



## 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-deposited version published in : <http://oatao.univ-toulouse.fr/>  
Eprints ID : 14310

**To link to this article** : DOI : 10.1002/app.42550  
URL : <http://dx.doi.org/10.1002/app.42550>

**To cite this version** : Giraud, Isabelle and Franceschi-Messant, Sophie and Perez, Emile and Lacabanne, Colette and Dantras, Eric [Influence of new thermoplastic sizing agents on the mechanical behavior of poly\(ether ketone ketone\)/carbon fiber composites](#). (2015) Journal of Applied Polymer Science, vol. 132 (n° 38). n/a-n/a. ISSN 0021-8995

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

# Influence of new thermoplastic sizing agents on the mechanical behavior of poly(ether ketone ketone)/carbon fiber composites

Isabelle Giraud,<sup>1,2</sup> Sophie Franceschi,<sup>1</sup> Emile Perez,<sup>1</sup> Colette Lacabanne,<sup>2</sup> Eric Dantras<sup>2</sup>

<sup>1</sup>Laboratoire des Interactions Moléculaires et de la Réactivité Chimique et Photochimique (IMRCP), Université Paul Sabatier, 31062 Toulouse Cedex 09, France

<sup>2</sup>Polymer Physics, Centre InterUniversitaire de Recherche et d'Ingénierie des Matériaux (CIRIMAT), Université Paul Sabatier, 31062 Toulouse Cedex 09, France

Correspondence to: E. Dantras (E-mail: eric.dantras@univ-tlse3.fr)

**ABSTRACT:** In this study, unidirectional poly(ether ether ketone)/carbon fiber (CF) composite sheets were elaborated with unsized, epoxy-sized, and thermoplastic-sized CFs by hot-press molding. The thermoplastic sizings that we used were poly(ether imide) (PEI) and poly(ether ketone ketone) oligomer aqueous dispersions. Scanning electron microscopy observation of the composites freeze fractures showed that unlike unsized or epoxy-sized CFs, the thermoplastic sizings improved the interaction between the fibers and the matrix. A comparative study of the mechanical relaxations by dynamic mechanical analysis was carried out on the different composites before and after immersion in kerosene. At low temperature, the PEI sizing had a significant influence on the  $\beta$  relaxation, particularly after kerosene immersion. The thermoplastic sizings did not modify the glass-transition temperature but improved the kerosene resistance on the composites.

**KEYWORDS:** composites; fibers; mechanical properties

**DOI:** 10.1002/app.42550

## INTRODUCTION

In the last 30 years, abundant literature has been devoted to poly(ether ether ketone) (PEEK)<sup>1–6</sup> because of interest in the development of high-performance thermoplastic composites.<sup>7–14</sup> More recently, enhancements in the mechanical properties with the introduction of hybrid fibers<sup>15</sup> or nanoparticles<sup>16–21</sup> have been reported. With electroactive particles, PEEK can also become a multifunctional matrix.<sup>22</sup> The strengthening of carbon fiber (CF)/PEEK composites has led to the development of new CF sizing agents. Indeed, sizing agents are important for making fiber handling but also for improving the compatibility between the matrix and CF.<sup>23–28</sup> Consequently, the sizing has to be adapted to the matrix. The formulation of the sizing is often hidden by CF manufacturers. Most of the composites have an epoxy resin matrix, and sizing agents are often an organic solution of prepolymers or polymers of the same nature.<sup>29–32</sup> With a degradation temperature around 250°C, such sizings are not tailored for high-temperature thermoplastics such as PEEK. In previous studies, on the basis of the general formulation of the sizing,<sup>33,34</sup> we elaborated new high-temperature thermoplastic sizing formulations; they were two aqueous dispersions, one based on poly(ether imide) (PEI) and the other based on poly(ether ketone ketone) (PEKK) oligomers.<sup>35,36</sup>

The aim of this study was to highlight the influence of these new thermoplastic sizings on the mechanical properties of PEEK/CF composites. Unsized CFs were coated by the PEI and PEKK aqueous dispersion by sputtering. Four series of unidirectional PEEK/CF sheets were processed by hot-press molding with commercially available unsized and epoxy-sized CFs and homemade PEI- and PEKK-sized CFs. Two different characterizations were carried out to determine the importance of a suitable sizing on the mechanical properties of the PEEK/CF composites. First, scanning electron microscopy (SEM) observation of the composites freeze fractures provided us with visual information on the matrix/CF interface. Then, a comparative study of dynamic mechanical analysis (DMA) highlighted the influence of the sizing agents on the mechanical behavior of the composites before and after kerosene immersion. This solvent was chosen as common aerospace fluid.

