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Electrical behavior of a graphene/PEKK and carbon black/PEKK nanocomposites in the vicinity of the percolation threshold

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ABSTRACT

Graphene and carbon black have been dispersed in a high performance thermoplastic polymer, the poly(ether ketone ketone), to improve its electrical conductivity. The dispersion of graphene has a significant influence on the percolation threshold. A simple exfoliation protocol to obtain graphene monolayers has led to a significant decrease of the percolation threshold from 4.2 to 1.9 vol%.

1. Introduction

High performance thermoplastic composites raise a growing interest for structural applications in aeronautical and space industries. In order to improve their electrical properties, the introduction of conductive particles (metal or carbon) within the polymer matrix has been the subject of many studies. Usually, metallic fillers like gold [1,2] or silver fillers [3-5] permit to reach high electrical conductivity ($\sigma = 10^{-2}-10^{-3}$ S·m$^{-1}$) but their high density implies an increase of the structure weight. Due to their low density, carbon fillers as carbon black [6], carbon nanotubes [7,8] or graphene [9] are of interest in a wide range of applications, where a high electrical conductivity for electrical dissipation ($\sigma = 0.1-1$ S·m$^{-1}$) is not required [10]. In order to maintain the mechanical properties of the matrix, for low particle content, conduction phenomenon may occur. The critical transition from an insulating to a conducting behavior is associated with the percolation threshold. It corresponds to the formation of an infinite conducting path within the material. The value of the percolation threshold only depends on the apparent conductive particle aspect ratio $\xi$ [11,12]. Lower percolation thresholds are reached for particles with a high aspect ratio. For example, percolation threshold is observed near 8–10 vol% [13] with carbon black ($\xi \approx 1$) and lower than 0.4 vol% [14] with carbon nanotubes ($\xi \approx 1000–10,000$).

In the present work, graphene was used for the elaboration of conductive nanocomposites. Graphene was recently highlighted by Novoselov and Geim in 2004 [15,16]. Its good electrical properties and high aspect ratio have aroused great interest among the scientific community [17-21]: high charge mobility (230,000 cm$^2$/Vs), low visible light absorption (2.3%), high thermal conductivity (3000 W/mK), high strength (130 GPa), high elastic modulus (1 TPa) and the highest theoretical specific surface area (2600 m$^2$/g). A reference sample processed with spherical carbon black was also elaborated to compare with graphene.

The poly(ether ketone ketone) (PEKK) was used as polymer matrix. It is a high performance thermoplastic polymer that belongs to the poly(aryl ether ketone) family. One of the main advantages of PEKK is that the melting point can be modulated, as reported by Gardner [22]. 100% para PEKK and para - iso PEKK show differences in the melting point temperature, whereas the glass transition temperature stays quasi constant. By increasing the proportion of meta isomers, defects in the crystal packing decrease the melting point temperature and enhance the processing conditions.

The processing of nanocomposite and, more specifically, the dispersion of particle is the most important challenge to obtain...
macroscopic homogeneous properties. Due to strong interactions between graphene sheets, it makes difficult to disperse them randomly in the polymer matrix. Especially in case of graphene, aggregates could be generated and decrease the apparent aspect ratio \([17,23,24]\). In order to improve the graphene dispersion in nanocomposites several exfoliation ways are studied. The solvent way, which uses commonly N-methyl-2-pyrrolidone \([25]\) or \(N,N\)-dimethylformamide \([26]\), is an easy process that can bring high graphene concentration (higher than \(1 \text{ mg mL}^{-1}\)) but leads to use solvent. An aqueous way have been proposed with an anionic surfactant as sodium dodecyl sulfate for example. In this case, high graphene concentration is more difficult to obtain \([27-29]\).

The manuscript presents the protocol to graphene exfoliation and the processing used for PEKK/graphene and PEKK/carbon black nanocomposites. The influence of the nature of conductive fillers on dielectric properties such as electrical conductivity and dielectric permittivity and mechanical properties such as storage and loss moduli were studied.

2. Experimental section

2.1. Materials

Poly(ether ketone ketone) PEKK (Arkema) (diameter of powder \(20 \mu\text{m}\)) and Carbon black (CB, glassy carbon from Sigma Aldrich), were supplied in powder, respectively. Graphene (GR from Avanzare) was supplied in ethanol suspension (EtOH) with a concentration of \(0.5\) wt%. The morphology of GR and CB was investigated by scanning electron microscopy (SEM - FEG JEOL JSM 7800F Prime) using secondary electron detector. Fig. 1 shows the SEM images of CB (a) and “as received” GR (b), respectively.

