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Adsorption of phenylalanine-rich sequence-defined oligomers onto Kevlar fibers for fiber-reinforced polyolefin composite materials

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ABSTRACT

Oligomers comprising four or sixteen phenylalanine residues with regularly intercalated aliphatic chains of different lengths prepared by solid-phase synthesis exhibit sufficient thermal stability to be used as interfacial agents and processed for the preparation of poly(propylene-co-ethylene)-based composite materials. The investigation of their adsorption on Kevlar fibers by SEM is difficult due to the surface heterogeneity of the bare Kevlar fibers. However, oligomers with four successive phenylalanine residues have been clearly observed suggesting their better adsorption on the fiber. The quantification of those oligomers adsorbed on the fibers performed gravimetrically on pellets of fibers has however revealed no significant impact of the length of the aliphatic chain.

KEYWORDS: Adsorption, phenylalanine, Kevlar fibers, interfacial agent, sequence-defined oligomer

1. INTRODUCTION

As recently highlighted, the future of polymer science requires the development of new generations of high-performance polymers as well as the rejuvenation of classical polymer materials.[1] Fiber-reinforced thermoplastic composite materials (FRTCM) are widely used in a large number of applications including civil engineering,[2, 3] aircraft,[4] and automotive[5, 6] industry. The growing interest for FRTCM, commonly using glass[7] and carbon[8] fibers, is driven by the substitution of metal components to develop materials having similar or higher performances compared to traditional materials like steel and aluminum. The main advantages of FRTCM are their higher strength-to-weight ratio used to decrease the weight of vehicles and thus fuel consumption and CO₂ production, their higher resistance to corrosion,

and the ability to tune the performances according to their composition and design. Para-aramid fibers provides lightweight, strength superior to steel, and high impact and abrasion resistance. While its tensile strength (3.6 GPa) and tensile modulus (131 GPa) are similar or superior to those of glass fibers (3.4 and 72 GPa respectively), but inferior to those of carbon fibers (4.1 and 242 GPa respectively),[9] its density is lower (1.4 g cm^{-3} as compared to 2.5 and 1.8 g cm^{-3} for glass and carbon fibers respectively) electing Kevlar fibers as a competitor to carbon fibers and showing superiority to glass fibers in terms of strength-to-weight ratio.

FRTCM involves fibers as reinforcement constituents embedded in a polymer matrix such as polypropylene that hold the reinforcement constituents together. The proper control of the interface between the fibers and matrix and thus the mechanism of interfacial adhesion are beneficial to reach FRTCM with improved structural integrity and mechanical properties.[10] Various approaches focused on the surface treatment of fibers have been developed to optimize the adhesion at the fiber-matrix interface through either chemical etching to induce fiber surface roughening or chemical modification to introduce functional groups at the fiber surface. In the case of Kevlar fibers, chemical etching has been conducted using different strategies such as bromination,[11] chlorosulfonation,[12, 13] and plasma treatment,[13-15] while amine,[16] alkoxy silane,[17] alkyl,[18] and phosphoric acid[19] groups have been inserted at the surface of Kevlar fibers.

In the field of polymer blends, a common approach is the compatibilization by addition. Various types of additives have been investigated including copolymers[20] and Janus particles.[21] These materials are tailored to have sections compatible to those of the polymers composing the blend through specific interactions such as hydrogen bond and dipole-dipole interactions.[22] The compatibilizer should place itself at the interface of the incompatible polymers modifying the molecular structure of the interface and reducing the interfacial tension for a better stabilization of the polymer blend morphology and interfacial adhesion. Examples of this approach applied to Kevlar fiber-reinforced thermoplastic composite materials are sparser focusing generally on the use of maleic anhydride-grafted polyolefins, a reactive compatibilizer, and combined in some cases to surface-modified Kevlar fibers, leading to improved tensile strength and modulus of the composite materials.[23-26]

It has been shown in recent years that sequence-defined oligomers open up interesting new avenues in materials science;[27-30] in particular for blends and composites compatibilization.[31] The group of Simmons has recently demonstrated by molecular dynamics simulations that the use of copolymers with specific sequences as interfacial agents in polymer blends can better reduce interfacial energy than block or random copolymers.[32] Furthermore, the group of Börner has identified peptide-polymer conjugates

with specific peptide sequences able to act as interfacial agents for poly(ethylene oxide)/magnesium fluoride nanoparticle composite materials.[33, 34] As the sequence of the repeat units constituting the interfacial agent has been identified as **beneficial** in the improvement of the interfacial adhesion in FRTCM, sequence-defined interfacial agents for Kevlar fiber-reinforced polyolefin composite materials have been designed considering as repeat units phenylalanine to interact with Kevlar fibers through π - π interaction and hydrogen bond, and alkyl chains to be compatible with the polyolefin (*i.e.* poly(propylene-co-ethylene)) matrix using an iterative synthesis on a solid support.[35] Herein, a library of sequence-defined oligomers (**Figure 1**) were prepared and deposited on Kevlar fibers by dip coating technique to investigate the effect of the number of successive phenylalanine units and the length of the alkyl chains on the coating integrity and quantity adsorbed on the fibers. A comparative study was conducted with model molecules in the attempt to understand which parameters drive the adhesion between Kevlar fibers and the polyolefin matrix.

