Surface Treatment of Kevlar® Polyaramid Fibers with Imidazolium-based Ionic Liquids

C. Moraes*, H.S. Schrekker** and S.C. Amico*

*Post-Graduation Program in Mining, Metallurgical and Materials Engineering
Federal University of Rio Grande do Sul, Porto Alegre, Brazil, carolina.moraes@ufrgs.br
**Laboratory of Technological Processes and Catalysis, Institute of Chemistry
Federal University of Rio Grande do Sul, Porto Alegre, Brazil

ABSTRACT

Polyaramid fibers have excellent mechanical properties, such as high tensile strength-to-weight ratio and high thermal stability, but its applicability as reinforcement for composite materials is limited due to its high crystallinity and inert and smooth surface. In this work, an imidazolium-based ionic liquid (1-Butyl-3-methylimidazolium chloride) was used to treat Kevlar polyaramid fibers with the aim of improving Kevlar and epoxy resin interaction. The fibers were characterized by infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM). Tensile strength tests were carried out to verify loss of mechanical properties caused by the treatment. Contact angle measurements and pull-out tests verified an improvement of the wettability and adhesion between the fibers and epoxy resin. The interfacial shear strength (IFSS) was improved by 37% and the contact angle was decreased from 35˚ to 22.

Keywords: aramid fibers, epoxy resin, imidazolium salts, ionic liquids, interfacial compatibilization

1 INTRODUCTION

Poly (paraphenylene terephtalamide), commonly known as aramid, is a low density polymeric fiber that has high symmetry and rigidity, excellent thermal and chemical stability, high tensile strength and modulus and a lower cost when compared to carbon fibers [1]. However, the inferior interfacial affinity toward polymeric matrices hampers their use in composite materials, since the properties of composite materials depend on the interfacial interaction between the fiber and the matrix. In order to overcome this disadvantage, chemical [2–7], plasma and irradiation treatments [8–13] have been developed. However, various treatments fail to achieve high-effective functionalization of the fiber and functional group aggregation [4]. Ionic liquids present a promising alternative as compatibilizer in polymeric matrix reinforced with aramid fibers because of their set of physical-chemical properties that can be tuned from their chemical structures [14]. Recently, ionic liquids are being studied as curing agents for epoxy networks [15–19], resulting in a polymer with improved final properties.

In this work, Kevlar®129 fibers are treated with an imidazolium-based ionic liquid, in an attempt to functionalize its surface. FTIR indicated presence of new chemical groups in the aramid fibers. SEM showed the appearance of the organic salts adsorbed on the surface of the fiber. The interaction of Kevlar and epoxy resin was enhanced by the treatment, as its wettability and IFSS were improved.

2 EXPERIMENTAL

2.1 Materials

Kevlar® 129 yarns were supplied by DuPont. Epoxy resin (AR260) and epoxy hardner (AH260) was obtained from Barracuda, Brazil. 1-Butyl-3-methylimidazolium chloride, further referred as BMImCl, was acquired from Sigma Aldrich.

2.2 Surface Treatment

The aramid fibers were previously washed with n-hexane using soxhlet extractor for 24 hours to remove a coating existent in the fiber, commonly refered as finish. BMImCl (imidazolium salt:fiber ratio = 0.1) was diluted in ethanol and the fibers were treated in this solution for 1 hour in an ultrasonic bath at 60˚C. The fibers were then dried for 12 hours at 110˚C. In addition, the same treatment process was applied to the fibers without the presence of ionic liquids (referred as KT0), in order to investigate the effect of the solvent on the fiber.

2.3 Pull-out Specimens Preparation

Aramid fiber bundle/epoxy microcomposites were prepared using a silicon mold. Epoxy resin was firstly degassed for 30 minutes at 60˚C, then mixtured with hardner at 26% weight basis and added to the mold. Microcomposites were then cured for 24h at room temperature and post cured for 2 hours at 60˚C. The embedded fiber length varied from 1 to 3 mm. 15 specimens was made for each sample (as received and BMImCl treated fibers).