The CB particles are spherical with a mean diameter of \(6.3 \mu\text{m} (d_{50})\) determined using a laser granulometer (Fig. 1a). Fig. 1b shows graphene stack due to the SEM resolution, which does not allow to observe GR monolayers. To analyze precisely the GR nanotexture, images were performed using a JEOL JEM 2100F electron microscope operated at 200 kV. Diffraction patterns were recorded using selected area electron diffraction (SAED) mode with a 150nm aperture.

Fig. 2 is a bright field image of GR and one monolayer is visible in the black circle, which indicates the selected area for the SAED pattern. This pattern is characteristic of one graphene layer (\(P63/mmc\), \(a = 2461 \text{ Å}\) and \(c = 6708 \text{ Å}\)). The wrinkled aspect and the grey contrast differences suggest that GR is also composed by a large amount of GR multilayers classically labelled exfoliated graphene nanoplatelets in the literature \([30]\). This local microscopic observation is not appropriate to characterize the entire GR batch. The number of GR layers modifies the apparent aspect ratio and has a significant influence on nanocomposite electrical properties. The electrical percolation threshold allows us to determine the apparent aspect ratio of these particles.

2.2. Nanocomposite processing

In order to manage the distribution of GR in the polymer, a simple protocol was applied. It consists in two steps process: a GR exfoliation followed by a decantation. For exfoliation an aqueous solution with sodium dodecyl sulfate (SDS) as surfactant was chosen \([29]\). SDS was solubilized in EtOH at \(2.4 \text{ mg mL}^{-1}\). It corresponds to the critical micellar concentration (CMC) in water. GR suspension was diluted in a solution containing EtOH and SDS following the 3/5 ratio, respectively. Suspension was sonicated for 1 min (power 300 W). After 10 min of decantation, GR suspension was collected to process the nanocomposite.

For the PEKK/GR (GR-NC) and PEKK/CB (CB-NC) nanocomposites processing, a premix powder was used. GR/EtOH or CB/EtOH suspensions and polymer powder (20 \(\mu\text{m}\) in diameter) were mixed. PEKK polymer powder is in suspension in this mix. Then it was sonicated with ultrasound to promote a homogeneous dispersion. EtOH
was evaporated with a rotary evaporator at 80°C. Nanocomposites were elaborated through melt blending at 360°C with mechanical mixing using a laboratory twin screw extruder (GR-NC1). GR-NC2, GR-NC3 and CB-NC were processed with hot press. GR-NC1 was elaborated from “as received” GR without any treatment. GR-NC2 was elaborated from GR exfoliated according to the previously described protocol. GR-NC3 was elaborated from GR exfoliated by the commercial supplier. As it has been reported in previous works, this protocol leads to a very good particle dispersion in polymer matrix even for high aspect ratio [1,4,5,14]. The nanocomposite electrical conductivity study, and more specifically, the percolation threshold value allows us to analyze the dispersion quality at a macroscopic scale. As the percolation threshold theoretical value of spherical particles dispersion is well known, CB-NC was elaborated to check the dispersion protocol.

2.3. Dielectric and mechanical analyses

Dynamic electrical conductivity and dielectric permittivity of nanocomposites were performed from −150°C to 200°C and 10⁻² Hz to 10¹ Hz using a Novocontrol Broadband Dielectric Spectrometer (BDS). Disk-shape samples (20 mm in diameter) have been processed by compression molding at 360°C to determine the bulk electrical conductivity. In order to promote a 3D conductivity, thick samples were hot pressed (1 mm thickness).

To extract the percolation threshold value the following Eq. (1) was used [31,32]:

\[ \sigma_{DC} = \sigma_0 (p - p_c)^t \]

where \( \sigma_{DC} \) is the static nanocomposite conductivity, \( \sigma_0 \) the GR pathway conductivity, \( p \) the GR content, \( p_c \) the percolation threshold and \( t \) the universal critical exponent that depends on the system dimensionality (1 < t < 1.3 for a 2D network and 1.5 < t < 2 for a 3D network [31,32]).

Dynamic mechanical analyses (DMA) were carried out on PEKK, GR-NC1 and CB-NC using an ARES G1 TA Instruments apparatus in shear mode, from −130°C to 270°C at 3°C/min⁻¹. The applied strain and frequency were fixed at 0.1% and 0.16 Hz (an angular frequency of 1 rad/s⁻¹), respectively. Parallelepipedic samples with 40 mm long, 10 mm wide and 0.6 mm thick were studied.