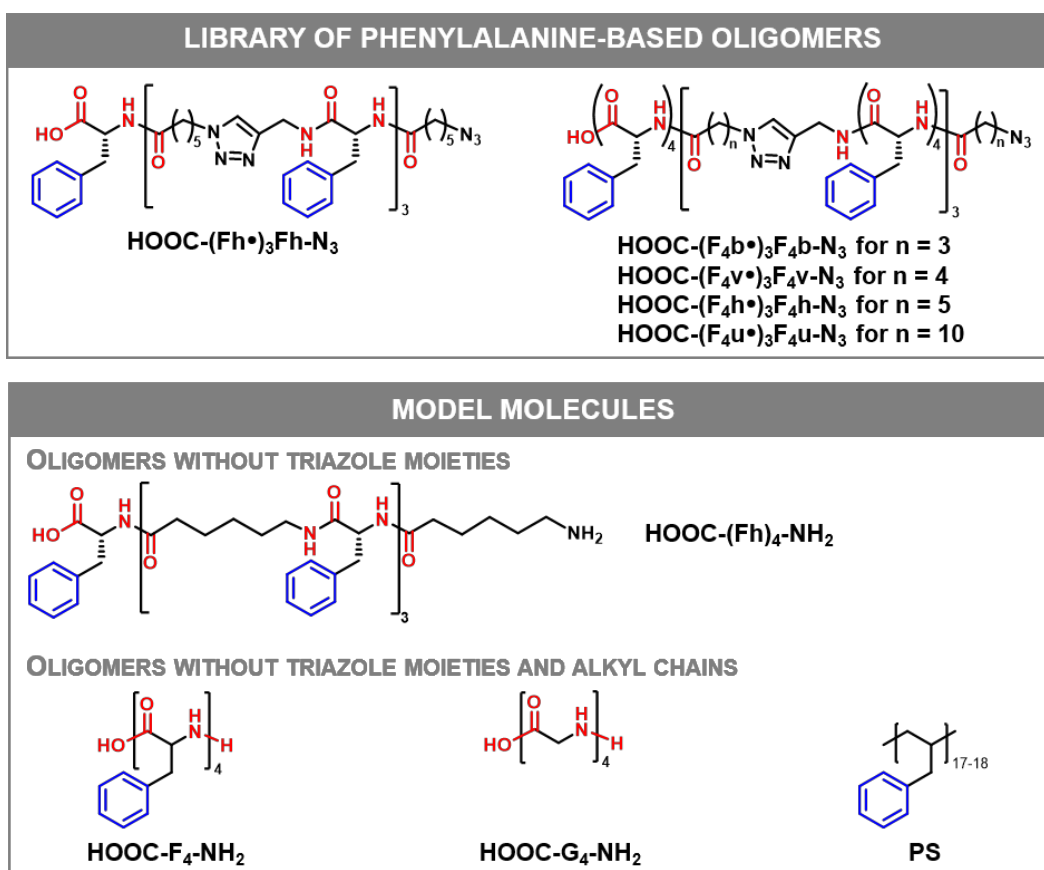


Figure 1. Library of phenylalanine-based oligomers synthesized and model molecules considered in this study as compatibilizers of Kevlar-reinforced composite polyolefin composite materials. The functional groups involved in hydrogen bond and π - π interactions are indicated in red and blue respectively.

2. RESULTS AND DISCUSSION

2.1. Synthesis and thermal characterization of phenylalanine-based oligomers

The oligomer $\text{HOOC}-(\text{Fh}\bullet)_3\text{Fh}-\text{N}_3$, where F stands for the phenylalanine unit, h the hexyl chain and \bullet for the triazole group, was prepared by performing four repeating cycles by successive addition of Fmoc-L-Phe-OH (followed by Fmoc removal), 6-azidohexanoic acid, and propargyl amine on a 2-chlorotrityl chloride resin as previously reported.[35] The library of oligomers was first extended to evaluate the influence of the presence of four successive phenylalanine units per repeating cycles affording $\text{HOOC}-(\text{F}_4\text{h}\bullet)_3\text{F}_4\text{h}-\text{N}_3$. Due to difficulties in synthesis, the 2-chlorotrityl chloride resin was replaced by Tentagel[®]-S-PHB prefunctionalized with Fmoc-Phe-OH with a low loading in phenylalanine (0.24 mmol per gram of resin), and the solvent used for the addition of Fmoc-Phe-OH and 6-azidohexanoic acid by a mixture of solvent consisting in dichloromethane, *N,N*-dimethylformamide, and 1-methyl-2-pyrrolidinone in equivolumes. Similarly, $\text{HOOC}-(\text{F}_4\text{b}\bullet)_3\text{F}_4\text{b}-\text{N}_3$, $\text{HOOC}-(\text{F}_4\text{v}\bullet)_3\text{F}_4\text{v}-\text{N}_3$, and $\text{HOOC}-(\text{F}_4\text{u}\bullet)_3\text{F}_4\text{u}-\text{N}_3$ were prepared to study the effect of the length of the alkyl chain by replacing 6-azidohexanoic acid (h) by 4-azidobutyric acid (b), 5-azidovaleric acid (v), and 11-azidoundecanoic acid (u) respectively. The oligomers were characterized by NMR spectroscopy and MALDI-ToF mass spectrometry (ESI, Figure S2-S5). Both characterization techniques indicated the presence of oligomers with deleted sequences (*i.e.* oligomers obtained with incomplete reaction steps) and PEG (*i.e.* PEG leakage due to acidic hydrolysis of ester linkage between PEG and polystyrene composing the Tentagel resin). The observation of the molecular peak of the oligomers was arduous due to the difficulty to ionize them. Due to their limited solubilities in common solvents and requiring the addition of a relatively large amount of acids (*i.e.* at least 5 vol%), their purification by standard techniques, *e.g.* high-performance liquid chromatography, could not be achieved and the oligomers were used without further purification.

The preparation of composite materials requires working at a temperature above the melting temperature of the polymer matrix. As poly(propylene-*co*-ethylene) was aimed as polymer matrix and its melting temperature is 137 °C, the working temperature to process the composite material was expected to be at least 167 °C. Thus, the molecules to be used as interfacial agents should not thermally degrade at or below this temperature. The thermal stability of the oligomers synthesized was studied by thermogravimetric analysis. $\text{HOOC}-(\text{Fh}\bullet)_3\text{Fh}-\text{N}_3$ was previously investigated showing at 167 °C a cumulative weight loss of 7 wt% attributed to the loss of the terminal groups,[35] while the other oligomers (*i.e.* $\text{HOOC}-(\text{F}_4\text{b}\bullet)_3\text{F}_4\text{b}-\text{N}_3$, $\text{HOOC}-(\text{F}_4\text{v}\bullet)_3\text{F}_4\text{v}-\text{N}_3$, $\text{HOOC}-(\text{F}_4\text{h}\bullet)_3\text{F}_4\text{h}-\text{N}_3$, and $\text{HOOC}-(\text{F}_4\text{u}\bullet)_3\text{F}_4\text{u}-\text{N}_3$) showed an initial degradation temperature between 214 and 230 °C (ESI, Figure S6). The inobservance of

earlier degradation for these oligomers could be attributed to their higher molecular weight and thus a contribution of the terminal groups corresponding to 2 wt% that may be difficult to detect.

