Mechanical Properties of Epoxies Reinforced with Chloride-Treated Aramid Fibers

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ABSTRACT: Surface treatment of aramid fibers by immersion in a solution of methacryloyl chloride in carbon tetrachloride was carried out, and the resulting material was examined by means of electron microscopy and chemical analysis in an attempt to record any changes in the morphology and nature of the surface. Mechanical testing of tensile, flexural, and interlaminar shear strength, as well as dynamic mechanical analysis (DMA), were performed in an attempt to explore the effect of this treatment on the strength of the fiber. In a subsequent stage, the performance of those fibers as reinforcement in composites of epoxy matrix was assessed. The aim of this study was to provide more information about the interactions between the chloride-treated aramid fibers and the epoxy resin and, more specifically, to compare the behavior of the epoxy matrix composites with those composed of unsaturated polyester, polyethylene, and polyurethane matrix, which were studied in the past. It was found that specimens containing chloride-treated aramids display better flexural properties, whereas their tensile strength is drastically reduced. Improved performance was also identified by the DMA experiments. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 267–276, 1997

Key words: aramid fiber; surface treatment; adhesion; reinforced epoxies

INTRODUCTION

It is well known that the mechanical properties of fiber-reinforced composites are highly dependent on the interactions between the fiber and the matrix. The primary role of the interface in composites is to transfer the load from the matrix to the fibers. To take full advantage of the mechanical properties of the fiber and matrix, the interfacial shear strength between the fiber and matrix must be greater than the failure shear strength of the matrix or of the fiber. Several mechanisms that contribute to adhesion have been identified, namely, mechanical, physical interaction, and chemical bonding at the fiber–matrix interface.

Due to the poor adhesion between aramid fibers and most matrices, aramid fiber-reinforced composites are characterized by relatively low off-axis properties. This limitation is further aggravated by the skin–core morphology and the weaker skin properties of aramid fibers. In fact, it was observed that aramid–epoxy interfacial failure involves failure by fibrillation at the fiber outer surface, which suggests the presence of a cohesive weak layer on the fiber exterior that can fail at low shear levels, resulting in low values of interfacial shear strength and, consequently, insufficient fiber–matrix load transfer.[1] In order to improve the interfacial bonding between the aramid fiber and polymer matrix, a variety of fiber surface modifications have been attempted, including grafting, use of coatings, chemical attack of hydrogen amide groups, and the formation of functionalities by plasma treatment.

In addition to the above procedures, plasma

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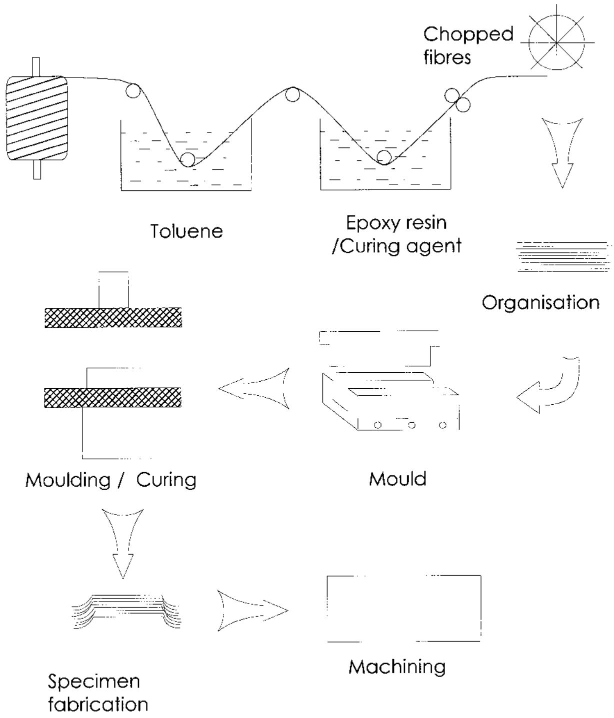
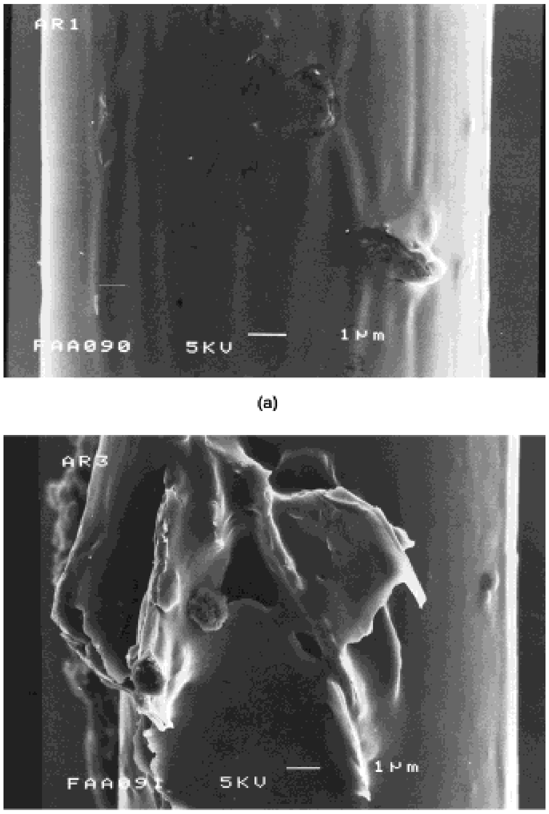