3. Results & discussion

3.1. Study of the dispersion quality by bulk electrical conductivity analysis

Fig. 3 represents the DC conductivity behavior at room temperature as a function of GR and CB content: GR-NC1 (PEKK/“as received” GR nanocomposites), GR-NC2 (PEKK/lab-exfoliated GR nanocomposites), GR-NC3 (PEKK/supplier exfoliated GR nanocomposites) and CB-NC (PEKK/CB nanocomposites).

For GR-NC1 the percolation threshold is determined near 4.2 vol%, the conductivity value above \( p_c \) reaches \( 4.9 \times 10^{-4} \) S·m⁻¹. The percolation threshold decreases until 3 vol% after the exfoliation/decantation protocol (GR-NC2) and the conductivity value above \( p_c \) is \( 6.5 \times 10^{-2} \) S·m⁻¹. For GR-NC3, the percolation threshold is even lower (1.9 vol%) with the highest conductivity value of \( 1.2 \) S·m⁻¹.

In order to compare these results with a reference material, CB nanocomposites were elaborated. The percolation threshold for CB-NC is determined at 16.2 vol%.

The percolation threshold value is highly dependent on the GR dispersion, which is associated with the elaboration process, the GR aspect ratio and its surface modification. Kim et al. [33] have shown the influence of elaboration process by comparing three techniques: in-situ polymerization and melt process. The first and second one lead to the lowest percolation threshold due to the very low viscosity of the mixture [34]. For example, Stankovich et al. [23] dispersed GR (chemically modified) in polystyrene (PS) and they reached a percolation threshold near 0.1 vol%.

Fig. 4 reports the linear fit of \( \log(\sigma_{DC}) \) as a function of \( (p - p_c) \). Extracted values of \( p_c, \sigma_0 \) and \( t \) were reported in the Table 1 for GR-NC1, GR-NC2, GR-NC3 and CB-NC.
Influence of graphene on the conductivity frequency and temperature

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This value was clearly dependent from the particle nature (carbonaceous as comparison with metallic particles).

Table 1

<table>
<thead>
<tr>
<th>Processing</th>
<th>(p_c) (vol%)</th>
<th>(\sigma_0) (S·m(^{-1}))</th>
<th>(t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR-NCl</td>
<td>4.2</td>
<td>(2.5 \times 10^{-9})</td>
<td>6.4</td>
</tr>
<tr>
<td>GR-NC2</td>
<td>3.0</td>
<td>(7.9 \times 10^{-4})</td>
<td>3.6</td>
</tr>
<tr>
<td>GR-NC3</td>
<td>1.9</td>
<td>(3.1 \times 10^{-1})</td>
<td>1.0</td>
</tr>
<tr>
<td>CB-NC</td>
<td>16.2</td>
<td>(6.3 \times 10^{-3})</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Universal critical exponent values of GR-NCl and GR-NC2 were 6.4 and 3.6, respectively. These values are higher than the estimated values (1.5 < \(t < 2\) for a 3D network [31,32]). In the literature, high \(t\) values have already been identified in GR/polymer nanocomposites: 5.8 for PEEK/GR nanocomposites [35], 3.8 for PVDF/GR nanocomposites [39], 3.2 for ABS/GR and SAN/GR nanocomposites [40]. Authors attributed this behavior to the inhomogeneity of the GR dispersion. Aggregates or folding limited the electronic transport within the nanocomposite and increased the \(t\) value. Thus, it is consistent with GR-NC3 results; i.e. a better dispersion leads to a decrease of \(t\) at 1.

GR-NCl nanocomposites, elaborated by extrusion from a premix nanocomposite powder, has a very low conductivity above the percolation threshold (\(10^{-9}\) S·m\(^{-1}\)). The shear and compression strengths during the extrusion process alter the electrical properties. These observations, already reported in the literature, were related to the reduction of exfoliated graphene nanoplatelets aspect ratio [41] and/or re-agglomeration phenomenon [42]. The conductivity above the percolation threshold is thereby greatly reduced. \(\sigma_0\) is related to the intrinsic conductivity of the pristine GR sheet [26] (generally known at \(10^{6}\) S·m\(^{-1}\) for carbon particles).

The GR-NC3 nanocomposite has the higher \(\sigma_0\). This elaboration protocol (exfoliation/decantation then hot press lamination) promote better GR electrical properties. Finally, as regards CB-NC nanocomposites, the CB intrinsic conductivity \(\sigma_0\) is \(6.3 \times 10^{-4}\) S·m\(^{-1}\). It is an intermediate value between GR-NCl and GR-NC3; \(t\) value is 1.6, which corresponds to a 3D network [31,32]. For GR-NCl (1.2 S·m\(^{-1}\) at 6 vol%) and GR-NC (1.0 S·m\(^{-1}\) at 50 vol%), we noticed that the maximum of conductivity above the percolation threshold was similar in both cases. This value was clearly dependent from the particle nature (carbonaceous as comparison with metallic particles).