2.2. Adsorption of interfacial agents on Kevlar fibers

Dip coating is a simple and widely used technique to deposit a substance dissolved in a solution onto a substrate as a film at its surface.[36] The deposition of the synthesized interfacial agents onto Kevlar fibers was considered through dip coating individual Kevlar fibers in 95/5 acetonitrile (ACN)/trifluoroacetic acid (TFA) solutions at a concentration of 1 mM of interfacial agent. After being air-dried overnight, the fibers were analyzed by SEM (**Figures 2-3**). For all the interfacial agents considered, the coating integrity on the fibers was low showing heterogeneous deposition as depicted for HOOC-(Fh•)₃Fh-N₃ in **Figure 2**. The adsorption of the oligomer on Kevlar was attempted to be further characterized by energy dispersive X-ray spectroscopy (EDS). However, the close chemical composition of the oligomers and Kevlar fibers (**ESI, Table S1**) and the effect of the nature of these samples (curved surface, heterogeneity of the coating, etc.) on the accuracy to determine the composition limited the possibility to discriminate precisely the oligomers from Kevlar fibers. For these reasons, the adsorption of all the oligomers on Kevlar fibers was thus conducted qualitatively and quantitatively by SEM and gravimetric analysis respectively.

To estimate the contribution of the triazole moiety through hydrogen bond and dipole-dipole interactions,[37] HOOC-(Fh)₄-N₃ was considered. No significant difference in the coating formation was observed between HOOC-(Fh•)₃Fh-N₃ and HOOC-(Fh)₄-N₃ indicating no significant influence of the triazole group on their adsorption on Kevlar fibers. Furthermore, as phenylalanine is expected to adsorb on Kevlar fibers thanks to potential π - π interactions and hydrogen bond, the relevance of the choice of phenylalanine as anchoring unit to promote the adsorption of the oligomers on Kevlar fibers was evaluated. The contribution of these interactions was investigated using oligostyrene (PS, possessing solely π - π interactions, solubilized in toluene instead of 95/5 ACN/TFA), tetraglycine (HOOC-G₄-NH₂, involving hydrogen bond), and tetraphenylalanine (HOOC-F₄-NH₂, combining π - π interactions and hydrogen bond). The fibers dipped in the solution of PS showed patches of coating on the fibers. The dewetting phenomenon observed (even more pronounced after six months after the deposition on the fiber, **ESI, Figure S7**) could be attributed to low interactions between PS and the fibers. The presence of HOOC-G₄-NH₂ deposited on Kevlar fibers was difficult to detect. The distinction between the bare Kevlar fibers and the fibers coated with HOOC-G₄-NH₂ was complexified by the inhomogeneity observed at the surface of bare Kevlar fibers (**ESI, Figure S8**) that may be due to some remaining finish on the fibers besides the treatment performed by the supplier. If HOOC-G₄-NH₂ was present on the fiber, the coating seemed to be thin and relatively smooth. The fibers treated with HOOC-F₄-NH₂ exhibited the presence of a coating

that seemed to be more prominent as compared to HOOC-G₄-NH₂ and more homogeneous than when PS was used. These experiments emphasize the need of the combined contribution of π - π and hydrogen bond interactions provided by phenylalanine residues for the adsorption of interfacial agents on Kevlar fibers.

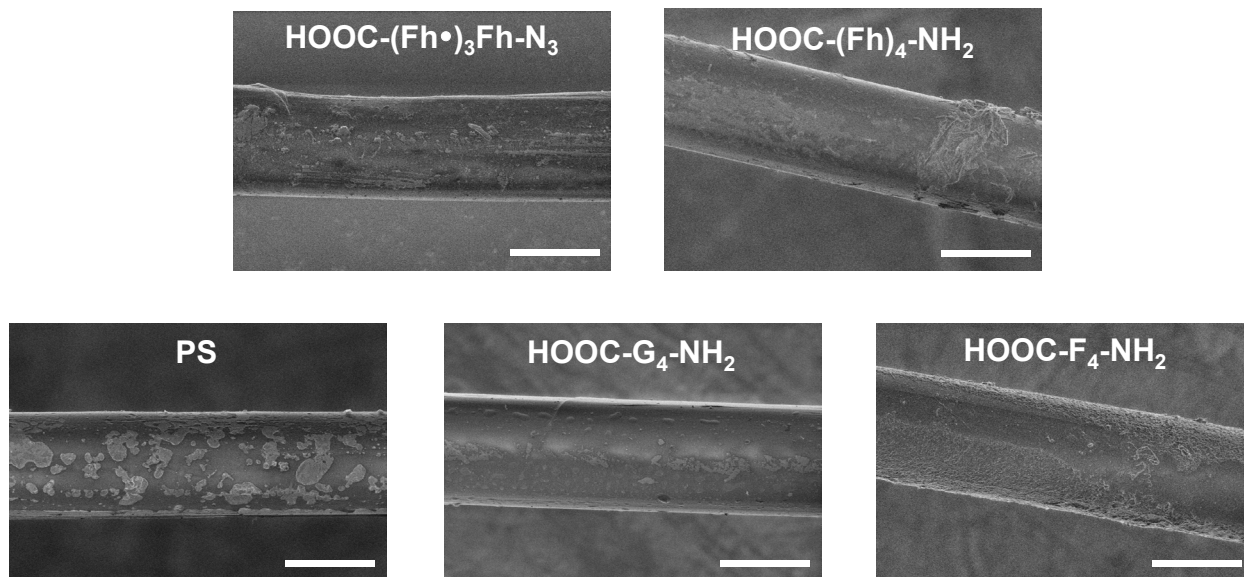


Figure 2. SEM images (scale bar = 10 μm) of one single Kevlar fiber treated by dip coating ($1 \mu\text{mol mL}^{-1}$ of interfacial agent in 95/5 ACN/TFA) with oligomer HOOC-(Fh•)₃Fh-N₃ in comparison to treatment conducted with HOOC-(Fh)₄-NH₂, PS, HOOC-G₄-NH₂, and HOOC-F₄-NH₂.

The structure of the oligomers synthesized was further tuned by first increasing the number successive phenylalanine units on the oligomer. HOOC-(F₄h•)₃F₄h-N₃ (*i.e.* oligomers with four successive phenylalanine units per repeating cycle) was deposited on Kevlar fibers by dip coating showing a more prominent presence on the fibers emphasized by the cracks observed on the coating that was relatively homogeneous (Figure 3). The influence of the length of the alkyl chains was then investigated using oligomers with spacing units comprising three, four, five, and ten methylenes (HOOC-(F₄b•)₃F₄b-N₃, HOOC-(F₄v•)₃F₄v-N₃, HOOC-(F₄h•)₃F₄h-N₃, HOOC-(F₄u•)₃F₄u-N₃ respectively). Among these oligomers, the fibers coated with HOOC-(F₄v•)₃F₄v-N₃ exhibited the roughest and thickest coating at the surface of Kevlar fibers (**Figure 3**). The roughness of the coating may be advantageous when embedding the fibers in the polymer matrix. The interfacial adhesion between the fiber and the polymer matrix may be enhanced acting as nucleating agents for the crystallization of the polymer matrix in the close proximity of the fiber.[38] The fibers treated with HOOC-(F₄v•)₃F₄v-N₃ were characterized again by SEM after six months to evaluate their stability: some fibers remained visually unchanged, while others exhibited some delamination (**ESI, Figure S9**).