Figure 1 Complete line for the preparation of composite specimens.



(a)

(b)

Figure 2 SEM micrograph of original aramid fiber: (a) perfect fiber; (b) fiber with some defects.

treatment has been used and is claimed to display an important advantage in comparison with other methods, which is that the surface modification can be achieved with minimal alteration of the bulk characteristics of the substrate polymer.

Thus, Allred et al.[2] have employed gas phase O_2 plasmas for the oxidation of Kevlar 49 fibers, whereas Wertheimer and Schreiber[3] used microwave plasma in atmospheres of O_2, N_2, and Ar to oxidize the surface of Kevlar incorporated into a triazine matrix polymer. They found that this treatment increased the strength of composite laminates. The mechanical performance of these materials seemed to be strongly dependent on the lapsed time between plasma reaction and sample preparation. The laminate strength was maximized when the time interval between plasma exposure and resin contact was minimized.

Allred et al.[4] presented a method to introduce amine groups into the filament surface by exposure to ammonia plasmas. Subsequent reaction of the amine groups with epoxides formed strong covalent bonds at the composite interface.

Some researchers claim that the surface modification of aramid fibers by plasma treatment alone is not enough to improve adhesion. Combined plasma treatment and coupling agent treatment with silicone adhesive was found effective in promoting adhesive bonding between aramid fibers and silicone rubber.[5] Wang et al.[6] applied the catalytic grafting technique to the oxygen plasma-treated aramid fibers–High Density Polyethylene (HDPE) system. The reactive sites introduced by the plasma treatment were used to

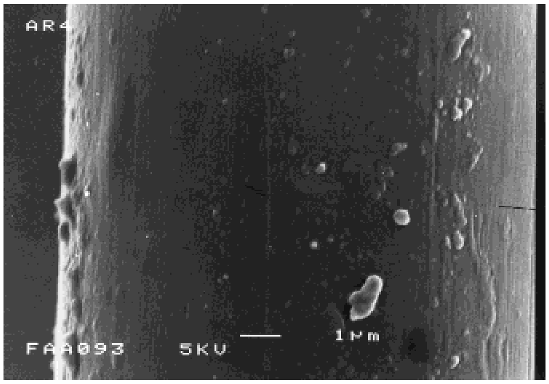


Figure 3 SEM micrograph of chloride-treated aramid fiber.

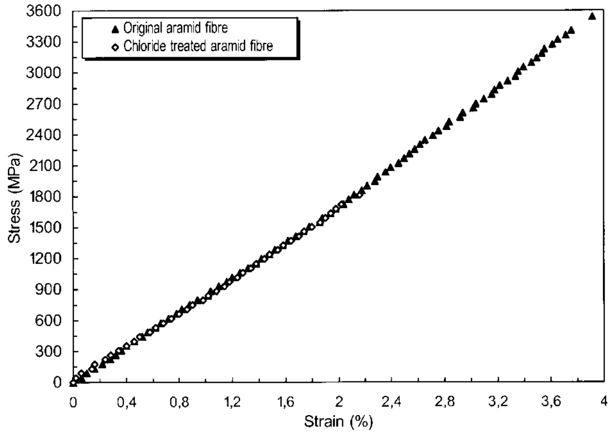


Figure 4 Stress–strain curve from tensile test in monofilaments.