## EXPERIMENTAL

### Materials

PEEK, provided by Victrex, was a 100  $\mu\text{m}$  thick film. AS4 CF-treated and unsized CF tows of 12,000 fibers, provided by Hexcel, were used. These CFs were sized with two different aqueous sizings, both elaborated by the emulsion–solvent evaporation method.<sup>36</sup> The first one was based on PEI, and the second one

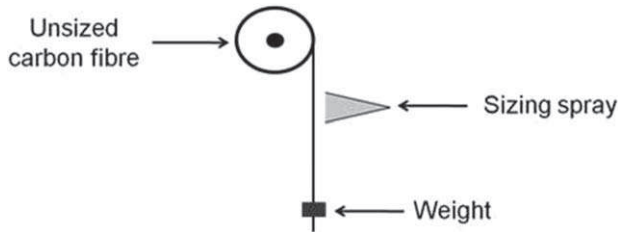


Figure 1. Schematic representation of the sizing process.

was based on the synthesized PEKK oligomer. The kerosene was provided by Sigma-Aldrich, and the remolding agent was CIREX 041WB from Sicomin.

### Sizing Coating Method

Even though the most common method for sizing is bath coating, we chose to spray the dispersion directly onto the unsize fiber surface, as shown in Figure 1. This method is well suited for a laboratory-scale processing. Usually, the sizing concentration is between 0.5 and 1 wt %.<sup>37,38</sup> Our previous work shows that the optimized concentration of the aqueous dispersion was 0.5 wt %.<sup>36</sup> Therefore, the PEI and PEKK sizing concentration used in this study was fixed at 0.5 wt %.

### PEEK/CF Composite Processing

PEEK/unidirectional CFs sheet samples were prepared at a laboratory scale, as described in our previous work.<sup>36</sup> The processing was realized in two steps. First, the sample, consisting of a strand of CFs in a folded PEEK film, was placed in an aluminum mold previously coated with the remolding agent. Then, the mold was placed between the plates of the press previously heated at 400°C.

### SEM Observation

The different samples were all examined with a scanning electron microscope (JEOL JSM 6700F) with an acceleration tension of 5 kV.

### DMA

The DMA were performed with an Advanced Rheometric Expansion System strain-controlled rheometer (TA Instruments) in torsion rectangular mode at an angular frequency of 1 rad/s.

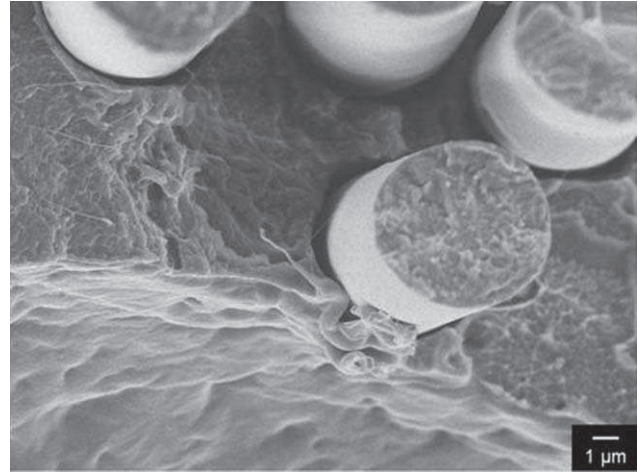


Figure 3. Freeze fracture of the epoxy-sized CF composite.

