



**HAL**  
open science

## Conductive sizing for improving electrical conductivity of carbon fiber/polyaryl ether ketone/AgNWs composites

Jérémie Audoit, Luis Enrique Quiroga Cortes, Sébastien Racagel, Antoine Lonjon, Eric Dantras, Colette Lacabanne

► **To cite this version:**

Jérémie Audoit, Luis Enrique Quiroga Cortes, Sébastien Racagel, Antoine Lonjon, Eric Dantras, et al.. Conductive sizing for improving electrical conductivity of carbon fiber/polyaryl ether ketone/AgNWs composites. *Journal of Applied Polymer Science*, 2019, 136 (34), pp.47872-47876. 10.1002/app.47872 . hal-02188144

**HAL Id: hal-02188144**

**<https://hal.science/hal-02188144>**

Submitted on 18 Jul 2019

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



## Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible

This is an author's version published in: <http://oatao.univ-toulouse.fr/24129>

**Official URL:** <https://doi.org/10.1002/app.47872>

### To cite this version:

Audoit, Jérémie<sup>ORCID</sup> and Quiroga Cortes, Luis Enrique<sup>ORCID</sup> and Racagel, Sébastien<sup>ORCID</sup> and Lonjon, Antoine<sup>ORCID</sup> and Dantras, Eric<sup>ORCID</sup> and Lacabanne, Colette<sup>ORCID</sup>  
*Conductive sizing for improving electrical conductivity of carbon fiber/polyarylether ketone/AgNWs composites.* (2019) *Journal of Applied Polymer Science*, 136 (34). 1-8 ISSN 0021-8995

Any correspondence concerning this service should be sent to the repository administrator: [tech-oatao@listes-diff.inp-toulouse.fr](mailto:tech-oatao@listes-diff.inp-toulouse.fr)

# Conductive sizing for improving electrical conductivity of carbon fiber/polyarylether ketone/AgNWs composites

J r mie Audoit, Luis Quiroga Cortes,\* S bastien Racagel, Antoine Lonjon, Eric Dantras , Colette Lacabanne

CIRIMAT, Universit  de Toulouse Paul Sabatier, Physique des Polym res, 118 route de Narbonne, 31062 Toulouse cedex 09, France  
Correspondence to: E. Dantras (E-mail: eric.dantras@univ-tlse3.fr)

**ABSTRACT:** The aim of this work is to enhance the electrical conductivity of PAEK/continuous carbon fiber (CF) composites while maintaining their mechanical properties. A conductive sizing was elaborated by mixing polyetherimide (PEI) with silver nanoplates (AgNpts) in suspension in dichloromethane. An aqueous PEI formulation was used as insulating sizing reference. The presence of AgNpts into the sizing enhances electrical conductivity up to  $0.2 \text{ S.m}^{-1}$  for a silver content  $\sim 0.2 \text{ vol } \%$  without any modification of mechanical properties. The influence of conductive sizing on PAEK-AgNWs/CF was observed. For low AgNWs content lower ( $<1 \text{ vol } \%$ ); the conductive sizing increases the electrical conductivity of the composite by one decade. This result shows that both types of Ag particles participate to the conductive path. For higher AgNWs content, electrical conductivity ( $200 \text{ S.m}^{-1}$ ) is independent from the AgNpts content: the conductive path is only constituted by AgNWs. Mechanical properties of such composites show that the value of the conservative modulus is almost the same, while the dissipative modulus slightly increases. The global mechanical properties of the composite are preserved despite the addition of the CF, AgNWs, and AgNpts.

**KEYWORDS:** carbon fiber/PAEK composites; conductive sizing; electrical conductivity; percolation; silver nanoplates; silver nanowires

DOI: 10.1002/app.47872

## INTRODUCTION

Multifunctional composites have received increasing interest in many application fields such as aeronautic, automotive or electronic devices. Carbon fiber reinforced polymers (CFRP) for structural purposes present high mechanical properties but poor transverse electrical conductivity. Multifunctional composites are excellent candidates to combine their high mechanical properties and sufficient electrical conductivity. Multifunctional CFRP are generally obtained by the introduction of conductive fillers such as carbon nanotubes,<sup>1-5</sup> graphene,<sup>6-11</sup> silver nanowires<sup>12</sup> or by metal deposition on CFs.<sup>13-15</sup> Graphene and carbon nanotubes are preferred for their mechanical reinforcement,<sup>5,9,16</sup> although their introduction as filler enables moderate enhancement of conductivity level.

Carbon nanotubes could be directly deposited on the CF<sup>1-3,5</sup>; their growth on the CF bundles is generally achieved by CVD.<sup>1,3</sup> Pozegic *et al.*<sup>1</sup> reported an enhancement of electrical properties about 400% in presence of carbon nanotubes. However, CVD technique is inconvenient and requires high temperature treatments of CF that generally causes thermal degradation of carbon fiber, and thus the composites have reduced mechanical properties compared to the reference samples.<sup>1,3</sup> In order to preserve

the mechanical properties of CF, the deposition of carbon nanotubes could be achieved by electrophoresis.<sup>2,5</sup> The low temperature process avoids the degradation of CFs, but it involves a preliminary functionalization of the CF surface.

Nickel deposition on the surface of CF was reported to enhance the electrical conductivity of the prepared composites,<sup>14,15</sup> but no mechanical enhancement was reported. Poor compatibility between the polymer matrix and the nickel-coated fibers suggests a possible delamination of the composites. The deposition of silver nanowires on carbon nanofiber was recently reported by An *et al.*<sup>17</sup>: the electrical conductivity of such composites presented a conductivity level increased by 3 decades compared to the reference.