chemically anchor a Ziegler–Natta catalyst followed by ethylene polymerization on the fiber surface. The grafted polyethylene acts as a transition layer between the polymer matrix and reinforcement and improves the interfacial adhesion. Improved mechanical properties were observed when a blend of polar polymers was used as matrix for the fabrication aramid fiber composites.[7]

Many procedures of chemical treatment have also been developed for aramid. Thus, Vaughan[8] studied the effect of coupling agents on the surface of aramid fibers in an attempt to improve the performance characteristics of aramid fiber-reinforced composites. Various organic sizings were tested, but no evidence of improvement upon the baseline adhesion between bare fiber and matrix was identified.[9]

The fracture toughness of Kevlar–epoxy resin composites with intermittent bonding with a silicon vacuum fluid (SVF-200) and a polyurethane varnish (Estapol 7008) has been studied over a range of temperatures and strain rates. Estapol 7008 was found to be more effective than SVF-200 in enhancing the toughness of the composites.[10]

Kim and Mai[11] reported that the transverse fracture toughness of unidirectional Kevlar–epoxy resin composites was substantially improved by coating the fibers with poly(vinyl alcohol) without any loss of flexural strength, but there was only a moderate improvement upon coating with a carboxyl-terminated butadiene-acrylonitrile copolymer and poly(vinyl acetate) with some reduction in flexural strength.

Menon et al.[12] studied the surface modification of Kevlar fibers with titanate coupling agents for improved adhesion to treated Kevlar–phenolic composites. The specimens exhibited improved flexural properties and greater resistance to moisture penetration.

In another work, the surface of aramid fibers was roughened by water treatment.[13] These fibers exhibited adhesion properties below those of the sized fibers but more superior than the untreated fibers. Another modification consists of a metalation reaction in dimethyl sulfoxide. The treated fibers were used as a reinforcement for the ionomer and polyethylene matrix.[14]

Keller et al.[15] have studied a solution reaction scheme for Kevlar fibers based on aqueous hydrolysis of the amide linkages with strong aqueous acidic and basic solutions. After hydrolysis, a bifunctional epoxy monomer was reacted with the free amine groups. Breznick et al.[16] observed significant improvement of the interlaminar shear strength (ILSS) of aramid fiber/epoxy matrix composites by bromination, which roughens the fiber surface. Penn et al.[17] investigated the surface energy and adhesion of modified Kevlar 29 fibers by a surface-controlled nitration reaction and by nitration–reduction sequence. Although the modification did not alter the surface energy, the interfacial adhesion was significantly increased.

The surface of aramid fibers was chemically modified using oxalylchloride to obtain an intermediate to which various secondary reactions took place with water, methanol, ethylenediamine, and glycidol. It was found that the introduction of epoxy groups was the most effective to

Table I Tensile Characteristics of Treated Aranid Fibers

Aramid Fiber Sample	Tensile Strength (MPa)	Standard Deviation	Tensile Modulus (GPa)	Standard Deviation	Strain at Breaking Point (%)	Standard Deviation
Original	3103.5	252.8	82.7	3.15	3.5	0.315
Chloride-treated	1927.5	298.9	80.9	5.15	2.0	0.271

Table II Tensile Test Results of Unidirectional Composite Materials Reinforced with Original Aramid Fibers

V_f (%)	Tensile Strength (MPa)	Standard Deviation	Tensile Modulus (GPa)	Standard Deviation	Strain at Breaking Point (%)	Standard Deviation
24.74	628.61	132.21	8.23	1.19	4.11	1.22
27.08	687.18	46.99	10.57	0.77	3.68	0.78
32.07	758.35	28.56	11.98	0.33	3.47	0.33
35.85	781.84	54.99	14.12	0.91	3.80	0.04
37.58	957.82	67.53	13.34	0.18	4.75	0.49
43.00	936.89	141.68	15.58	1.44	3.57	0.26
48.97	1053.02	3.51	—	—	—	—

improve adhesive properties with epoxy resin.[18] Briscoe and Williams reported the successful grafting of propane-diol, alkyl, epoxy, and trimethyl silane groups into the surface of Kevlar fibers via an anhydrous reaction route. The changes in the contact angle and the works of adhesion for water and methylene iodide with the modified fibers confirmed the potential success of the grafting reactions.[19]

Chou and Penn[20] attached molecular chains with different chemical structures to the surface of aramid fibers and studied the effect on the fiber's adhesion to the epoxy matrix. They came to the conclusion that inert chains did not alter the fiber–matrix adhesion. Chains capable of chemically bonding with the matrix increased the adhesion significantly. Briscoe and Williams[21] studied the effect of acid–base interactions in the fracture toughness of aramid epoxy composites and found that the fracture process is not directly influenced by the interface quality but rather by the structure of the system and, hence, the size and the dissipative character of the deformation zone associated with the crack.

