ethanol solution. The mixture was sonicated in order to promote the dispersion and then evaporated in a rotary evaporator at 80 °C. The volume fraction p of Ag NWs was ranging from to 0 to 5 vol%. The mixture obtained after evaporation was melted at 340 °C during 15 min. After slow cooling of about 10 °C.min^{-1}, the bulk material obtained was cut into very small pellets and pressed again to obtain the samples, at 340 °C during 15 min at a pressure of 3 MPa, for the DSC, DMA and conductivity measurements.

The volume fraction of AgNWs was determined by density measurements from the following mixture law: $d_{\text{composite}} = (1-\varphi)\, d_{\text{PEKK}} + \varphi d_{\text{AgNWs}}$ where $d_{\text{PEKK}} = 1.3$, $d_{\text{AgNWs}} = 10.5$ and φ is the volume ratio ranging from 0 to 5 %.

2.2. Scanning electron microscopy (SEM)

SEM analysis was carried out on a JEOL JSM 6700F instrument. Images were collected under 10 keV accelerating voltage. Nanowires images were obtained using the secondary electron detection mode. Nanocomposites images were obtained using backscattered electron mode in order to enhance the contrast between organic matrix and metallic nanowires. Ag NWs were well dispersed in ethanol suspension and deposited on an SEM pin.

2.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements were performed using a calorimeter 2920 from Thermal Analysis instrument. The samples weight varied from 5 to 15 mg. They were first heated in the DSC at 370 °C in order to erase the thermal history of the polymer. The cooling rate was 10 °C.min^{-1}. The second heating was considered for data analysis. The scanning rate was 10 °C.min^{-1} and the temperature range 30 °C to 350 °C. The crystallinity X_c of a polymer can be estimated with

$$\chi_c = \frac{\Delta H_m\text{-}\Delta H_{cc}}{\Delta H_{100\%}} \times 100 \tag{1}$$

with ΔH_m melting enthalpy, ΔH_{cc} cold crystallization enthalpy and ΔH_{100} melting enthalpy of the theoretical 100 % crystalline polymer.

2.4. Dynamic mechanical analysis (DMA)

The dynamic mechanical properties of PEKK/Ag NWs composites were determined using an ARES strain control rheometer from Thermal Analysis instruments in the torsion rectangular mode. Dynamic mechanical storage modulus and loss modulus G' and G'' of PEKK and PEKK/Ag composites were recorded as a function of temperature. The scanning rate was 3 °C.min^{-1} between −125 °C and 165 °C. Test were carried out over the linear elasticity range with $\omega = 1$ rad · s^{-1} (angular frequency) and $\gamma = 10^{-1}$ % (strain). Test samples were parallelepiped with length between 35 and 40 mm, 10 mm width and thickness between 0.6 and 0.7 mm. Samples preparation was described earlier.

2.5. Electrical conductivity

For conductivity measurements, samples were prepared at 340 °C in disc form with 20 mm diameter and 1 mm thick. They were coated with silver paint to ensure good electrical contact with electrodes.

- Low electrical conductivity values
  The electrical conductivity measurements were carried out with the Novocontrol broadband spectrometer by recording the complex conductivity $\sigma^*(\omega)$. Measurements were performed at room temperature, covering a frequency range of 10^{-2}–10^6 Hz. The real part $\sigma'(\omega)$ of the complex conductivity $\sigma^*(\omega)$ was recorded. The value of $\sigma'(\omega)$ at 10^{-2} Hz was taken as dc conductivity σ_{dc} according to Barrau [16].
- 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.
  In the percolation zone, the data were fitted by a power law where the evolution of conductivity is defined by four parameters [31,32]:

$$\sigma = \sigma_0 (p\text{-}p_c)^t \tag{2}$$

where σ_0 is a constant, p is the Ag NWs volume fraction, p_c is the Ag NWs volume fraction at the percolation threshold and t is the critical exponent depending on the network dimensionality d; $t = 1.1$–1.3 for $d = 2$ and $t = 1.6$–2 for $d = 3$.