The storage modulus ( $G'$ ) and loss modulus ( $G''$ ) were recorded as a function of the temperature between  $-135$  and  $250^\circ\text{C}$  at a scanning rate of  $3^\circ\text{C}/\text{min}$ . The measurements were realized in the linear zone with the strain  $\gamma = 0.1\%$ . The sample dimensions were 40 mm long, 10 mm wide, and 250  $\mu\text{m}$  thick.

## RESULTS AND DISCUSSION

### Final Mechanical Properties

To determine the influence of the new sizings on the composites, we observed their freeze fractures by SEM. Figures 2 and 3 present the freeze fractures of the unsize and epoxy-sized CF composites, respectively. Both figures clearly show a void between the fiber and matrix: there was no cohesion between the fibers and the matrix. Therefore, it appeared that there was a lack of affinity between the fibers and the matrix; this confirmed the necessity of a sizing compatible with both materials.

Figures 4 and 5 present the freeze fractures of the PEI-sized CF and PEKK-sized CF composites, respectively. Molecules constituting the sizing created continuity at the interface. Here, we observed that the fiber was connected to the matrix. This observation showed that not only did the sizing not degrade during the composite processing, but it also created continuity between

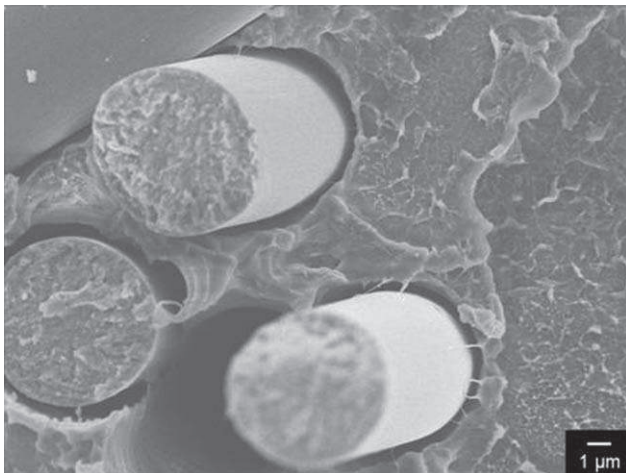


Figure 2. Freeze fracture of the unsize CF composite.

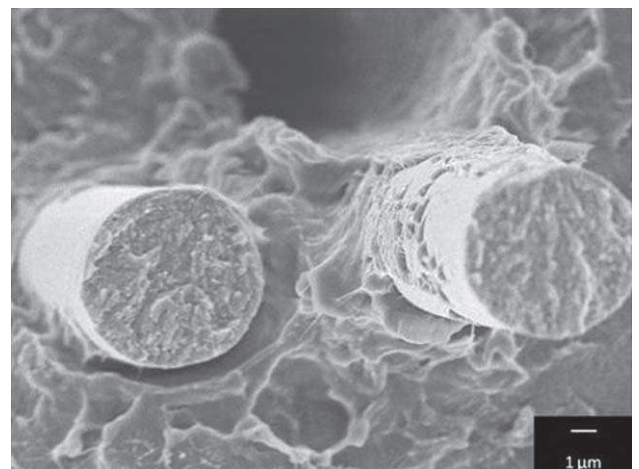


Figure 4. Freeze fracture of the PEI-sized CF composite.

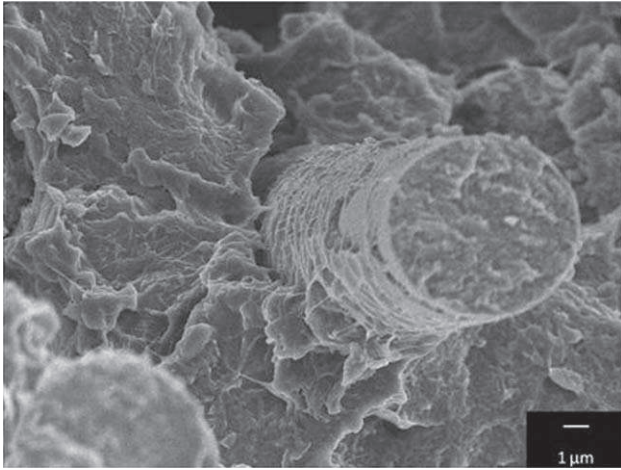


Figure 5. Freeze fracture of the PEKK-sized CF composite.

the fiber and the matrix by interacting with them. Both sizings were constituted by the same chemical groups as the matrix, so their density was analogous: Consequently, they could not be distinguished on the SEM images.