To our knowledge, few works concern the dispersion of conductive fillers into the polymer matrix prior to fiber impregnation. Lonjon *et al.*<sup>4</sup> obtained enhanced electrical property for polyepoxy/CF composites by dispersing carbon nanotubes, especially at the interlayer interface of prepreg plies. Liu *et al.*<sup>18</sup> reported an enhancement of thermal conductivity of poly(ether ether ketone) (PEEK)/CF composites with graphene filler. Quiroga Cortes *et al.*<sup>12</sup> dispersed silver nanowires into a Poly(ether ketone ketone) (PEKK) matrix and then impregnated the CF tapes. Very high

\*Present address: IRT Saint Exup ry, Toulouse, France

electrical conductivity level was obtained ( $\sigma \approx 10^2 \text{ S.m}^{-1}$ ) as a result of a percolation mechanism induced by metallic fillers, also observed in their previous work on composites matrix/filler without any CF.<sup>19</sup>

The aim of this work is to enhance the electrical conductivity while maintaining mechanical properties of continuous CFs composites. The previously cited works generally require the removal of the commercial sizing deposited onto CF surface. One of the functionalities of sizing agent is to promote the CF/matrix continuity.<sup>20,21</sup> The sizing agent, which promotes load transfer from the polymer matrix to the CFs, is selected to be miscible with the polymer matrix. A poly(aryl ether ketone) (PAEK) thermoplastic matrix was chosen due to their excellent mechanical properties and their thermal stability. Compatible sizing agents are limited because of the high processing temperature<sup>21</sup> (>350 °C): poly(etherimide) (PEI)<sup>11,22</sup> or poly(phthalazinone ether ketone) (PPEK)<sup>23</sup> sizing have been recently developed since they are compatible with the high processing temperature of PEEK. The electrical functionalization was established by two methods: (1) the functionalization of the sizing, that was achieved by dispersing silver nanoplates into the PEI; and (2) the dispersion of silver nanowires into the matrix with CF sized with the previously mentioned functionalized sizing. To our knowledge, silver nanoplates have been only used for their optical properties,<sup>24,25</sup> and in some rare cases as conductive filler,<sup>26</sup> but never used in high performance thermoplastic matrices such as PAEK. Both mechanical and electrical properties of the different composites have been compared.

## MATERIALS AND METHODS

### Materials

**PAEK Matrix and Silver Nanowires.** The low-melting PEEK-like polymer VICTREX AE™ 250 was kindly supplied by Victrex as ultra-fine powder. The polymer presents a lower melting temperature than PEEK that facilitates composite processing. The polymer would be designated as PAEK in the following sections.

The silver nanowires (AgNWs) were synthesized by a polyol process in the presence of poly(vinyl pyrrolidone) as previously described.<sup>19</sup> Their diameter is approximately 200 nm and their aspect ratio is  $\xi = 250$  [Figure 1(a)]. Their electrical conductivity

is close to the one of bulk silver. The matrix loading values ranged from 0.5 to 4.0 vol %. The loading values are always given in relation with the polymer matrix.

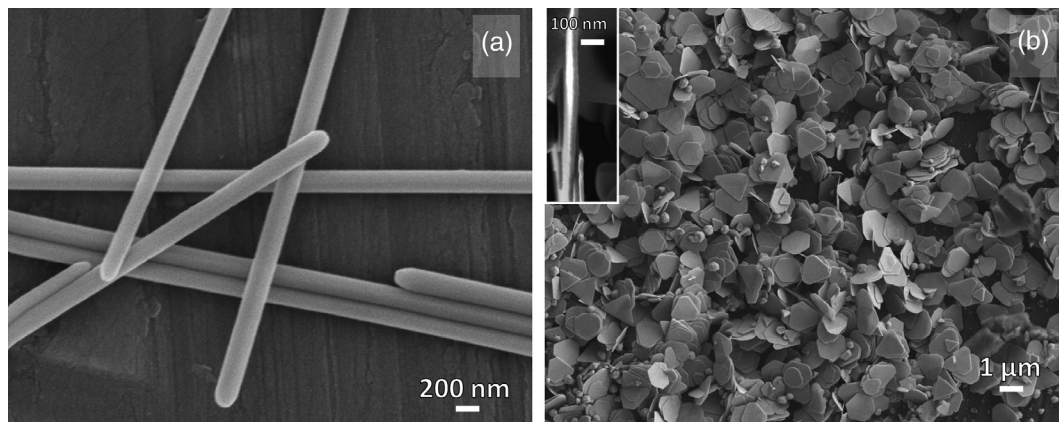
**Carbon Fiber and Sizing.** Unsized AS4 CF tow of 12 000 monofilaments was supplied by Hexcel. Two sizings were used: formulated sizing and functionalized sizing. Formulated sizing was realized by an emulsion-solvent evaporation method.<sup>22,27</sup> The sizing process was carried out by dip-coating into the sizing solution. Functionalized sizing was obtained by the dispersion of large silver nanoplates into dissolved PEI in dichloromethane. The filler ratio of the functionalized sizing was fixed at 30 vol % to ensure a maximized electrical conduction. The as obtained PEI/AgNpts solution was then diluted to adjust PEI concentration to  $0.65 \text{ g.L}^{-1}$ . CF was then sized by bath-coating, into the PEI/AgNpts sizing solution. Filmification of the PEI was effective after drying fiber at 50 °C. The visual aspect of the sized CF is shiny and slightly silver-colored.

Large silver nanoplates were obtained by a modified seed-mediated protocol<sup>28–31</sup> that enables us to control their edge length and size distribution.<sup>32</sup> The obtained silver nanoplates are presented on Figure 1(b).

**Carbon Fiber Polymer Composites.** Carbon reinforced composites (Table I) were achieved by a powder impregnation of CF (sized or unsized). The polymer powder was firstly mixed and sonicated with ethanol (ratio PAEK / EtOH = 0.092 w/w). The solution was then incorporated into the CF bundle (length between 8 and 10 cm), under fluid pressure. The impregnated bundle is then placed into a 360°C hot press system. A mild pressure ( $\sim 20 \text{ MPa}$ ) was applied and maintained for 3 min on the melt polymer. Unidirectional CFRPs with a fiber content around 40 wt% were obtained.

### Methods

**Scanning Electron Microscopy.** Morphology of silver nanoplates and cryofractured composites were observed with a JEOL 7800F Prime. Acceleration voltage was set between 5 and 10 kV. Silver nanoplates and nonconductive composites images were obtained with a secondary electron detector; while polymer composites with metallic fillers were observed with back scattered detector.