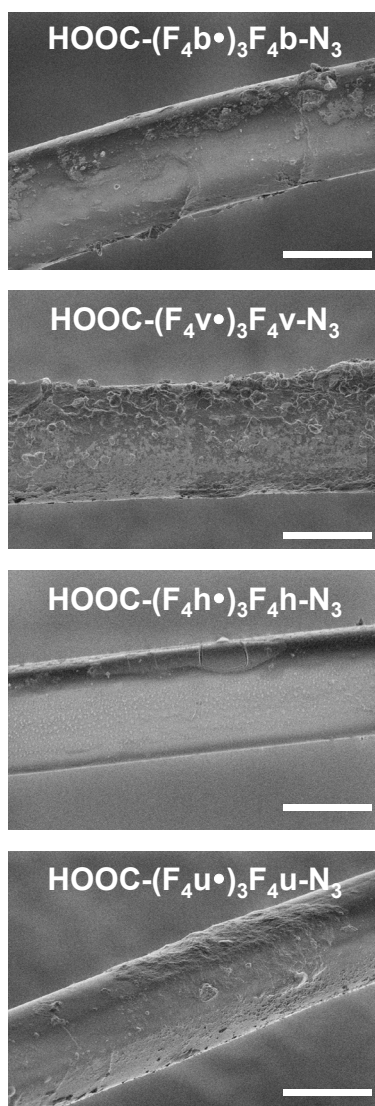


Figure 3. SEM images (scale bar = 10 μm) of one single Kevlar fiber treated by dip coating ($1 \mu\text{mol mL}^{-1}$ of interfacial agent in 95/5 ACN/TFA) with oligomers having spacing units of various lengths: HOOC-(F₄b•)₃F₄b-N₃, HOOC-(F₄v•)₃F₄v-N₃, HOOC-(F₄h•)₃F₄h-N₃, and HOOC-(F₄u•)₃F₄u-N₃.

2.3. Quantification of interfacial agents deposited onto Kevlar fibers

The previously prepared fibers were not suitable for gravimetric quantification due to the weight of one Kevlar fiber (*i.e.* approximately 9 μg per fiber having a length of 5 cm). Kevlar fiber pellets were thus prepared by placing approximately 75 mg of fibers (*i.e.* corresponding to an estimated number of 8000 fibers) in a stainless-steel crucible and compressing them using a hydraulic press. The pellets obtained had a diameter of 13.37 ± 0.13 mm and a height of 1.15 ± 0.03 mm (ESI, Figure S10 and Table S2). These pellets were then immersed in a solution containing one of the synthesized oligomers. The deposition of the interfacial agent onto the fibers constituting the pellets was confirmed by SEM as illustrated on

Figure 4 using HOOC-(F₄u•)₃F₄u-N₃. The pellets exhibited loose and flattened areas with a smooth coverage of the interfacial agent deposited at the surface of the Kevlar fibers.

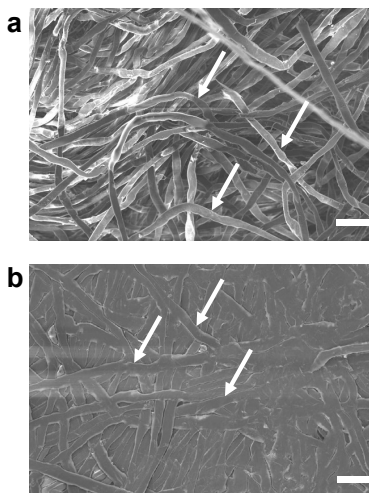


Figure 4. SEM images of fiber pellets that have been submerged in a solution of HOOC-(F₄u•)₃F₄u-N₃ (1 μmol mL⁻¹ of interfacial agent in 95/5 ACN/TFA) highlighting a) loose and b) flattened areas. The white bars represent 100 μm. White arrows are highlighting three of the Kevlar fibers.

The quantification was conducted by weighing these pellets before and after immersing them into a solution for 5 min and then letting them air dry overnight. As control, pellets were treated with the solvent (*i.e.* 95/5 ACN/TFA) using this protocol permitting to determine the amount of residual solvent present in the pellets. The amount of solvent per pellet was estimated as 0.41 mg (ESI, Table S3), value used for correction in the quantification study to determine the amount of oligomer deposited on the fibers. The pellets in triplicate were also treated with one of the synthesized oligomers having sixteen phenylalanine residues (*i.e.* HOOC-(F₄b•)₃F₄b-N₃, HOOC-(F₄v•)₃F₄v-N₃, HOOC-(F₄h•)₃F₄h-N₃, HOOC-(F₄u•)₃F₄u-N₃) by immersion in a solution of oligomer at a concentration of 1 mM in 95/5 ACN/TFA. The number of moles of oligomer adsorbed on the fibers was determined by gravimetry (Table 1). The results for the pellets treated with the oligomers were relatively consistent. The average value of the number of moles of oligomers adsorbed per gram of fibers was similar for these oligomers ranging from 3.84 to 5.21 μmol g⁻¹ without any identified trend associated to the length of the spacing unit. However, it seemed that the rougher surface of HOOC-(F₄v•)₃F₄v-N₃ might be associated to higher adsorption density in the oligomer.