Another approach was to impregnate aramid fibers with acetic acid anhydride, sulfuric acid–acrylamide, and methacryloyl chloride. The latter treatment seemed to be very interesting as it increases the fiber–matrix adhesion when these fibers were used as reinforcement for unsaturated polyester.[22] Also, aramid pulp was treated with methacryloyl chloride, which has shown to be an effective technique for promoting the fiber–matrix adhesion. In fact, the treated fiber is an efficient reinforcing agent for crosslinked polyethylene; and since PE is a nonpolar polymer, this performance could suggest some chemical grafting.[23] A direct chemical reaction would be possible between acid chloride and the secondary hydrogen of the amide bonds present in aramids, as already reported.[18] However, in our previous work,[22,23] no obvious evidence of such interactions was recorded. It would be of interest, therefore, to extend this research to other polymeric matrices in order to collect data capable of elucidating the effect.

In this work, aramid fibers were treated with methacryloyl chloride according to the above established technique. The resulting material was examined by means of electron microscopy and chemical analysis in an attempt to record any

Table III Tensile Test Results of Unidirectional Composite Materials Reinforced with Chloride-Treated Aramid Fibers

V_f (%)	Tensile Strength (MPa)	Standard Deviation	Tensile Modulus (GPa)	Standard Deviation	Strain at Breaking Point (%)	Standard Deviation
25.33	321.49	21.90	8.88	0.59	3.84	0.11
34.84	406.53	46.77	11.80	1.12	3.39	0.39
44.78	551.49	39.34	15.65	1.07	3.62	0.52
53.23	579.35	8.16	17.39	2.56	3.75	0.54

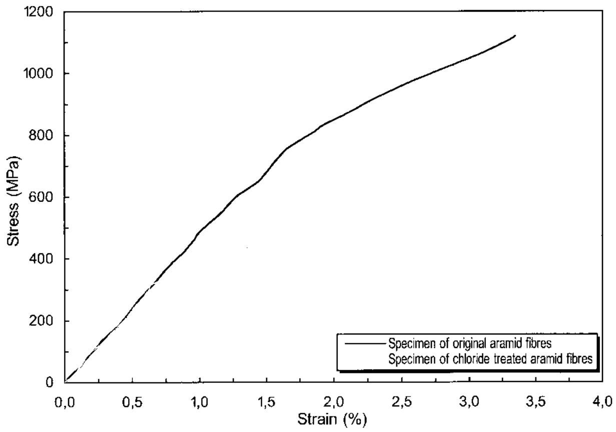


Figure 5 Stress–strain curve of unidirectional composite specimens in tension.

changes in surface morphology and nature. Mechanical testing was also carried out, which was expected to show whether this treatment deteriorates the strength of the fiber. In a subsequent stage, the performance of those fibers as reinforcement in composites of epoxy matrix was assessed. The aim of this study was to provide more information about the interactions between the chloride-treated aramid fibers and the epoxy resin and, more specifically, to compare the behavior of the epoxy matrix composites with those composed of unsaturated polyester, polyethylene, and polyurethane matrix, which were studied in the past.[22–24]

EXPERIMENTAL

Materials

The aramid fiber Twaron 1000 supplied by AKZO (The Netherlands) was used in this study. For the preparation of composites, a low initial viscosity epoxy resin was used (Epikote 828, Shell Chemicals Hellas) intended for use in high-strength composites. Curing was carried out at 40°C for 1 h and 60°C for 3 h, using an oligomeric amide (Epilink 175) as a hardener at a weight ratio to epoxy 1 : 2. In a subsequent stage, postcuring took place at 150°C for 1 h.