**Figure 1.** SEM images of (a) silver nanowires (AgNWs) used as conductive filler into the PAEK matrix. (b) Silver nanoplates (AgNpts) used into the conductive sizing solution.

**Table I.** List of the Composites Short Names and Their Full Components Description Used in the Text

Composite short name	Composite/component full name	Analysis performed
PAEK	Low-melting PAEK matrix	Mechanical and electrical
PAEK/ <i>CF</i>	PAEK matrix/unsized carbon fiber	Mechanical and electrical
PAEK/ <i>CF</i> <sub>PEI</sub>	PAEK matrix/carbon fiber with PEI sizing	Mechanical and electrical
PAEK/ <i>CF</i> <sub>PEI + AgNpts</sub>	PAEK matrix/carbon fiber with PEI/AgNpts sizing	Mechanical & electrical
PAEK + AgNWs/ <i>CF</i> <sub>PEI</sub>	PAEK matrix + silver nanowires/carbon fiber with PEI sizing	Mechanical & electrical
PAEK + AgNWs/ <i>CF</i> <sub>PEI + AgNpts</sub>	PAEK matrix + silver nanowires/carbon fiber with PEI+ AgNpts sizing	Mechanical & electrical

**Dynamical Mechanical Analysis.** Dynamical mechanical shear modulus was measured using a rheometer ARES G1 from Rheometric Scientific. Polymer or composites samples were obtained by hot-pressing process using a parallelepiped aluminium mold (35 mm × 10 mm × 250 μm). Strain of 0.1% is applied with an angular frequency  $\omega=1 \text{ rad.s}^{-1}$ . The analysis was carried out in the temperature range – 135 to 250°C with a heating rate of 3°C.min<sup>-1</sup>.

**Electrical Conductivity.** A Keithley 2420 source meter with a four wires configuration was used as precision ohmmeter. The transverse electrical conductivity  $\sigma$  of the composites was deduced from the measured transverse resistance  $R$  of samples taking into account the electrode geometry.

$$\sigma = \frac{t}{R.S}$$

Where  $R$  is the electrical resistance,  $S$  is the surface of the electrode, and  $t$  is the thickness of the sample. The voltage value was between 2.0 and 20.0 V (automatic calibration mode).

## RESULTS AND DISCUSSION

### SEM Observations of PAEK/*CF* Composites

The sizing deposit was controlled during the composite manufacturing process. The weight of the sized fiber bundle was normalized to the unsized *CF*. The mean amount of deposited sizing was 4 wt % for formulated PEI sizing, and 3 wt % for dichloromethane PEI + AgNpts sizing.

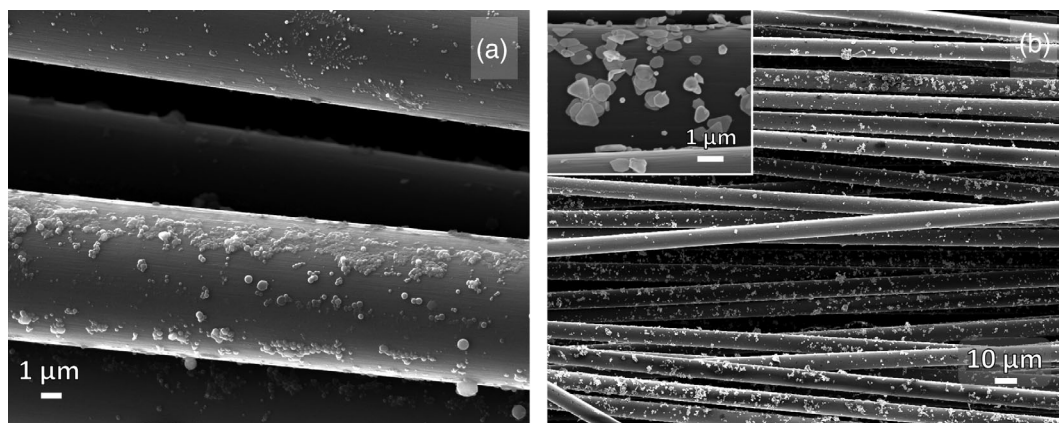
The presence of sizing was examined by scanning electron microscopy (Figure 2). The SEM image of cartoon A suggests the deposit

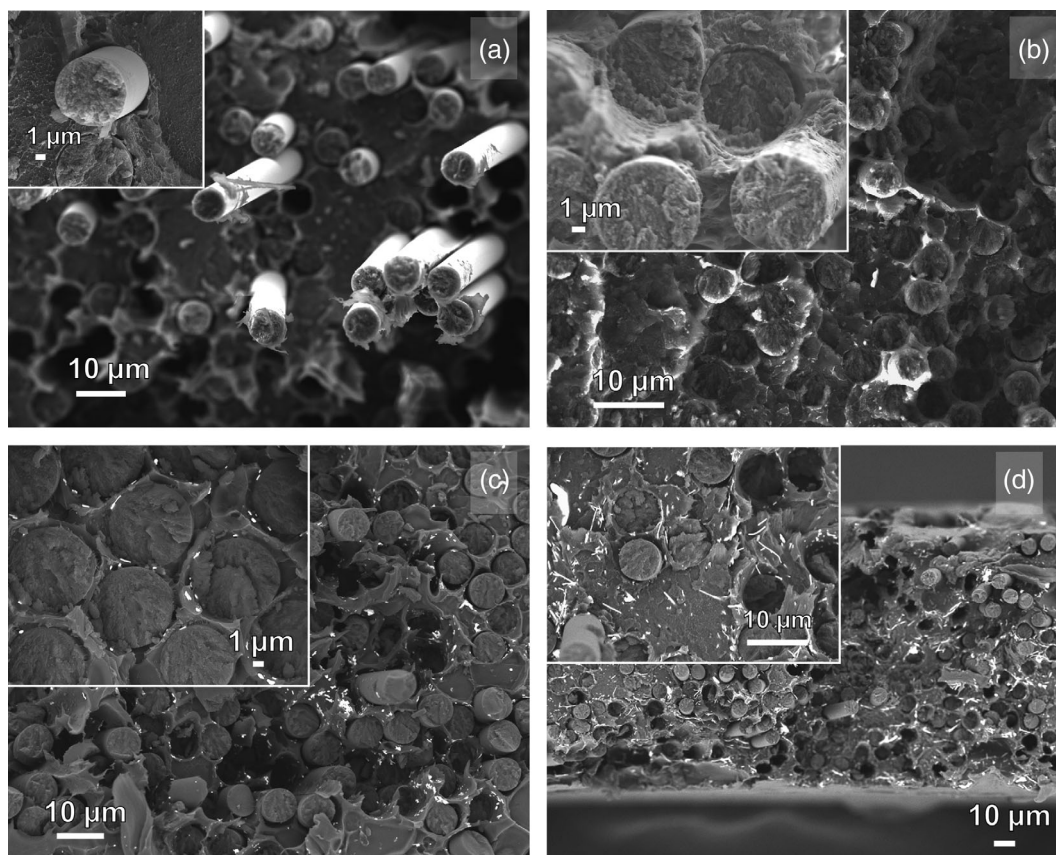
of PEI. To ensure PEI coating, *CFs* were thermally treated at 360°C during 5 min. The surfactants are thermally removed and the polymer coating is then possible. On cartoon B, the AgNpts of the sizing are observed onto the fiber surface. This functionalized sizing does not require a thermal treatment since the film forming takes place when the dichloromethane was evaporated.