#### Influence of Kerosene on the Mechanical Relaxation

**Dynamic Mechanical Relaxation of the Neat PEEK.** Before the comparative study of the composites, a preliminary DMA was realized to identify the different relaxations of the neat PEEK. Figure 6 shows the dynamic mechanical response of the PEEK at 0.1% strain from  $-135$  to  $250^\circ\text{C}$ .

The conservative modulus ( $G'$ ) decreased slightly at low temperature on the vitreous plateau; then, a sharp decrease was observed at  $150^\circ\text{C}$  to reach the rubbery plateau. The dissipative modulus ( $G''$ ) showed two main relaxations. The relaxation at  $150^\circ\text{C}$ , named  $\alpha$ , corresponded to the anelastic manifestation of the PEEK glass transition. At low temperature, we can observe a broad peak around  $-80^\circ\text{C}$ , which corresponded to a  $\beta$  relaxation.<sup>39-41</sup> This relaxation was associated with the intramolecular flipping of the phenyl rings.<sup>42</sup> The dielectric relaxation mode associated with this anelastic mode was solved into two submodes by thermally stimulated current analyses.<sup>43</sup> The submode  $\beta_a$ , at  $-100^\circ\text{C}$ , was associated with the crystallizable amorphous

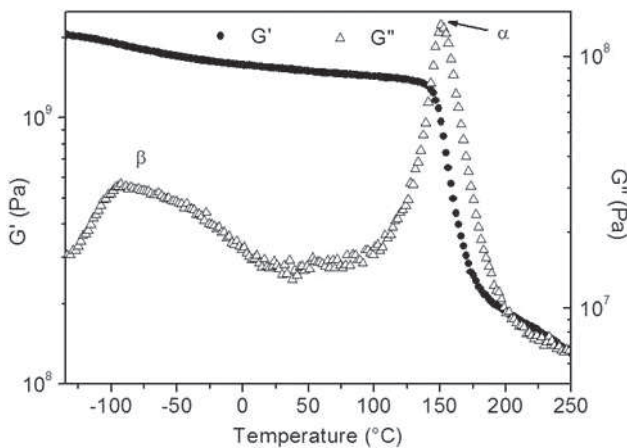


Figure 6. Dynamic mechanical relaxations of PEEK ( $3^\circ\text{C}/\text{min}$ ,  $1 \text{ rad/s}$ ).

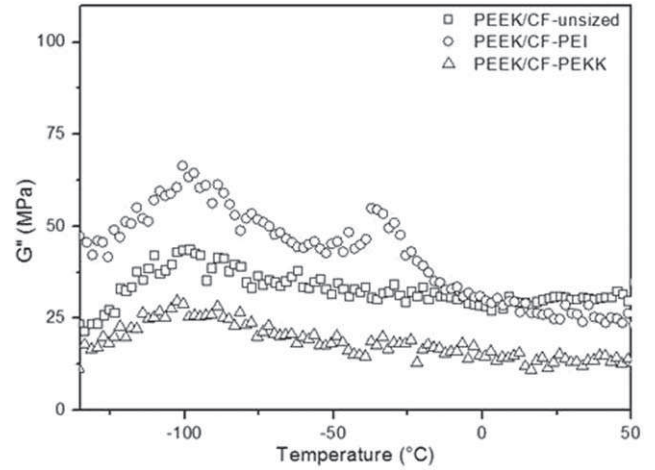


Figure 7.  $G''(T)$  between  $-135$  and  $50^\circ\text{C}$ .

phase, and the submode  $\beta_c$ , around  $-75^\circ\text{C}$ , was located in the crystalline zones. Both submodes have also been observed by mechanical relaxation. According to David and coworkers,<sup>44,45</sup> the relaxation  $\beta_1$  corresponded to the local intrachain mobility in the amorphous phase, and the  $\beta_2$  relaxations corresponded to the local mobility in the ordered regions of the amorphous phase. All data converged to the assignment of the splitting to the physical structure of the environment of the phenyl rings.