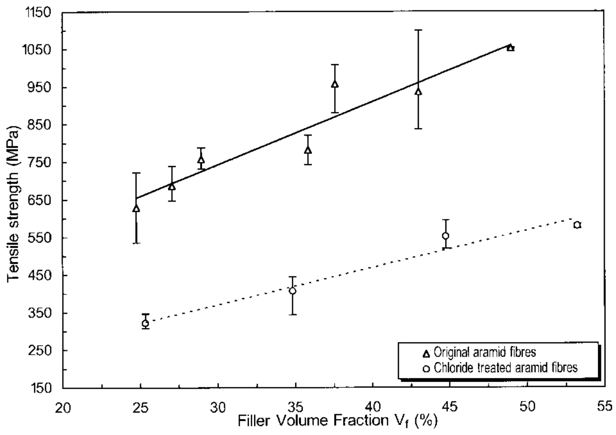


Figure 6 The tensile strength of unidirectional composites as a function of filler volume fraction.

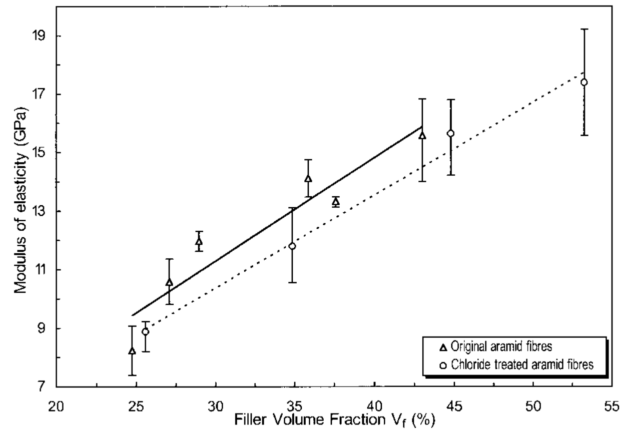


Figure 7 The tensile modulus of unidirectional composites as a function of filler volume fraction.

Treatment and Characterization of Reinforcement

Methacryloyl chloride (Purum, Fluka AG) and carbon tetrachloride (CCl_4, chemically pure, Mallinckrodt Chemical Works) were used. The acid chloride was dissolved in CCl_4 (10/90 v/v solution) in order to prepare a less reactive means for treatment of the aramid fibers. CCl_4 and similar chlorinated hydrocarbons are frequently used for removal of lubricants or sizing present on the ara-

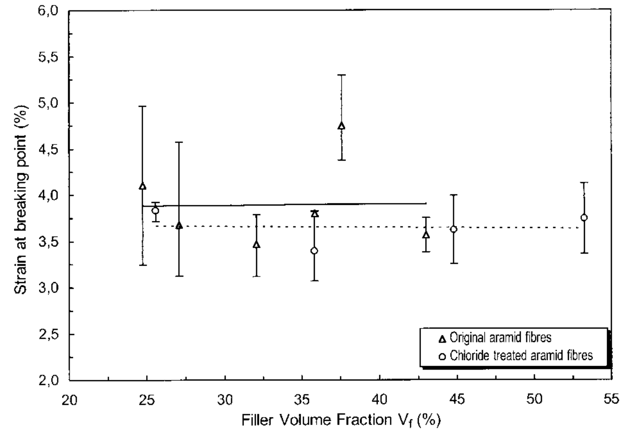


Figure 8 The ultimate strain of unidirectional composites as a function of filler volume fraction.

Table IV Flexural Properties of Unidirectional Composite Materials Reinforced with Original Aramid Fibers

V_f (%)	Flexural Strength (MPa)	Standard Deviation	Flexural Modulus (GPa)	Standard Deviation	Deflexion (mm)	Standard Deviation
27.87	243.60	4.46	11.94	0.10	14.15	1.78
31.25	236.36	4.08	12.05	0.65	14.58	0.77
34.28	257.69	2.46	14.03	0.06	13.56	0.10
36.52	290.16	4.38	16.32	0.95	13.97	0.27
42.90	290.56	8.71	17.91	0.46	12.71	0.97

mid surface[18,22] and have not been reported to affect the fiber. A JSM-300 microscope, capable of high resolution was employed for scanning electron microscopy (SEM). The mechanical properties of the treated fibers were compared to those of untreated monofilaments using a 20 kN Hounsfield screw-driven tensile tester machine. Individual monofilaments were mounted across a hole in a paper card. At each end, the fiber was twisted around a bar and stacked in a card using the HY 5161/CY 210 (Ciba Geigy) epoxy resin system. The curing was carried out at room temperature. The monofilaments had to be strongly fixed in the card in order to avoid fiber's gripping during the experiment. Samples of 250 mm gauge length were tested in tension at room temperature at a rate of 0.5 mm min^{-1}.