After the impregnation process, the composites were cryofractured and the surface was observed by SEM. Low magnification images validate the impregnation technique: reference samples with unsized *CF* shows that the thermoplastic polymer matrix correctly penetrate the bundle of fiber [Figure 3(a)]. Similar results were obtained for both nonconducting or conducting sizing, even when silver nanowires are introduced into the polymer matrix. Figure 3 (cartoons B, C, and D) shows the corresponding cryofracture. The last results are consistent with our previous work.<sup>12</sup>

A qualitative comparison of the different composites was performed by SEM at higher magnification. Composites with unsized *CF* [insert Figure 3(a)] present no matter-continuity at the matrix–fiber interface. Contrarily, composites with sized fiber [inset Figure 3(b-d)], the SEM images show a matter-continuity between *CF* and polymeric matrix that suggest the existence of physical interactions between the polymer matrix and the *CF*. This observation is less visible for the conductive sizing because the PEI film on the *CF* surface form a very smooth surface [inset Figure 3(c,d)].

The composites obtained with PEI/AgNpts sizing, revealed the presence of silver nanoplates, most of them are located at the matrix–fiber interface [inset Figure 3(c)]. The migration of

**Figure 2.** Sized carbon fiber with (a) PEI sizing; (b) PEI + AgNpts sizing. The silver nanoplates are observable at the surface of carbon fibers.

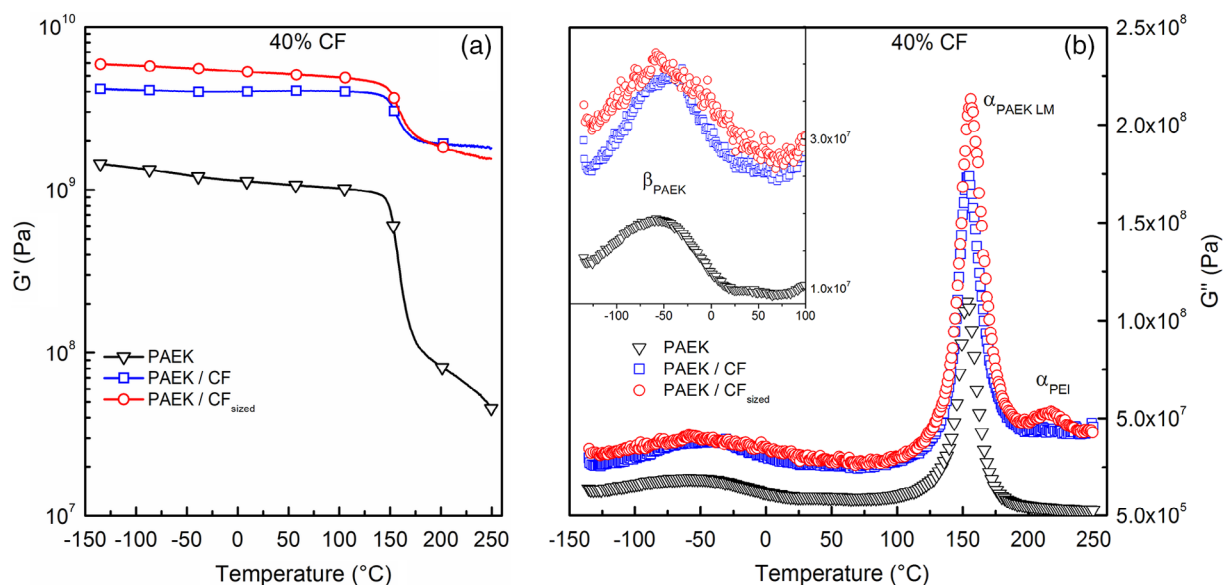


**Figure 3.** Cryofracture of (a) PAEK/CF unsized, (b) PAEK/CF<sub>PEI</sub>; (c) PAEK/CF sized with PEI + AgNpts conductive sizing. (d) PAEK+AgNWs/CF sized with PEI + AgNpts.

nanoplates into polymer matrix was rarely observed. These observations suggest that the impregnation process is compatible with functionalized sizing and prevents the migration of silver nanoplates.

### Physical Properties of PAEK/CF-Sized and PAEK/CF-Unsigned Composites

**Mechanical Modulus.** The dynamic mechanical modulus of the different composites was compared to the bulk polymer. The



**Figure 4.** (a) Storage and (b) loss modulus of PAEK/CF composites compared to PAEK reference. Carbon fiber content is fixed at 40 wt % Inset of Figure B is focussed on local mobility of the polymer and composites. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

PAEK storage modulus is  $\sim 1.5$  GPa on the vitreous plateau [Figure 4(a)]. The viscoelastic transition is observed around  $150^\circ\text{C}$ .<sup>33–35</sup> The rubbery plateau is located between 0.05 and 0.1 GPa. Figure 4(b) shows the loss modulus versus temperature for the PAEK. The main  $\alpha$  relaxation is observed at  $154^\circ\text{C}$ , which is consistent with the DSC glass transition.<sup>36</sup> Previous work on PAEK showed that both  $\beta$  and  $\alpha$  relaxations are analogous with the ones of PEEK<sup>34,37,38</sup>: the  $\beta$  relaxation of PAEK was attributed to the localized mobility of aromatic rings and the  $\alpha$  relaxation to the delocalized molecular mobility of the main chain.