#### Dynamic Mechanical Relaxation of the PEEK Composites.

The temperature range being large and the different relaxations of PEEK being well distinct, the mechanical study of the composites was divided into two domains. The first one, from  $-135$  to  $50^\circ\text{C}$ , corresponded to the relaxations in the glassy state, and the second one, from  $50$  to  $250^\circ\text{C}$ , corresponded to the relaxation associated with the glass transition. For each temperature range, a comparative analysis was carried out between the samples before and after 1 month of immersion in kerosene.

Figures 7 and 8 present the dynamic mechanical relaxations from  $-135$  to  $50^\circ\text{C}$ , respectively, before and after immersion in kerosene. We can see on Figure 7, that the  $\beta$  relaxation of PEEK

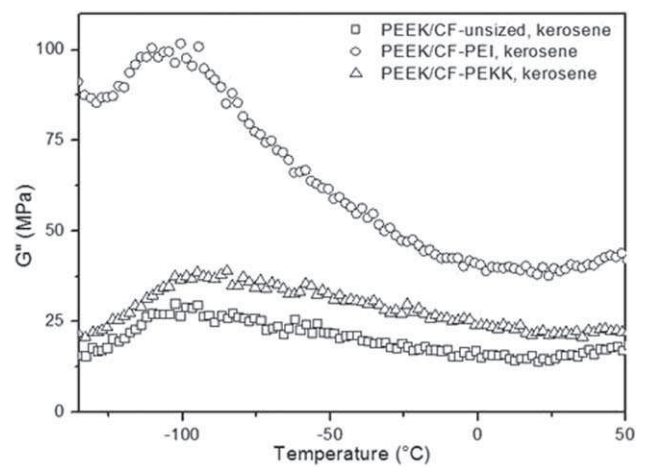


Figure 8.  $G''(T)$  between  $-135$  and  $50^\circ\text{C}$  after 1 month in kerosene.

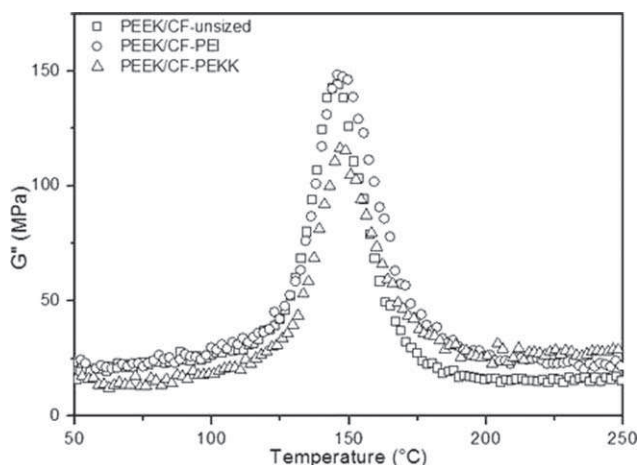


Figure 9.  $G''(T)$  between 50 and 250°C.

is modified according to the sizing used. Indeed, the PEI sizing brings up clearly two relaxations named  $\beta_1$  at  $-100^\circ\text{C}$  and  $\beta_2$  at  $-34^\circ\text{C}$ . The increase of the magnitude of the  $\beta_1$  mode might be related to a better toughness due to a continuity of the polymeric matter at the interface. The PEI sizing amplifies also the  $\beta_2$  relaxation meaning that it tends to increase the coupling with crystalline domains. This result highlights interactions between the fiber, the PEI sizing and the matrix. Concerning the PEKK sizing, no significant modifications of the  $\beta$  mode is observed. It is probably due to the chemical immiscibility of PEKK with PEEK, contrary to PEI.