Preparation of Composites

The unidirectional fiber composites were prepared by the leaky mould technique. This technique involves the use of an open-ended two-part mould, as shown in Figure 1, which produces a single composite bar. The procedure adopted was as follows.

The fibers were soaked/impregnated with the epoxy resin/curing agent system. After coating the mould with a silicone release agent (Frekote 1711, Dexter Corporation), the fibers were laid down in the groove, and liquid resin was poured in until soaking was complete. The upper part of the mould was then placed in position, and the mold was then placed in hydraulic press with the appropriate spacers to produce 2 mm thick specimens. The excess resin was expelled by squeezing the mould.

The desired fiber volume fraction (V_f) was achieved by changing the number of aramid yarns in the mould. The samples prepared were cut into specimens with a fine band saw. The fiber volume fraction obtained ranged from 10 to 50%.

Mechanical Measurements on Composites

Mechanical testing of unidirectional composite specimens was carried out in an INSTRON 11706 TT-CM tensometer. The tensile specimens were prepared according to ASTM D3039/D3039M-93. In order to avoid the problems of stress transfer between the composite sample and the Instron grips, tabs made from the glass fiber–epoxy resin system were used.

The flexural properties of the composites were measured by three-point bending tests, according to ASTM S D790-92. The selected support span-

Table V Flexural Properties of Unidirectional Composite Materials Reinforced with Chloride-Treated Aramid Fibers

V_f (%)	Flexural Strength (MPa)	Standard Deviation	Flexural Modulus (GPa)	Standard Deviation	Deflexion (mm)	Standard Deviation
27.40	264.00	7.99	13.440	1.51	15.79	0.41
30.57	249.27	1.94	14.778	0.41	14.33	0.65
36.49	264.92	9.08	16.460	0.58	13.23	2.00
43.95	306.99	2.37	19.210	1.19	14.05	0.93

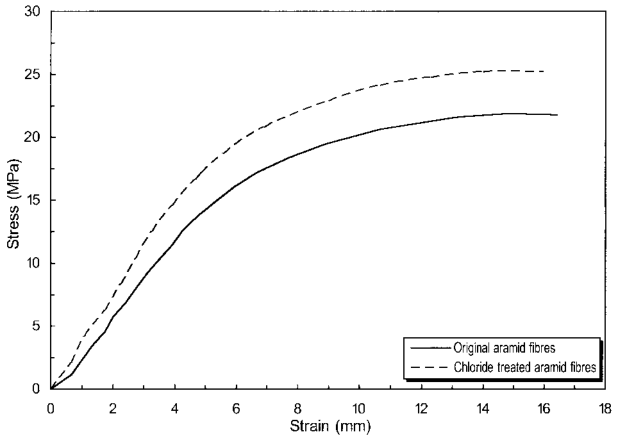


Figure 9 Typical three-point flexural stress versus deflection curves.

to-depth ratio was $L : d = 32 : 1$ with a specimen length of 100 mm. The ILSS was determined using a short-beam bending rig, according to ASTM D2344-84. The specimen support span to thickness ratio was 4, and the specimen length to thickness ratio was 6.

Dynamic Mechanical Analysis

The DMA tested were carried out in a DuPont V4.2C machine at a temperature range of 20–120°C and vibrational frequency 1 Hz. An amplitude of 0.50 mm was used; and the shear modulus, the complex modulus, and loss of tangent were determined.

RESULTS AND DISCUSSION

The SEM micrograph of the as-received fibers reveals, in general, a very smooth surface, as shown in Figure 2(a), although some defects can be identified [Fig. 2(b)]. Figure 3 shows that after treatment with methacryloyl chloride, small flaws and randomly distributed grooves were created on the fiber surface. The changes in the surface morphology suggest that mechanical interlocking of the treated fibers and the epoxy matrix is possible to occur. Furthermore, it would be of interest to explore the nature of those changes in the fiber surface morphology by performing chemical analyses with higher sensitivity than that of infrared (IR) spectroscopy, which was used in the past.[22,23] Such tests would be of interest in order to explore whether surface irregularities are simply the result of etching of the fiber via a hydrolytic attack of the amide bond.