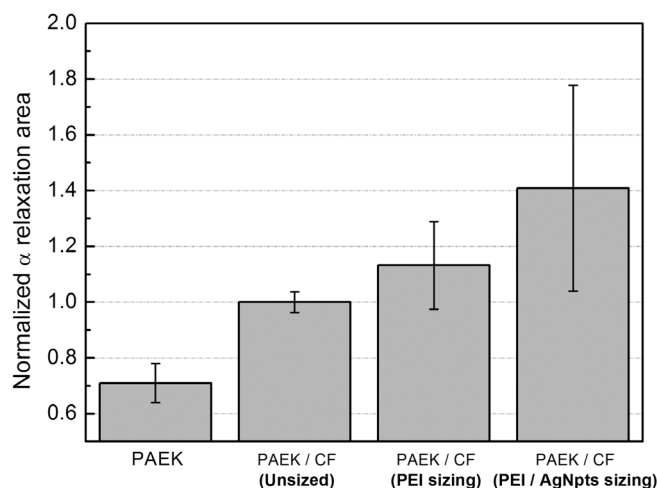
The storage modulus  $G'$  essentially showed the reinforcing effect of  $CF$  regardless of the sizing. The presence of  $CF$  in the composites increases the storage modulus of the polymer matrix from 400 to 500%. The reinforcing effect is emphasized on the rubbery plateau: the relative drop of storage modulus (taken between  $T_{\alpha-50}$  and  $T_{\alpha+50}$ ) is 12.5, 2.1, and 2.7 for PAEK, PAEK/ $CF$ , PAEK/ $CF_{\text{sized}}$ , respectively. This comparison indicates that the reinforcing effect of the  $CF$  is the predominant effect. The influence of the sizing on the viscoelastic transition is more visible on the loss modulus [Figure 4(b)]. The PAEK thermograms show two anelastic relaxations. PAEK/ $CF$  composites with unsized and sized  $CF$  exhibit a higher modulus on the entire temperature range. Main  $\alpha$  relaxation is observed at  $156^\circ\text{C}$ , slightly higher than for the bulk polymer. PEI-sized  $CF$  composites exhibit a supplementary mechanical relaxation beyond the main  $\alpha$  relaxation. It has been attributed to PEI  $\alpha$  relaxation. Analyses of bulk PEI under the same conditions confirmed the presence of the main  $\alpha_{\text{PEI}}$  relaxation in the vicinity of  $220^\circ\text{C}$ . Because of low sizing content in the whole PAEK/ $CF$  composite ( $< 1$  wt %), the observation of  $\beta_{\text{PEI}}$  and  $\gamma_{\text{PEI}}$  relaxations of PEI is not possible. Only the main (and more intense) relaxation is observed. Furthermore, it is thought that polymer sizing is under mechanical constraint at the interface between  $CF$  and polymer matrix that enhance PEI relaxation.

Despite the miscibility between PAEK and PEI, the high melt viscosity of PEI and PAEK is responsible for phase segregation remaining after composite processing. As suggested by SEM images, PEI remains at the fiber–matrix interface. For coated PEI sizing, the mechanical relaxation of PEI is not distinguishable, probably due to the very thin interface between the  $CF$  and the polymeric matrix.

Figure 5 reports the integrated area of the mechanical  $\alpha$  relaxation that could be associated with an amount of dissipated energy. It has been normalized to the value of the composites with unsized  $CF$ . An increase of the dissipated energy is observed for sized  $CF$ , which suggest a better mechanical coupling. This propensity is enhanced when silver nanoplates are introduced into the sizing agent. This increase associated with the silver nanoplates might be due to local heterogeneities emphasizing the stick–slip phenomenon.

The introduction of AgNpts into the PEI sizing does not modify the characteristics of the dynamic mechanical relaxations of PAEK/ $CF$  sized with coated PEI sizing. Thus, the introduction of conductive silver nanoplates into the PEI sizing allows to maintain the integrity of the PAEK matrix.

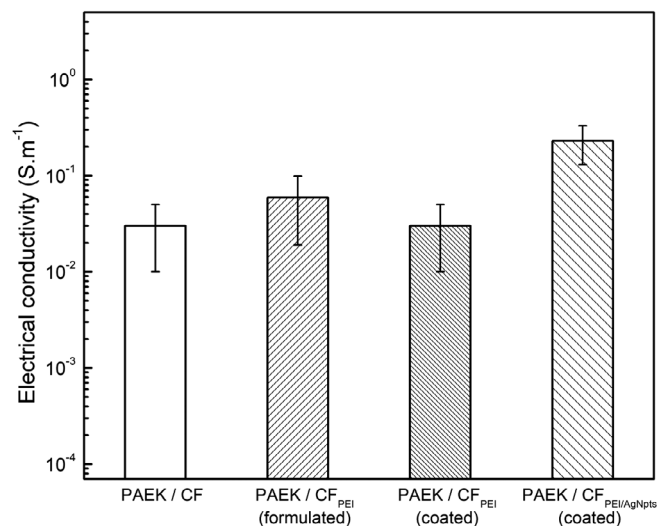
**Transverse Electrical Conductivity.** The transverse electrical conductivity of the composites has been compared in Figure 6. The



**Figure 5.** Normalized  $\alpha$  relaxation peak area. The area of unsized carbon fiber composite was used as reference.

polymer matrix has a low conductivity around  $10^{-15}$   $\text{S}\cdot\text{m}^{-1}$ . The electrical conductivity of CFRP are in the range of  $10^{-2}$  to  $10^{-1}$   $\text{S}\cdot\text{m}^{-1}$ , which is consistent with the conductivity of composites filled with carbonaceous fillers such as carbon nanotubes,<sup>39,40</sup> graphene,<sup>41,42</sup> or carbon black.<sup>43,44</sup> The  $CF$  content is about 40 wt % ( $\sim 33$  vol %) for the elaborated composites. A through thickness schematic representation of the composites may consider  $CF$  as spheres and matrix as the continuous medium.  $CF$  content is far above the percolation threshold for randomly dispersed spheres (15 vol %).<sup>45</sup> Hence there is a through thickness backbone of conductive carbon filler that is commonly observed.<sup>1,2,6,12</sup> The presence of PEI sizing agent was found to have no influence on the transverse conductivity of the composites. Composites with both sizings (formulated or coated) have a conductivity level in the same range ( $0.02$  to  $0.06$   $\text{S}\cdot\text{m}^{-1}$ ) than composites with unsized  $CF$ .