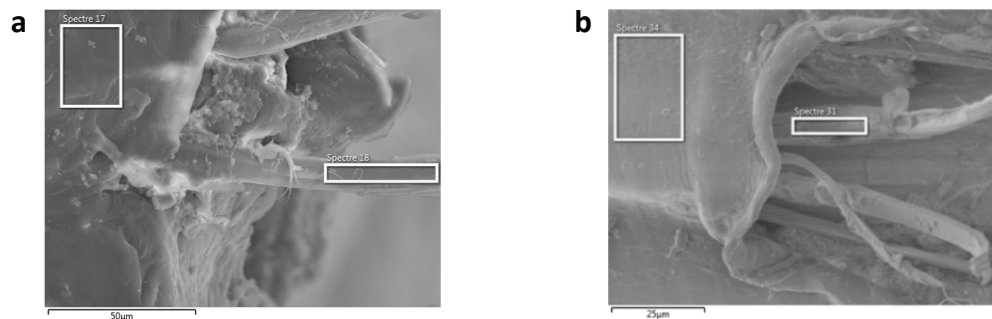
Table 1: Quantification of the amount of oligomer deposited on Kevlar fiber pellets after immersion in a solution of oligomer at a concentration of 1 mM in 95/5 ACN/TFA for 5 min and air-drying overnight.

oligomer	$m_{\text{oligomer}}^{\text{a}}$ (mg)	$m_{\text{pellet}}^{\text{b}}$ (mg)	m_{f}^{c} (mg)	adsorption density ^d ($\mu\text{mol g}^{-1}$)	
				individual pellet	average
HOOC-(F ₄ b●) ₃ F ₄ b-N ₃	5.99	74.52	75.81	3.96	4.46 ± 0.71
	6.03	74.48	76.06	5.27	
	6.02	74.47	75.80	4.15	
HOOC-(F ₄ v●) ₃ F ₄ v-N ₃	6.14	74.25	75.81	5.10	5.21 ± 0.89
	6.09	74.45	76.25	6.15	
	6.08	74.59	75.99	4.37	
HOOC-(F ₄ h●) ₃ F ₄ h-N ₃	6.24	74.07	75.36	3.84	3.84 ± 0.34
	6.20	74.36	75.73	4.18	
	6.18	74.56	75.78	3.51	
HOOC-(F ₄ u●) ₃ F ₄ u-N ₃	6.80	74.68	76.26	4.64	4.84 ± 0.21
	6.76	74.50	76.18	5.05	
	6.81	74.26	75.88	4.83	

^a mass of oligomer dissolved in 2 mL of 95/5 ACN/TFA, ^b weight of the Kevlar fiber pellet before treatment, ^c weight of the Kevlar fiber pellet after immersion and drying, ^d number of moles of oligomer adsorbed per gram of Kevlar fibers (adsorption density = $(m_{\text{f}} - m_{\text{pellet}} - 0.41 \text{ mg}) / (M_{\text{oligomer}} \cdot m_{\text{pellet}})$)

2.4. Preliminary investigation of the composite material

Preliminary investigations on fiber-reinforced composite materials were conducted with bare Kevlar fibers and fibers treated with HOOC-(F₄v●)₃F₄v-N₃. After embedding the fibers in a matrix of poly(propylene-co-ethylene) upon thermal treatment at 180 °C, the composite materials were investigated by fracture test. The fragments were analyzed by EDS selecting for each sample at least one spot on the matrix and one on the fiber (**Figure 5**). The results seem to suggest an enrichment of the presence in matrix on the fiber when the interfacial agent was used.



	%C	%N	%O
Calculated values			
Poly(propylene-co-ethylene) (PP-co-PE) matrix	100	0	0
Kevlar fibers	78	11	11
Experimental values			
<i>Composite material without interfacial agent (image a)</i>			
PP-co-PE matrix (spectre 17)	98	0	2
Fiber (spectre 18)	76	11	13
<i>Composite material with HOOC-(F₄v●)₃F₄v-N₃ (image b)</i>			
PP-co-PE matrix (spectre 34)	95	0	5
Fiber (spectre 31)	89	4	7

Figure 5. SEM images and EDS data of Kevlar-reinforced composite material with a poly(propylene-co-ethylene) matrix a) without adding an interfacial agent and b) upon treatment of the fiber with HOOC-(F₄v●)₃F₄v-N₃. The white rectangles are highlighting the spot analyzed by EDS, for which the experimental values are reported in the table.

3. CONCLUSION

Oligomers based on phenylalanine have been designed as potential candidates as interfacial agents for Kevlar fiber-reinforced polyolefin composite materials. The evaluation of their adsorption on Kevlar fibers has been evaluated visually by SEM on individual fibers and gravimetrically on pellets of fibers. While the use of a larger number of successive phenylalanine residues on the oligomers increased the adsorption of the oligomer on Kevlar fibers, the length of the aliphatic chains did not seem to have a notable influence. This work is the first step in determining the potential of these oligomers by evaluating their adsorption, however it will be also essential to further study their interaction with the polymer matrix to validate their potential as interfacial agents for fiber-reinforced composite materials.

4. EXPERIMENTAL

4.1. Materials

Sodium azide (NaN₃, 99 %), 6-bromohexanoic acid (>98%), 5-bromovaleric acid (97%), 4-bromobutyric acid (97%), piperidine (99%), phenol (>99%), copper(I) bromide (CuBr, 98%) and 1-methyl-2-pyrrolidinone

(NMP, 99%) were purchased from Alfa Aesar. 11-Bromoundecanoic acid (>98%), *N*-ethyl-diisopropylamine (DIPEA, 99%), propargylamine (>95%), acetyl chloride (98%) were purchased from TCI. 1-Hydroxybenzotriazole hydrate (HOBT, >97%), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99%), dimethylsulfoxide (DMSO, 99.9%), thionyl chloride (99.9%), trifluoroacetic acid (TFA, 99%), potassium cyanide (ACS reagent, 97%), anhydrous dichloromethane (>99.8%), triisopropylsilane (TIPS, 99%), ninhydrin (99%), and α -cyano-4-hydroxycinnamic acid (matrix substance for MALDI-MS, $\geq 99.0\%$) were purchased from Sigma-Aldrich. 2-(1H-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU, 99%) and Fmoc-L-Phe-OH (>99%) were purchased from Iris Biotech GmbH. Methyl-4-bromobutyrate (>98%) was purchased from Acros Organics. *N,N*-Dimethylformamide (DMF, 99.5%), methanol (99.9%), toluene (99.9%), acetonitrile (ACN, 99.9%) and acetone (99.9%) were purchased from Fisher chemicals. Diethyl ether (>99.5% pure grade, stabilized with BHT 5-7 ppm) was purchased from Carlo Erba Reagents. Tentagel[®] S PHB resin functionalized with a protected phenylalanine residue (Fmoc-Phe-Tentagel[®] S PHB resin) with a loading density in phenylalanine of 0.24 mmol per gram of resin was purchased from Rapp Polymere. CupriSorb[™] (Seachem[®]) was bought from Recif at home. All the reagents were used as received except if otherwise noted. Copper(I) bromide was purified by stirring in acetic acid overnight, washing with methanol, and drying under vacuum at room temperature.

All the syntheses on solid support were performed in solid phase extraction (SPE) tubes (60 mL polypropylene tubes with polyethylene frits, 20 μ m porosity, SUPELCO[®] purchased from Sigma-Aldrich) and shaken using a modified IKA KS 130 basic shaker.