2.4 Characterization

Surface morphologies of the as received, washed and treated aramid fibers were analyzed by scanning electron microscopy with X-ray microanalysis SEM/EDS (Phenon-World Pro-X). Fourier transform-infrared (FTIR) spectroscopy was performed on the fibers before and after finish extraction and treatment. Tensile strength test was performed in a universal testing machine (EMIC-Instron 23-5D), following the standard test ASTM D7269. Epoxy contact angle of the fiber surface was obtained by observing epoxy droplet on a single fiber in an optical microscope (Carl Zeiss axio Lab.A) and the photographs were processed using Image J software. The contact angle was calculated by the method of the droplets geometry in cylindrical filaments [14]. For each sample, ten contact angle measurements were obtained and values within one standard deviation were considered. Fiber bundle pull-out test was performed in an universal testing machine (EMIC-Instron 23-5D). The specimens were tested at the speed of 2mm min^{-1}. Interfacial shear strength (IFSS) was calculated by the following equation:

$$\tau_{IFSS} = \frac{F_{max}}{\pi \cdot d_f \cdot l_e} \tag{1}$$

where F_{max} is the maximum value of the pull out force, d_f is the diameter of the fiber beam and l_e is the fiber embedded length in epoxy. Fiber beam diameter and embedded length were measured using an optical microscope.

3 RESULTS AND DISCUSSION

3.1 Characterization of the Treated Fibers

Error! Reference source not found.(a) illustrates the IR spectra for the Kevlar fibers after finish extraction and the treated fibers, and Figure 1(b) the spectra of the ionic liquid and treat fiber. BMImCl is a hygroscopic salt, so the broad band that appeared on the treated fiber spectrum regards the O-H stretching of water. According to literature [15,16], the peaks at 3138, 3064, 2955, 2864, 1160 cm^{-1} are characteristics of imidazolium salts. The peak at 3300 cm^{-1} corresponds to N-H stretching vibrations in secondary amide of the aramid fiber. There was a slight shift of the peak corresponding to the N-H stretching vibrations. According to literature [17], chloride anion has a strong interaction with the amide groups of aramid fibers, so the shift could have been a consequence of this interaction. The FTIR spectra suggest successful functionalization of Kevlar surface.

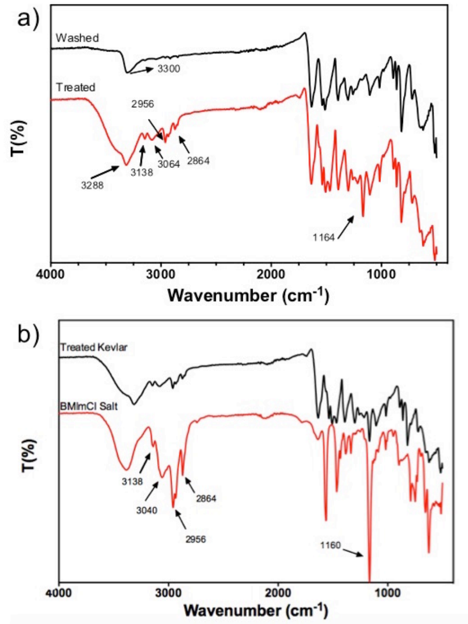

Figure 1 - FTIR spectra of Kevlar fibers after finish removal and treatment (a) and of the BMImCl salt and treated fibers (b)

Figure 2 shows SEM micrographs of the as received fibers (Figure 2a) and after the extraction of the finish with hexane (Figure 2b). The removal of the finish did not affect the filaments, as its morphology remained the same. The ethanol seems to have detached Kevlar blades, as it can be seen in **Figure 3**(a). It is possible to identify on **Figure 3**(b) the presence of the imidazolium salt on the surface of the fibers, which can be confirmed by the presence of chlorine on EDS analysis shown in **Table 1**. It was also observed filaments with damage on its surfaces, as it can be seen on Figure 3(b).