Composites elaborated with PEI/AgNpts sizing were found to have higher conductivity level of about  $0.2$   $\text{S}\cdot\text{m}^{-1}$ . This conductivity



**Figure 6.** Transverse electrical conductivity of composites. The contribution of AgNpts sizing is about one decade.

level is about 5 to 10 times the conductivity of other composites, that is, with unsized or PEI-sized CF. It is important to underline the relative low mean content of silver ( $\sim 0.2$  vol %) of the whole composite. According to previous work on composites with silver nanoplates,<sup>32</sup> the silver content is far below the percolation threshold of randomly dispersed nanoplates. The consequence is that there is no percolative network of metallic particles, but rather, a CF percolative network assisted by the presence of silver nanoplates. It is thought that their disposition around the CF is important to create electrical connections between CF. Bekyarova *et al.*<sup>2</sup> reported a similar enhancement for a low carbon nanotubes content in CFRP composites. The hopping conduction mechanism might be facilitated by the presence of silver nanoplates.

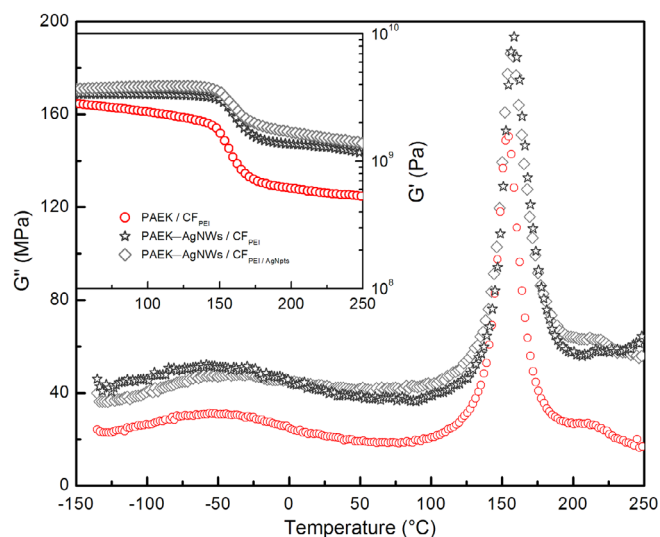
#### PAEK–Ag NWs/CF with PEI + AgNpts Sizing Composites

Silver nanowires were introduced into the PAEK/CF composites to enhance the electrical conductivity. The influence of AgNpts in the sizing of PAEK/AgNWs/CF composites was tested. Both neat PEI and PEI/AgNpts sizing were compared.

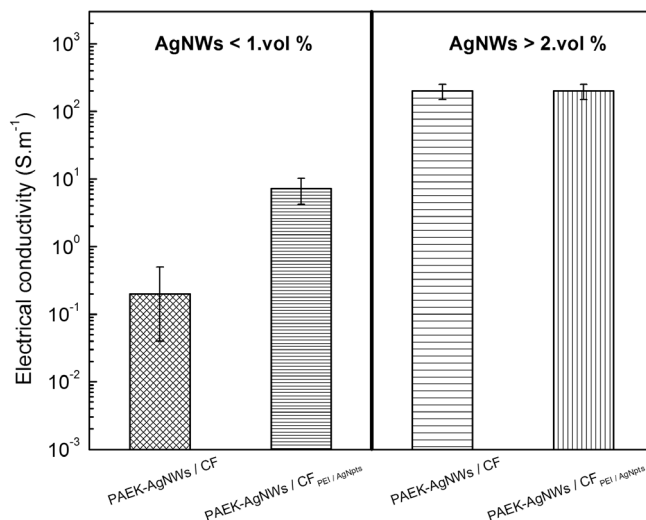
**Mechanical Modulus.** Figure 7 shows the influence on the composites mechanical behaviour of Ag nanowires (4 vol %) in the matrix and AgNpts in the sizing.

The major event of the mechanical moduli is the viscoelasticity at the  $\alpha$  relaxation temperature  $T_\alpha$ . The introduction of 4 vol % AgNWs induced an increase of the storage modulus on the entire temperature range. This mechanical reinforcement is more pronounced on the rubbery plateau that increases from 0.6 to 1.4 GPa. This observation is attributed to the formation of a physical network by silver nanowires. The value of  $G'$  was taken at  $T_\alpha - 50^\circ\text{C}$  and  $T_\alpha + 50^\circ\text{C}$  for all composites. An increase of the storage modulus from 2.4 to 3.9 GPa was observed. It is attributed to the stiffening of the polymer due to the presence of both fiber bundle and silver nanowires.

The presence of AgNWs does not influence the  $\beta$  sub glass relaxation at low silver content; we only noticed a slight increase of



**Figure 7.** Loss shear modulus of (O) PAEK/CF sized with PEI, (\*)PAEK+AgNWs/CF sized with PEI, and (<>) PAEK+AgNWs/CF sized with PEI + AgNpts. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**Figure 8.** Electrical conductivity of composites with matrix containing AgNWs.

the  $\beta$  relaxation temperature at high silver loading ( $\geq 3$  vol %). For the  $\alpha$  relaxation even with 4 vol % of Ag nanowires, we do not observe any significant evolution.