4-Azidobutyric acid[39] (b), 5-azidovaleric acid[40] (v), and 6-azidohexanoic acid[41] (h) were synthesized as previously reported.

Tetraglycine (HOOC-G₄-NH₂, >99.9%) and tetraphenylalanine (HOOC-F₄-NH₂, >97%) were purchased from Bachem. Polystyrene standard (PS) having an average number-molecular weight (M_n) of 2100 g mol⁻¹ (\mathcal{D} = 1.05) was purchased from PSS-Polymer. HOOC-(Fh)₄-NH₂ (>90%) was purchased from Laboratoire Altergen. HOOC-(Fh•)₃Fh-N₃ was synthesized as previously reported.[35] Kevlar[®] short fiber aramid (SFA A) fibers, having an average length of 50 mm and diameter of 12 μ m and pre-treated by the supplier to remove the finish present at their surface, were received as a sample from DuPont de Nemours S.A. Aceso[®] Lumicene[®] MR10MM0 (random copolymer of propylene and ethylene) was obtained from Total.

4.2. Characterization

Nuclear magnetic resonance (NMR) spectra were recorded in DMSO-*d*₆ on a Bruker Avance I 400 MHz spectrometer equipped with an Ultrashield[™] magnet.

Mass measurements were carried out on an Autoflex™ MALDI-TOF mass spectrometer (Bruker Daltonics GmbH, Bremen, Germany). This instrument was used at a maximum accelerating potential of 20 kV in positive mode and was operated in mode reflector at 19 kV. The delay extraction was fixed at 80 ns and the frequency of the laser (nitrogen 337 nm) was set at 5 Hz. The acquisition mass range was set to 400-4000 m/z with a matrix suppression deflection (cut off) set to 500 m/z. The equipment was externally calibrated with a standard peptide calibration mixture that contained seven peptides (Bruker Peptide Calibration Standard #206196, Bruker Daltonics GmbH, Bremen, Germany) covering the 1000-3200 m/z range. Each raw spectrum was opened with flexAnalysis 2.4 build 11 (Bruker Daltonics GmbH, Bremen, Germany) software and processed using the following parameters: signal-to-noise threshold of 1, Savitzky-Golay algorithm for smoothing, median algorithm for baseline subtraction, and SNAP algorithm for monoisotopic peak detection and labelling in reflectron mode. In all cases, resolution was higher than 9000. Sample preparation was performed with the dried droplet method using a mixture of 0.5 µL of sample with 0.5 µL of matrix solution dry at room temperature. The matrix solution was prepared from a saturated solution of α -cyano-4-hydroxycinnamic acid in water/acetonitrile 50/50 diluted three times in water/acetonitrile/trifluoroacetic acid 50/49.9/0.1. The sample solution was prepared by dissolving ~5 mg of oligomer in 1 mL of a solution of concentrated HCl in tetrahydrofuran (1/9).

Thermogravimetric analyses (TGA) were performed on a Mettler-Toledo TGA2 thermogravimeter at a heating scan rate of 50 °C min⁻¹ using alumina crucibles using an atmosphere of N₂ (gas flow rate: 100 mL min⁻¹). The TGA curves were recorded from 50 °C to 850 °C. The temperature of the onset of degradation (T_{d, onset}) was determined as the crossing point of the tangents of the first weight loss observed on each TGA curve.

Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vertex 70 spectrometer using the attenuated total reflectance (ATR) technique.

Energy dispersive X-ray spectroscopy (EDS) measurements were performed on a JEOL JSM6490LV microscope (max resolution 3 nm) equipped with an Oxford instruments AZTEC (lateral resolution 200 nm) EDS module at 5 keV with a spot size of 62 and measuring time of 60 s. The average atomic composition and standard deviation were determined on nine measurements.

For quantification experiments, all weights were recorded on a vibration-stabilized Mettler-Toledo AX 205 analytical balance located in an air-conditioned room.

4.3. Synthesis of 11-azidoundecanoic acid (u)

The synthesis of 11-azidoundecanoic acid was adapted from the protocol used to prepare 6-azidohexanoic acid.[41] Briefly, 11-bromoundecanoic acid (28 g, 106 mmol) and sodium azide (17 g, 264 mmol) were

added to a solution of 100 mL of acetone (100 mL) and 200 mL of reverse-osmosed water in a round bottom flask. The solution was stirred in an oil bath thermostated at 60 °C for 5 h. The reaction mixture was then cooled in an ice bath to 0 °C and acidified with concentrated HCl until pH 2 was reached. The mixture was then extracted with ethyl acetate three times. The organic layers were combined, washed with brine, dried over anhydrous sodium sulphate, concentrated by rotary evaporation and dried overnight under vacuum. The final product was obtained as an off-white solid (23 g, 96 %).

^1H NMR: δ (CDCl_3 , 7.26 ppm) 11.28 (bs, 1H), 3.24 (t, 2H), 2.34 (t, 2H), 1.53-1.68 (m, 4H), 1.21-1.43 (m, 12H). ^{13}C NMR: δ (CDCl_3 , 77.16 ppm) 180.54, 51.51, 34.14, 29.43, 29.34, 29.22, 29.15, 29.06, 28.87, 26.74, 24.68. FT-IR (ATR): 2091 cm^{-1} (azide).

Caution: Organic azides are potentially explosive substances. Routine precautions were taken to minimize the effect of possible explosions at all stages in the preparation and handling of any ω -azidoalkanoic acids. These compounds are stored in the fridge.

4.4. Synthesis of oligomers $\text{HOOC-(Fx}_4\bullet)_3\text{Fx}_4\text{-N}_3$

The oligomers were prepared using the Fmoc-Phe-Tentagel[®] S PHB resin by adding iteratively the different building blocks using the protocol described below illustrated for oligomers with a hexyl linker (h).

i) Resin deprotection. 3 g of Fmoc-Phe-Tentagel[®] S PHB resin (0.72 mmol of functional groups) was weighted in a SPE tube, swollen in 10 mL of CH_2Cl_2 for 10 min and washed three times with 10 mL of CH_2Cl_2 . The Fmoc-protecting groups were removed by agitation for 3 min with 10 mL of a 25% piperidine solution in DMF followed by filtration and agitation with a fresh cleavage solution for 20 min. The resin was then washed six times with 10 mL of DMF and six times with 10 mL of CH_2Cl_2 .