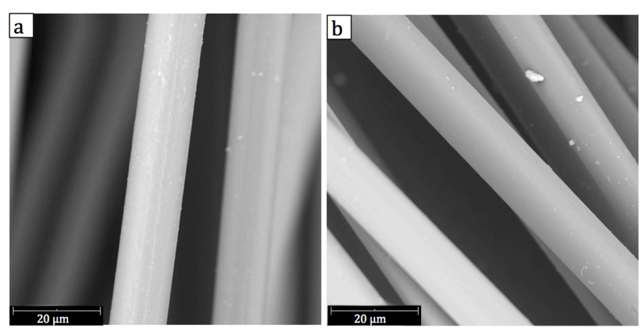

Figure 2 - SEM images of as received aramid fiber (a) and washed fiber (b)

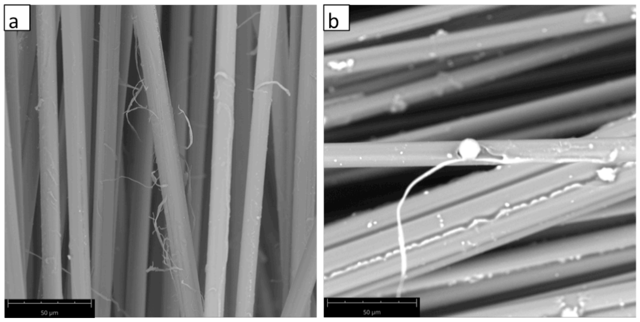

Figure 3 - SEM images of ethanol treated and BMImCl treated aramid fibers

Element	Atomic Concentration
C	61.79
N	22.88
O	14.52
Cl	0.8

Table 1 - EDS analysis of treated Kevlar fibers

TGA analyses (**Figure 4**) were made to quantify the presence of BMImCl adsorbed on the fiber. The mass loss at around 100˚C is result of humidity present in the fiber. At around 250˚C, BMImCl starts to decompose and is completely decomposed at around 400˚C. In this region, the mass loss is estimated to be 5%.

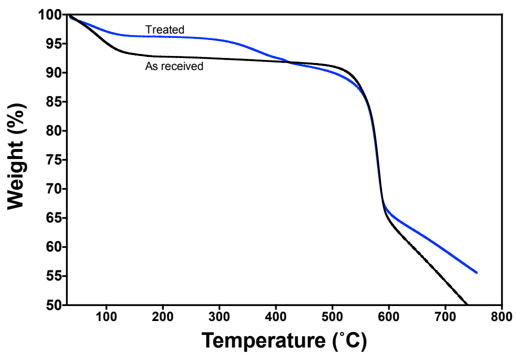

Figure 4 - TGA diagram of as received and treated fibers

3.2 Wettability of Kevlar Fiber by Epoxy Resin

The influence of treatment on the wettability of the aramid fibers by epoxy was investigated by measuring the contact angle of epoxy resin on the fiber. **Figure 5** shows the droplets of epoxy resin on the aramid filament for washed fiber (Figure 5a), as received fiber (Figure 5b), ethanol treated fiber (Figure 5c) and BMImCl treated fiber (Figure 5d). **Figure 6** illustrates the effect of the different treatments on the wettability of Kevlar by epoxy. The contact angle of washed aramid fibers increased, probably due to finish removal, which contains anhydrides that might have a better interaction with epoxy resin, or due to a hexane residue on the fiber. The contact angles of KT0 fiber decreased slightly, which could be explained by ethanol residue, which might have a better affinity with epoxy resin. The presence of the ionic liquid on the fiber decreased the contact angle from 35˚ (as received) and 31˚ (ethanol treated) to 22˚, improving the wettability of the aramid fibers.