**Transverse Electrical Conductivity.** The influence of AgNpts on the electrical properties is strongly dependent on nanowires content. As a matter of fact, the contribution of silver nanoplates only occurs when the nanowires content is low. The electrical conductivity was measured as a function of AgNWs content, between 0.5 and 4 vol %. As shown in Figure 8, two electrical behaviors were distinguished depending only on the AgNWs content. At lower silver content, the electrical conductivity depends on the filler content while, at higher silver content, the electrical conductivity becomes independent of the silver content.

The behavior at high silver content ( $>2$  vol %) may be easily explained. The conductivity reaches a constant level of  $200 \text{ S.m}^{-1}$  due to the percolation of the silver nanowires independently from the presence of nanoplates. This kind of behavior is often reported in the literature<sup>19,32,40–42,46</sup> as classical electrical percolation that is fitted by a power law.<sup>47</sup> The observed high electrical conductivity could be explained by the percolation of metallic nanowires independently of the fiber bundle presence. We propose that there is a metallic-filler percolation that govern the conductivity value. As percolation threshold of the silver nanowires is in the vicinity of 0.6 vol %, <sup>19,48</sup> our high values are situated on the high conductivity plateau that is consistent with the observations of Quiroga *et al.*<sup>12</sup> for such silver loading.

The influence of the silver nanoplates in the sizing is only seen at low silver nanowires content. For a nanowires content of 0.75 vol %, the measured electrical conductivity was increased by one decade when CFs were treated with PEI + AgNpts sizing. We suggest that the enhancement of electrical conductivity depends on all the entities (silver nanowires, silver nanoplates, and CF). When silver nanoplates are introduced in the sizing, it favors a connection between all the conductive elements of the composite (fibers, nanowires, and nanoplates). In that case, there is a percolation phenomenon that involves all conductive entities, which



explains its dependency regarding the AgNpts content. Such behavior has been previously described for carbonaceous fillers.<sup>49</sup> It is important to note that the increase can be seen because we remain below the percolation threshold. From the composite point of view, the total silver loading may vary from 0.75 vol % (AgNWs) to 0.95 vol % (AgNWs + AgNpts). When the amount of AgNWs is above the percolation threshold, the increase of conductivity of PAEK+AgNWs/CF<sub>PEI + AgNpts</sub> composites is not observed.

## CONCLUSIONS

The main objective of this work was to enhance the electrical conductivity of PAEK/continuous CF composites while maintaining their mechanical properties. Our study focused on the elaboration of an electrically conductive sizing, constituted of PolyEtherImide (PEI) and silver nanoplates (AgNpts), as suspension in dichloromethane prior the deposition on the CF. An aqueous PEI formulation was used as insulating sizing reference. According to SEM observations on the composites cryofractures, both sizing presented a continuity of matter at the fiber/matrix interface.

The presence of AgNpts into the sizing enhances electrical conductivity up to 0.2 S.m<sup>-1</sup> for a silver content ~0.2 vol % without any modification of mechanical properties. The influence of conductive sizing on PAEK+ AgNWs/CF was also observed. For AgNWs content lower than 1 vol %; conductive sizing increases the electrical conductivity of the composite by one decade. In that case, both types of Ag particles participate to the conductive path. For higher AgNWs contents, electrical conductivity (~ 102 S.m<sup>-1</sup>) is independent from the AgNpts content: the conductive path is only constituted by AgNWs.

The introduction of Ag particles in the matrix and the sizing of PAEK/CF composites looks very promising for promoting electrical conductivity while maintaining mechanical performances.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of BPI/France and Conseil Régional Midi Pyrénées/France through the MACOTHEC FUI program. The authors gratefully acknowledge the courtesy of Victrex that kindly supplied the PAEK VICTREX AE 250™.