ii) Addition of 6-azidohexanoic acid. 6-Azidohexanoic acid (0.35 g, 2.19 mmol), HBTU (0.83 g, 2.18 mmol), HOBT (0.29 g, 2.17 mmol), DIPEA (0.70 mL, 4.05 mmol) and a 1/1/1 mixture of CH_2Cl_2 /DMF/NMP (10 mL) were added to the vessel and agitated for 1 h. After filtration, the resin was washed six times with 10 mL of DMF and six times with 10 mL of CH_2Cl_2 . The completion of this step was monitored using the Kaiser test[42] that should be negative (yellow solution), and a measurement by FT-IR spectroscopy that should show an absorbance band at 2100 cm^{-1} characteristic of the asymmetric stretching vibration of azide groups. If the tests indicate an incomplete reaction, this step was repeated.

iii) Copper-assisted alkyne-azide cycloaddition with propargylamine. CuBr (27 mg, 0.19 mmol) was added to the vessel, which was then degassed through three vacuum/argon cycles. Anhydrous CH_2Cl_2 (10 mL) were added to the vessel, followed by PMDETA (0.07 mL, 0.34 mmol) and propargylamine (0.14 mL, 2.23 mmol). The solution was agitated under argon for 1 h. After filtration, the resin was washed six times with 10 mL of DMF and six times with 10 mL of CH_2Cl_2 . The completion of this step was monitored by FTIR

spectroscopy that should show the disappearance of the absorbance band at 2100 cm^{-1} characteristic of the asymmetric stretching vibration of azide groups. If the test indicates an incomplete reaction, this step was repeated.

iv) Addition of Fmoc-L-Phe-OH. Fmoc-L-Phe-OH (0.84 g, 2.19 mmol), HBTU (0.83 g, 2.18 mmol), HOBT (0.29 g, 2.17 mmol), DIPEA (0.70 mL, 4.05 mmol) and a 1/1/1 mixture of $\text{CH}_2\text{Cl}_2/\text{DMF}/\text{NMP}$ (10 mL) were added to the peptide vessel, and agitated for 1 h. After filtration, the resin was washed six times with 10 mL of DMF. The completion of this step was monitored using the Kaiser test that should be negative (yellow solution). If the test indicates an incomplete reaction, this step was repeated. The Fmoc-protecting group was removed by agitation with 10 mL of a 25% piperidine in DMF solution for 3 min followed by filtration and agitation with a fresh solution of piperidine for 20 min. The resin was then washed six times with 10 mL of DMF and six times with 10 mL of CH_2Cl_2 .

v) Cleavage from the resin and isolation of the phenylalanine-based macromolecule. The resin was washed twelve times with 10 mL of CH_2Cl_2 before transferring the resin to a round-bottom flask and adding the cleavage solution (10 mL of 95/2.5/2.5 TFA/TIPS/ H_2O) to the flask. The resin was agitated with the cleavage solution for 2 h and collected in a clean round-bottom flask. These tasks were performed three times. The resin was then washed six times with 10 mL of CH_2Cl_2 . The filtrates were combined, stirred with CupriSorb™ overnight to remove residual copper, concentrated into a viscous solution by rotary evaporation and precipitated in diethyl ether to remove TFA and TIPS followed by precipitation in reverse-osmosed water. Aggregates of oligomers were crushed to obtain a finely dispersed powder, which was washed six times with 10 mL of reverse-osmosed water. The product was then frozen in liquid nitrogen and subjected to six vacuum-argon cycles (these tasks were performed three times) before drying it under vacuum overnight at room temperature.

HOOC-(F_{4b}●)F_{4b}-N₃. 427 mg (31 % yield). ¹H NMR: δ (DMSO-*d*₆, 2.50 ppm) 12.77 (bs, 1H), 8.26-8.44 (m, 5H), 7.92-8.26 (m, 14H), 7.46-7.54 (m, 3H), 6.99-7.33 (m, 80H), 4.41-4.62 (m, 16H), 3.99-4.41 (m, 12H), 3.50 (PEG), 2.54-3.12 (m, 32H), 1.91-2.05 (m, 8H), 1.75-1.89 (m, 8H). ¹³C NMR: δ (DMSO-*d*₆, 39.52 ppm) 172.63, 171.09, 171.02, 170.86, 170.78, 170.68, 170.59, 170.47, 144.39, 137.97, 137.58, 137.49, 137.44, 137.33, 129.20, 129.08, 128.19, 128.05, 127.98, 127.92, 126.44, 126.29, 126.21, 126.15, 126.11, 122.50, 69.78 (PEG), 53.83, 53.64, 53.50, 53.46, 49.93, 48.60, 37.85, 37.63, 37.50, 37.41, 36.75, 34.29, 31.83, 24.39. MALDI MS (m/z): [M+H]⁺ calculated from C169H182N31O21 2981.41, found 2982.16.

HOOC-(F_{4v}●)F_{4v}-N₃. 450 mg (29 % yield). ¹H NMR: δ (DMSO-*d*₆, 2.50 ppm) 12.77 (bs, 1H), 8.27-8.46 (m, 4H), 7.87-8.27 (m, 15H), 7.50-7.57 (m, 3H), 6.97-7.37 (m, 80H), 4.37-4.66 (m, 16H), 4.08-4.37 (m, 12H), 3.50 (PEG), 3.17 (t, 2H), 2.56-3.11 (m, 32H), 1.89-2.05 (m, 8H), 1.40-1.60 (m, 8H), 1.14-1.40 (m, 8H). ¹³C

NMR: δ (DMSO- d_6 , 39.52 ppm) 172.64, 171.36, 171.16, 171.08, 170.86, 170.64, 170.55, 170.47, 169.08, 144.36, 137.95, 137.54, 137.50, 137.46, 137.33, 129.19, 129.09, 128.19, 128.04, 127.99, 127.92, 127.86, 126.43, 126.27, 126.21, 126.15, 126.07, 122.42, 69.78 (PEG), 53.83, 53.64, 53.58, 53.49, 53.45, 53.40, 50.27, 48.84, 37.84, 37.63, 37.53, 37.41, 36.73, 34.40, 34.29, 34.22, 34.15, 28.96, 27.45, 22.45, 22.19, 21.88. MALDI MS (m/z): [M+H]⁺ calculated from C173H190N31O21 3037.48, found 3037.65