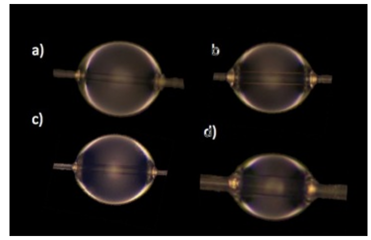

Figure 5 - Droplet of epoxy resin on Kevlar single fiber

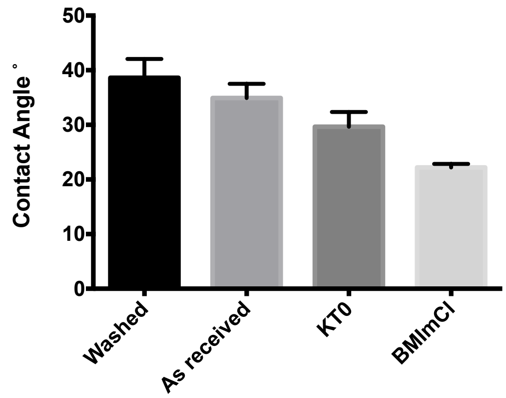

Figure 6 - Contact angle measurements obtained by observation of epoxy droplets on single fiber

3.3 Mechanical Properties

The finish removal by soxhlet extraction did not affect the mechanical properties of Kevlar. Detachment of blades of ethanol treated fibers observed in SEM images did not decrease the overall tensile strength of the fibers. However, treated fibers had a reduction of 15% of the tensile strength ($p = 0.0051$), which might have been caused by the break of hydrogen bonds of the amide groups of aramid fibers by chloride anion, explaining the rupture observed in SEM micrographs.

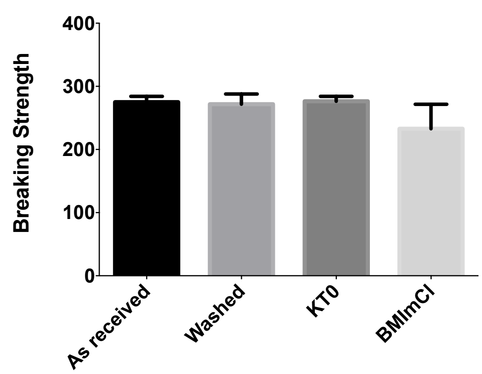

Figure 7 – Breaking strength of the fibers before and after treatments

3.4 Adhesion Properties

Pull-out tests were carried out in order to estimate the IFSS between Kevlar and epoxy resin and the results can be seen in **Figure 8**. IFSS was improved by 37% (p=0.005), increasing from 29.4 to 40.4 MPa. This confirms the BMImCl capacity of compatibilizing aramid fibers in epoxy resin.

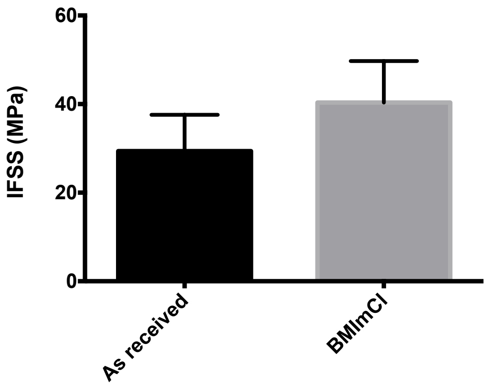

Figure 8 - IFSS results from pull-out test

4 CONCLUSION

Ionic liquid 1-Butyl-3-methylimidazolium chloride was able to enhance the interaction between aramid and epoxy. The wettability of the fiber increased as it was treated with the ethanolic solution of BMImCl. As expected, IFSS also raised, increasing its value by 37% in comparison with as received fibers. This improvement can lead to the manufacture of an aramid/epoxy composite with better mechanical properties. The tensile strength decline of 10% performed by BMImCl treated fiber could be the result of the breakage of hydrogen bonds of the amide groups due to its high interaction with chloride anion.

5 ACKNOLEGMENTS

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