After 1 month of immersion in kerosene (Figure 8), only the  $\beta$  relaxation of the PEI-sized CF composite was highly modified, particularly the  $\beta_1$  submode. This result highlights a modification of the localized molecular mobility in the amorphous phase. Sasuga *et al.* observed the same phenomenon on quenched amorphous PEEK<sup>40</sup> and associated it with the molecular mobility of water bound to the main chain. PEI is known for its solvent sensitivity, so it is possible that the small aliphatic chains of kerosene penetrated into the sizing and decreased the local interchains interactions in the amorphous phase.

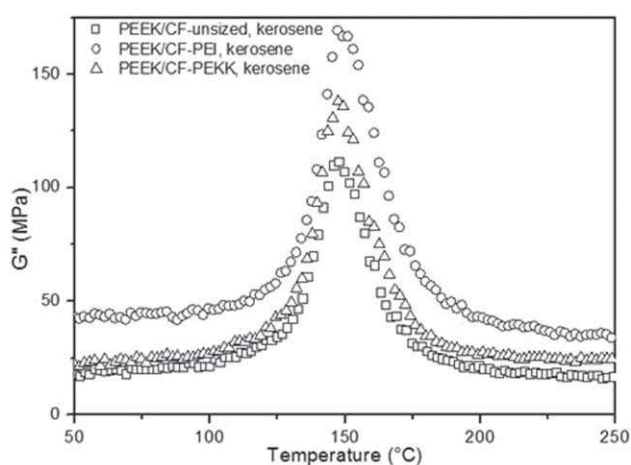


Figure 10.  $G''(T)$  between 50 and 250°C after 1 month in kerosene.

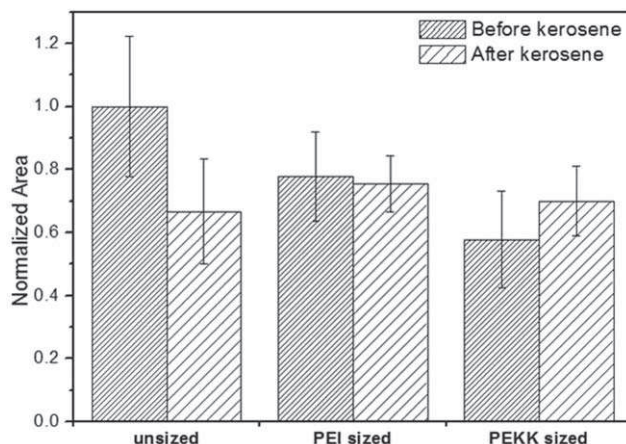


Figure 11. Normalized area under the  $\alpha$  peak before and after immersion for each composite.

Figures 9 and 10 present the imaginary part of the mechanical modulus  $G''(T)$  from 50 to 250°C, respectively, before and after 1 month of immersion in kerosene. The sizings had no impact on the  $\alpha$  relaxation always being centered at 150°C before or after immersion in kerosene. These results show that, in the viscoelastic zone, there was no modification of the matrix by the sizings, but also these sizings were not affected by kerosene.

The histograms (Figure 11) correspond to the normalized area under the  $\alpha$  peak before and after kerosene immersion for each composite. They were calculated 50°C below and above  $T_g$ , the mechanical manifestation of the glass transition, and averaged on a series of three samples.

Before immersion, the dissipated energy was lower for the sized composites. The sizing agents created physical entanglements with the matrix on one side and interacted with CFs on the other side. Such interactions stiffened the matrix.<sup>46</sup> After immersion, the energy loss for the unsized composite decreased significantly, whereas for the sized composites, it remained practically unchanged. Both sizing agents made the PEEK composite totally inert to kerosene.