3.3. Influence of graphene on the dielectric permittivity in the vicinity of the percolation threshold

Dielectric permittivity has been studied for GR-NCl nanocomposites in order to analyze behaviors within the gradual percolation threshold. Fig. 6(a) presents the evolution of permittivity measured at 1 Hz as a function of temperature for different GR contents: at room temperature, near the glass transition temperature and above 20 °C, 160 °C and 180 °C, respectively. The inset graph in Fig. 6(a) represents the DC conductivity as a function of GR content, each composite relative to the percolation threshold: tunneling effect below -50°C and hopping activation process above. At low temperature, tunneling effect is not temperature dependent whereas hopping is thermally activated. In both case, electronic transport through the conductive path do not require a surface contact between GR or CB particles.

Fig. 5. Real part of the conductivity versus frequency for PEKK/home-exfoliated graphene (GR-NC2) 3 vol% (solid line) and 4 vol% (dashed line) for isotherms from -150°C to 200°C.
Ta -soc, Ta and Ta + soc. Inset: PEKK matrix thermogram between graphene (GR-NCl) at room temperature: (a) 20 °C, (c) 160 °C and (A) 180 °C. Inset: DC conductivity versus GR content at room temperature. (b) Real part of the dielectric permittivity versus frequency for PEKK and PEKK/“as received” graphene (GR-NCl) at room temperature: (□) 2 vol% graphene, (△) 4.5 vol% graphene, (▲) 5 vol% graphene and (▼) 6 vol% graphene. Solid lines are guide for the eye.

Fig. 6. (a) Real part of the dielectric permittivity versus graphene vol% for PEKK and PEKK/“as received” graphene (GR-NCl) at (■) 20 °C, (○) 160 °C and (▲) 180 °C. Inset: DC conductivity versus GR content at room temperature. (b) Real part of the dielectric permittivity versus frequency for PEKK and PEKK/“as received” graphene (GR-NCl) at room temperature: (□) 2 vol% graphene, (△) 4.5 vol% graphene, (▲) 5 vol% graphene and (▼) 6 vol% graphene. Solid lines are guide for the eye.

Fig. 7. Storage modulus G' and loss modulus G'' of unfilled PEKK, PEKK/2 vol% GR, PEKK/4 vol% GR, PEKK/6 vol% GR and PEKK/4 vol% CB, measured at Ta = 50 °C, Ta and Ta + 50 °C. Inset: PEKK matrix thermogram between −130 °C and 270 °C.

3.4. Influence of graphene on the mechanical properties below the percolation threshold

The improvement of electrical properties of high performance thermoplastic should be done without altering their mechanical properties. The influence of carbon particles (GR-NCl or CB-NC) on the conservative and dissipative moduli has been determined in comparison with unfilled PEKK. G' and G'' values were determined at Ta = 50 °C (vitreous plateau), Ta (in the viscoelastic relaxation domain) and Ta + 50 °C (rubbery plateau) and reported in Fig. 7. The inset graph in Fig. 7 shows the PEKK thermogram over all the temperature range. The study of the mechanical relaxations have been extensively detailed in a previous paper [46].

Mechanical properties of PEKK and its composites are presented in Fig. 7. Considering the error bars, the particles until 6 vol% do not influence significantly the mechanical moduli even for graphene. Thus, the high performance mechanical properties of the polymer matrix is maintained.

4. Conclusion

Commercial graphene and carbon black were satisfactory dispersed in a high performance thermostable thermoplastic PEKK polymer in order to improve their electrical properties. Particle aspect ratio has a strong influence on the percolation threshold value. It decreased from 16.2 vol% with carbon black (ξ = 1) to 4.2 vol% with an “as received” graphene (GR-NCl) and 1.9 vol% after a graphene exfoliation/decantation process (GR-NCl3). Exfoliation/decantation improved the graphene dispersion by limiting the number of layer and increasing the graphene aspect ratio. Above the percolation threshold, high conductivity values (1–1.2 S·m−1) were obtained for graphene and carbon black. It was one decade higher than the conductivity measured for carbon nanotubes nanocomposites. Graphene pathway also increased dielectric permittivity from 2.6 for PEKK to 83 for the PEKK/6 vol% GR nanocomposite. Finally, until 6 vol% graphene and 4 vol% carbon black, nanocomposite mechanical behaviors are not significantly modified.

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