HOOC-(F₄h●)F₄h-N₃. 601 mg (28 % yield). ¹H NMR: δ (DMSO- d_6 , 2.50 ppm) 12.77 (bs, 1H), 8.24-8.53 (m, 4H), 7.77-8.28 (m, 15H), 7.52-7.65 (m, 3H), 6.82-7.45 (m, 80H), 4.38-4.67 (m, 16H), 4.07-4.38 (m, 12H), 3.50 (PEG), 3.20 (t, 2H), 2.56-3.11 (m, 32H), 1.84-2.01 (m, 8H), 1.56-1.74 (m, 6H), 1.21-1.43 (m, 10H), 0.91-1.10 (m, 8H). ¹³C NMR: δ (DMSO- d_6 , 39.52 ppm) 172.61, 171.68, 171.10, 170.84, 170.53, 137.98, 137.54, 137.49, 137.46, 137.33, 135.87, 129.19, 129.08, 128.18, 128.04, 127.97, 127.91, 127.86, 126.42, 126.19, 126.14, 126.05, 122.38, 69.77 (PEG), 53.83, 53.57, 53.44, 50.43, 49.05, 37.60, 37.51, 37.31, 36.74, 34.92, 34.86, 34.31, 29.46, 27.84, 25.45, 25.22, 24.58, 24.46. MALDI MS (m/z): [M+H]⁺ calculated from C177H198N31O21 3093.54, found 3095.79.

HOOC-(F₄u●)F₄u-N₃. 366 mg (26 % yield). ¹H NMR: δ (DMSO- d_6 , 2.50 ppm) 12.77 (bs, 1H), 8.35-8.42 (m, 2H), 8.28-8.35 (m, 2H), 8.14-8.21 (m, 2H), 8.02-8.12 (m, 4H), 7.82-6-8.01 (m, 9H), 7.59-7.65 (m, 3H), 7.02-7.31 (m, 80H), 4.39-4.63 (m, 16H), 4.18-4.39 (m, 12H), 3.50 (PEG), 3.29 (t, 2H), 2.55-3.11 (m, 32H), 1.87-1.99 (m, 8H), 1.66-1.78 (m, 8H), 1.45-1.55 (m, 2H), 0.91-1.35 (m, 54H). ¹³C NMR: δ (DMSO- d_6 , 39.52 ppm) 172.60, 172.00, 171.94, 171.25, 171.13, 170.82, 170.65, 170.52, 170.46, 169.10, 144.46, 138.01, 137.55, 137.50, 137.33, 129.19, 129.08, 128.18, 128.04, 127.98, 127.91, 127.84, 126.42, 126.41, 126.18, 126.13, 126.01, 122.42, 69.78 (PEG), 54.90, 53.90, 53.75, 53.58, 53.51, 53.46, 53.45, 49.24, 37.75, 37.62, 37.50, 37.23, 36.73, 35.16, 34.33, 34.18, 29.80, 28.84, 28.78, 28.74, 28.40, 25.85, 25.09. MALDI MS (m/z): [M+H]⁺ calculated from C197H238N31O21 3373.85, found 3373.78.

4.5. Dip coating procedures

Handling of the fibers was performed PTFE or PTFE coated tweezers, purchased respectively from COWIE and Bochem, to reduce their corrosion due to the use of acidic solutions.

Individual fibers: Ten individual aramid short fibers were placed for 30 min in the coating solution prepared by dissolving 2 μ mol of coating molecule in 2 mL of 95/5 ACN/TFA, except PS in pure toluene. The fibers were then pooled out the solution individually using tweezers and tapped at one of their extremities to a small piece of paper hanged to air dry overnight.

Fiber pellets: Pellets from aramid fibers were prepared using a Specac manual hydraulic press with a stainless-steel crucible having a diameter of 13 mm. Aramid fiber (SFA A) pellets were held in place by tweezers, fastened through the use of tie-wrap. Coating solution was prepared by dissolving 2 μ mol of

interfacial agent or model molecule in 2 mL 95/5 ACN/TFA (toluene in the case of **PS**). Subsequently the solution was emptied into a Petri dish (diameter = 3.5 cm, height = 1 cm) and fiber pellets were dipped into solution to fully submerge for 5 min, turning the pellet midway through. After treatment, coated fibers were left to dry on the tweezers overnight, after which the weight difference was recorded. All weights recorded were a result of an average of 2-3 separate instances of the same sample being weighted. In the case of a large standard deviation, more than triplicate experiments were performed. All weighted differences have been corrected for with a constant mass of solvent ($\langle m_s \rangle = 0.41$ mg) that was determined dip coating pellets in 2 mL of the solvent used for dip coating. Three sets of pellets were treated with 95/5 ACN/TFA and two sets with toluene that were weighed before (m_{pellet}) and after 16-18 h of soaking in the solution (m_f). The measurements were performed in triplicate to obtain average values for mass differences.

4.6. SEM measurements

For the individual fibers, the fibers placed on the sample holder were held in with carbon tape (Agar Scientific). Scanning electron microscopy (SEM) experiments were performed on a FE-SEM Hitachi SU8010 with a voltage of 1 kV.

For the fiber pellets, the pellet was placed on a carbon substrate and treated with platinum sputter coating (Emitech K575 sputter coater was used with the following settings: platinum as metal, pressure of 10^{-3} mbar, current of 65 mA, and sputter distance of 3 cm). Scanning electron microscopy (SEM) experiments were performed on a JEOL JSM6490LV microscope (max resolution 3 nm) under a pressure of $\sim 10^{-5}$ mbar with a voltage of 15 kV with a spot size of 55.

4.7. Fracture test

Untreated or treated aramid fibers were sandwiched between two layers of poly(propylene-co-ethylene) using eight to ten granules for each layer in a ceramic crucible (bottom diameter of 13 mm). The crucible was placed in a thermostated oven at 180 °C for 15 min to melt the polymer, after which the crucible was removed and allowed to cool to room temperature for 15 min. The composite was then removed from the crucible by gently pulling. The composite was then plunged into liquid nitrogen for 10 min after which it was fractured using a hammer and pick. Fragments of the composite were placed on several carbon substrates. Subsequently, the substrate was treated with platinum sputter coating. SEM/EDS analysis followed with SEM images taken at 15 keV with a spot size of 55 and EDS spectra taken at 5 keV with a spot size of 62 and measuring time of 35 s using X-Max X-ray module.

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Jeroen Louwsma: methodology, investigation, writing; **Alain Carvalho:** methodology, investigation; **Jean-François Lutz:** funding acquisition, conceptualization; **Stéphane Joly:** funding acquisition, conceptualization, supervision; **Delphine Chan-Seng:** conceptualization, supervision, visualization, writing.

DATA AVAILABILITY

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

APPENDIX A. Supplementary material

Supplementary data to this article can be found online at .

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