## CONCLUSIONS

This study highlighted the importance of a CF sizing compatible with the thermoplastic matrix PEEK. Indeed, the SEM observation showed that there was no continuity of matter between the fiber and the matrix when there was no sizing or unsuitable sizing. The use of PEI- and PEKK-sized CFs allowed this continuity by interacting with the CFs and the matrix and creating a continuous interface. The DMA of PEEK showed two main relaxations that were very distinct, the  $\beta$  relaxation at low temperature, corresponding to the intramolecular motion of the aromatic rings, and the  $\alpha$  relaxation, at high temperature, which was the mechanical manifestation of the glass transition. The mechanical analysis of the composites showed that the PEI and PEKK sizings had a significant influence on the different relaxations. At low temperature, the PEI sizing modified the relaxation with the apparition of two submodes,  $\beta_1$  and  $\beta_2$ ; this brought out the interactions between the fibers, the sizing, and the matrix. The kerosene created a modification of the  $\beta$

relaxation for the PEI-sized CFs composite by increasing the  $\beta_1$  submode; this was probably due to the solvent sensitivity of the PEI. The PEKK sizing showed no influence on the  $\beta$  relaxation. In the viscoelastic zone, the temperature of the  $\alpha$  relaxation was not influenced by the sizings or the kerosene. The study of the dissipated energy highlighted the interaction between the matrix, the sizing, and the CF, which played the role of physical crosslinking. This explained that the PEI- and PEKK-sized composites were inert in kerosene.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of Bpifrance and Conseil Régional Midi Pyrénées through the Innovative Material (INMAT 2) program. They are grateful to J. M. Bergerat from AIRBUS France for helpful discussions and advice during all of the work. They also thank D. Kemmish and A. Wood from Victrex, Inc. (United Kingdom) for relevant comments and fruitful discussions.