## REFERENCES

- Pozegic, T. R.; Hamerton, I.; Anguita, J. V.; Tang, W.; Ballocci, P.; Jenkins, P.; Silva, S. R. P. *Carbon N. Y.* **2014**, *74*, 319.
- Bekyarova, E.; Thostenson, E. T.; Yu, A.; Kim, H.; Gao, J.; Tang, J.; Hahn, H. T.; Chou, T.-W.; Itkis, M. E.; Haddon, R. C. *Langmuir*. **2007**, *23*(7), 3970.
- De Greef, N.; Zhang, L.; Magrez, A.; Forró, L.; Locquet, J. P.; Verpoest, I.; Seo, J. W. *Diamond Relat. Mater.* **2015**, *51*, 39.
- Lonjon, A.; Demont, P.; Dantras, E.; Lacabanne, C. *J. Non Cryst. Solids*. **2012**, *358* (Iss 15), 1859.
- Moaseri, E.; Karimi, M.; Maghrebi, M.; Baniadam, M. *Int. J. Solids Struct.* **2014**, *51*(Iss 3–4), 774.
- Ashori, A.; Rahmani, H.; Bahrami, R. *Polym. Test.* **2015**, *48*, 82.
- Cheng, X.; Yokozeki, T.; Wu, L.; Wang, H.; Zhang, J.; Koyanagi, J.; Weng, Z.; Sun, Q. *Compos. Part A Appl. Sci. Manuf.* **2016**, *90*, 243.
- Kandare, E.; Khatibi, A. A.; Yoo, S.; Wang, R.; Ma, J.; Olivier, P.; Gleizes, N.; Wang, C. H. *Compos. Part A Appl. Sci. Manuf.* **2015**, *69*, 72.
- Zang, C. G.; Zhu, X. D.; Jiao, Q. J. *J. Appl. Polym. Sci.* **2015**, *132*(19), 1.
- Zhang, X.; Fan, X.; Yan, C.; Li, H.; Zhu, Y.; Li, X.; Yu, L. *ACS Appl. Mater. Interfaces*. **2012**, *4*(3), 1543.
- Chen, J.; Wang, K.; Zhao, Y. *Compos. Sci. Technol.* **2018**, *154*, 175.
- Cortes, L. Q.; Racagel, S.; Lonjon, A.; Dantras, E.; Lacabanne, C. *Compos. Sci. Technol.* **2016**, *137*, 159.
- Ahmad, M. S.; Zihlif, A. M.; Martuscelli, E.; Ragosta, G.; Scafora, E. *Polym. Compos.* **1992**, *13*(1), 53.
- Hua, Z.; Liu, Y.; Yao, G.; Wang, L.; Ma, J.; Liang, L. *J. Mater. Eng. Perform.* **2012**, *21*(Iss March), 324.
- Tzeng, S.-S.; Chang, F.-Y. *Mater. Sci. Eng. A*. **2001**, *302* (2), 258.
- Wang, P.; Yang, J.; Liu, W.; Tang, X.-Z.; Zhao, K.; Lu, X.; Xu, S. *Mater. Des.* **2017**, *113*, 68.
- An, X.; Ma, J.; Wang, K.; Zhan, M. *J. Appl. Polym. Sci.* **2016**, *133*(9), 1.
- Liu, L.; Xiao, L.; Zhang, X.; Li, M.; Chang, Y.; Shang, L.; Ao, Y. *RSC Adv.* **2015**, *5*(71), 57853.
- Cortes, L. Q.; Lonjon, A.; Dantras, E.; Lacabanne, C. *J. Non Cryst. Solids*. **2014**, *391*, 106.
- Gerard, J. *Polym. Eng. Sci.* **1988**, *28*(9), 568.
- Veazey, D.; Hsu, T.; Gomez, E. D. *J. Appl. Polym. Sci.* **2017**, *134*(6), 19.
- Giraud, I.; Franceschi, S.; Perez, E.; Lacabanne, C.; Dantras, E. *J. Appl. Polym. Sci.* **2015**, *132*(38), 42550.1.
- Liu, W. B.; Zhang, S.; Hao, L. F.; Jiao, W. C.; Yang, F.; Li, X. F.; Wang, R. G. *J. Appl. Polym. Sci.* **2013**, *128*(6), 3702.
- Zeng, J.; Roberts, S.; Xia, Y. *Chem. - A Eur. J. Vol.* **2010**, *16* (42), 12559.
- Jiang, F.; Hsieh, Y. *Biomacromolecules*. **2014**, *15*, 3608.
- Ren, H.-M.; Guo, Y.; Huang, S.-Y.; Zhang, K.; Yuen, M. M. F.; Fu, X.-Z.; Yu, S.; Sun, R.; Wong, C.-P. *ACS Appl. Mater. Interfaces*. **2015**, *7*(24), 13685.
- Malho Rodrigues, A.; Franceschi, S.; Perez, E.; Garrigues, J.-C. *J. Mater. Sci.* **2015**, *50*(1), 420.
- Zhang, Q.; Li, N.; Goebel, J.; Lu, Z.; Yin, Y. *J. Am. Chem. Soc.* **2011**, *133*(46), 18931.
- Zeng, J.; Xia, X.; Rycenga, M.; Henneghan, P.; Li, Q.; Xia, Y. *Angew. Chem. Int. Ed. Engl.* **2011**, *50*(1), 244.
- Zhang, Q.; Hu, Y.; Guo, S.; Goebel, J.; Yin, Y. *Nano Lett.* **2010**, *10*(12), 5037.

31. Li, N.; Zhang, Q.; Quinlivan, S.; Goebel, J.; Gan, Y.; Yin, Y. *Chemphyschem.* **2012**, *13*(10), 2526.
32. Audoit, J.; Laffont, L.; Lonjon, A.; Dantras, E.; Lacabanne, C. *Polymer.* **2015**, *78*, 104.
33. Quiroga Cortés, L.; Caussé, N.; Dantras, E.; Lonjon, A.; Lacabanne, C. *J. Appl. Polym. Sci.* **2016**, *133*(19), 43396.
34. David, L.; Etienne, S. *Macromolecules.* **1992**, *25*(17), 4302.
35. Goodwin, A.; Hay, J. *J. Polym. Sci. Part B Polym. Phys.* **1998**, *36*, 851.
36. Audoit, J.; Rivière, L.; Dandurand, J.; Lonjon, A.; Dantras, E.; Lacabanne, C. *J. Therm. Anal. Calorim.* **2018**, *135*(4), 2147.
37. de Candia, F.; Michele, A.; Renzulli, A. *J. Macromol. Sci. Part B.* **1994**, *33*(3), 307.
38. Krishnaswamy, R. K.; Kalika, D. S. *Polymer.* **1994**, *35*(6), 1157.
39. Carponcin, D.; Dantras, E.; Aridon, G.; Levallois, F.; Cadiergues, L.; Lacabanne, C. *Compos. Sci. Technol.* **2012**, *72* (Iss 4), 515.
40. Sandler, J. K. W.; Kirk, J. E.; Kinloch, I. A.; Shaffer, M. S. P.; Windle, A. H. *Polymer.* **2003**, *44*, 5893.
41. Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. *Nature.* **2006**, *442*(7100), 282.
42. Yang, L.; Zhang, S.; Chen, Z.; Guo, Y.; Luan, J.; Geng, Z.; Wang, G. *J. Mater. Sci.* **2013**, *49*(5), 2372.
43. Huang, J. C. *Adv. Polym. Technol.* **2002**, *21*(4), 299.
44. Psarras, G. C. *J. Polym. Sci. Part B Polym. Phys.* **2007**, *45* (18), 2535.
45. Scher, H.; Zallen, R. *J. Chem. Phys.* **1970**, *53*(9), 3759.
46. Untereker, D.; Lyu, S.; Schley, J.; Martinez, G.; Lohstreter, L. *ACS Appl. Mater. Interfaces.* **2009**, *1*(1), 97.
47. Stauffer, D. *Introduction to Percolation Theory*; Taylor & Francis Ltd: London, **1985**.
48. Nguyen, T. H. L.; Quiroga Cortes, L.; Lonjon, A.; Dantras, E.; Lacabanne, C. *J. Non Cryst. Solids.* **2014**, *385*, 34.
49. Paszkiewicz, S.; Szymczyk, A.; Sui, X. M.; Wagner, H. D.; Linares, A.; Ezquerro, T. A.; Roslaniec, Z. *Compos. Sci. Technol.* **2015**, *118*, 72.