## REFERENCES

- Kemmish, D. J.; Hay, J. N. *Polymer* **1985**, *26*, 905.
- Velisaris, C.; Seferis, J. *Polym. Eng. Sci.* **1986**, *26*, 1574.
- Harris, J. E.; Winslow, P. A.; Botkin, J. H.; Maresca, L. M.; Clendinning, R. A.; Cotter, R. J.; Matzner, M.; Kwiatkowski, G. T. *Macromolecules* **1993**, *26*, 2366.
- Tregub, A.; Karger-Kocsis, J.; Könnicke, K.; Zimmermann, H. *J. Macromolecules* **1995**, *28*, 3890.
- Li, W.; Wang, G.; Jiang, Z.; Liu, C.; Huo, P.; Zhang, S. *J. Appl. Polym. Sci.* **2014**, *131*, 40172.
- Schwartz, M.; Lemonnier, S.; Carrado, A.; Vallat, M.-F.; Nardin, M. *J. Appl. Polym. Sci.* **2014**, *131*, 40783.
- Denault, J.; Vu-Khanh, T. *Polym. Compos.* **1992**, *13*, 361.
- Bishop, S. *Compos. Struct.* **1985**, *3*, 295.
- Lin, H.; Lee, R.; Liu, C.; Wu, J.; Huang, C. *Compos. Sci. Technol.* **1994**, *52*, 407.
- Li, T. Q.; Zhang, M. Q.; Zeng, H. M. *Compos. A* **2001**, *32*, 1727.
- Tierney, J. J.; Gillespie, J. W., Jr. *Compos. A* **2004**, *35*, 547.
- Saleem, A.; Frommann, L.; Iqbal, A. *Polym. Compos.* **2007**, *28*, 785.
- Haanappel, S.; Ten Thije, R.; Sachs, U.; Akkerman, R. *Compos. A* **2014**, *56*, 80.
- Ray, D.; Comer, A. J.; Lyons, J.; Obande, W.; Jones, D.; Higgins, R. M. O.; McCarthy, M. A. *J. Appl. Polym. Sci.* **2015**, *132*, 41643.
- Schmitt-Thomas, K.; Yang, Z.; Malke, R. *Compos. Sci. Technol.* **1998**, *58*, 1509.
- Sattari, M.; Molazemhosseini, A.; Naimi-Jamal, M. R.; Khavandi, A. *Mater. Chem. Phys.* **2014**, *147*, 942.
- Zhang, G.; Chang, L.; Schlarb, A. K. *Compos. Sci. Technol.* **2009**, *69*, 1029.
- Sandler, J.; Philipp, W.; Shaffer, M. S. P.; Demchuk, V.; Altstädt, V.; Windle, A. H. *Compos. Part A* **2002**, *33*, 1033.
- Díez-Pascual, A. M.; Naffakh, M.; Gómez, M. A.; Marco, C.; Ellis, G.; Martínez, M. T.; Ansón, A.; González-Domínguez, J. M.; Martínez-Rubi, Y.; Simard, B. *Carbon* **2009**, *47*, 3079.
- Hwang, Y.; Kim, M.; Kim, J. *Compos. A* **2013**, *55*, 195.
- Cortes, L. Q.; Lonjon, A.; Dantras, E.; Lacabanne, C. *J. Non. Cryst. Solids* **2014**, *391*, 106.
- Carponcin, D.; Dantras, E.; Laffont, L.; Dandurand, J.; Aridon, G.; Levallois, F.; Cadiergues, L.; Lacabanne, C. *J. Non. Cryst. Solids* **2014**, *388*, 32.
- Gao, S.-L.; Kim, J.-K. *Compos. A* **2000**, *31*, 517.
- Sharma, M.; Bijwe, J.; Mäder, E.; Kunze, K. *Wear* **2013**, *301*, 735.
- Li, T. Q.; Zhang, M. Q.; Zeng, H. M. *Polymer* **1999**, *40*, 4307.
- Gao, S.-L.; Kim, J.-K. *Compos. A* **2001**, *32*, 775.
- Drzal, L. T.; Rich, M. J.; Koenig, M. F.; Lloyd, P. F. *J. Adhes.* **1983**, *16*, 133.
- Dai, Z.; Shi, F.; Zhang, B.; Li, M.; Zhang, Z. *Appl. Surf. Sci.* **2011**, *257*, 6980.
- Paipetis, A.; Galiotis, C. *Compos. A* **1996**, *27*, 755.
- Dai, Z.; Zhang, B.; Shi, F.; Li, M.; Zhang, Z.; Gu, Y. *Appl. Surf. Sci.* **2011**, *257*, 8457.
- Ren, P.; Liang, G.; Zhang, Z. *Polym. Compos.* **2006**, *27*, 591.
- Mironov, V.; Park, M.; Kim, J.; Lim, S.; Choe, C. *J. Mater. Sci. Lett.* **2001**, *20*, 1211.
- Dilsiz, N.; Wightman, J. P. *Carbon* **1999**, *37*, 1105.
- Guan, R.; Yang, Y.; Zheng, J.; He, F. *Fiber Compos.* **2002**, *1*, 23.
- Giraud, I.; Bergerat, J. M.; Dantras, E.; Perez, E.; Lacabanne, C. [To (Airbus) Operation, Centre National de la Recherche Scientifique (CNRS).] U.S. Pat. 20113 (2011).
- Giraud, I.; Franceschi-Messant, S.; Perez, E.; Lacabanne, C.; Dantras, E. *Appl. Surf. Sci.* **2013**, *266*, 94.
- Fernandez, B.; Arbelaiz, A.; Valea, A.; Mujika, F.; Mondragon, I. *Polym. Compos.* **2004**, *25*, 319.
- Hughes, J. D. H. *Comp. Sci. Technol.* **1991**, *41*, 13.
- Stober, E. J.; Seferis, J. C.; Keenan, J. D. *Polymer* **1984**, *25*, 1845.
- Sasuga, T.; Hagiwara, M. *Polymer* **1985**, *26*, 501.
- Sasuga, T.; Hagiwara, M. *Polymer* **1986**, *27*, 821.
- Wu, Z.; Zheng, Y. B.; Ni, Z.; Nakamura, T.; Yosomiya, R. *Angew. Makromol. Chem.* **1988**, *164*, 103.
- Mourgues-Martin, M.; Bernès, A.; Lacabanne, C. *Thermochim. Acta* **1993**, *226*, 7.
- David, L.; Etienne, S. *Macromolecules* **1992**, *25*, 4302.
- David, L.; Girard, C.; Dolmazon, R.; Albrand, M.; Etienne, S. *Macromolecules* **1996**, *29*, 8343.
- Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, **1970**; p 433.