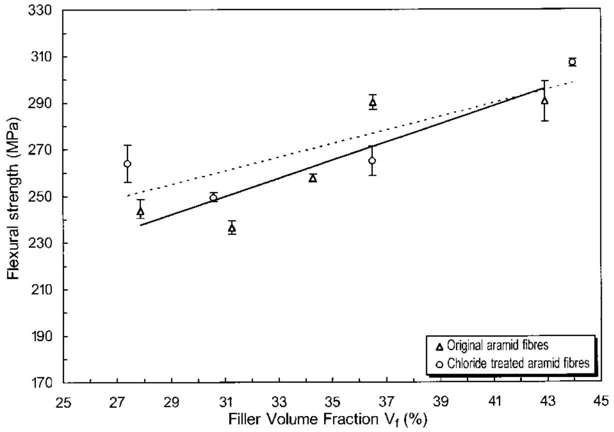


Figure 10 The flexural strength of unidirectional composites versus filler volume fraction.

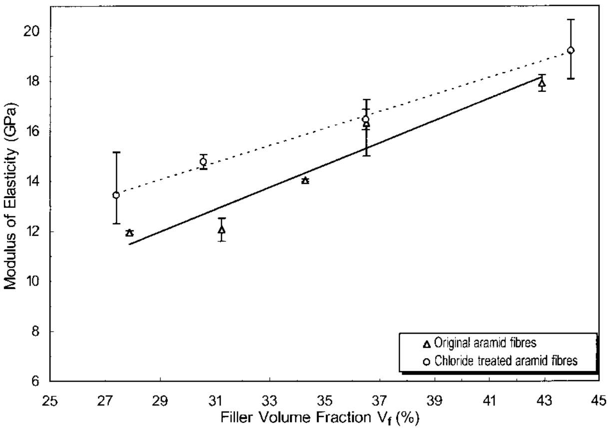


Figure 11 The flexural modulus of unidirectional composites as a function filler volume fraction.

The stress–strain curve obtained by the testing of individual monofilaments in tension is presented in Figure 4. It can be seen that the treated fibers display lower strength compared to the original aramid fibers, which can obviously be attributed to stress concentration in the flaws created by chloride treatment. It also can be observed that the application of tensile load leads to strain hardening effects. This was explained by the fact that the aramid fiber as a chain of crystallites was slightly misoriented with respect to the fiber axis and the application of tensile load results in the alignment of crystallites in the loading direction. The results obtained from the above tests are presented in Table I.

Similarly, the tensile properties of composites reinforced with treated and original fibers were examined. The results in terms of strength, modulus, and elongation, as well as their standard deviation, are shown in Tables II and III. Further-

Table VI Interlaminar Shear Strength in Aramid Fiber Composites

Composite Specimens with Aramid Fibers	Fiber Volume Fraction V_f (%)	Interlaminar Shear Stress (MPa)	Standard Deviation
Original fibers	38.72	32.70	1.08
Chloride-treated fibers	38.15	33.06	0.52

more, the stress-strain curves are presented in Figures 5 and 6. It is clear that there is a significant deterioration in the strength of specimens reinforced with chloride-treated aramid fibers, which is consistent with the decrease in strength determined for the treated fiber. Also, the strength obtained by the tensile tests is considerably lower than that expected according to the law of mixtures. This is most enhanced at high fiber volume fractions because this consistency does not allow enough volume of resin for the complete wetting and embedding of every single fiber. Similar results have been presented by other researchers too.[25] On the other hand, the tensile modulus and the elongation at break for specimens with original and treated fibers remain almost unchanged, as shown in Figures 7 and 8. This suggests that the fracture mechanism of those specimens involves crack propagation through the epoxy resin.

In order to explore the effect of the observed improvement on the adhesive bonding between treated aramid fibers and the epoxy matrix by running pull-out experiments, the flexural properties were recorded by performing the three-point bending test (Tables IV and V). Figure 9 shows the typical three-point flexural stress versus deflection curves for composites containing original and chloride-treated aramid fibers. The curve of the fiber fracture mode is characterized by a yielding stage and a larger ultimate deflection. It is reported that this curve is characteristic for failure by longitudinal fracture of fibers in the tensile side and is controlled by the fiber volume fraction. In fact, at 0.45 V_f, a change occurs; that is, the transition fracture mode is transformed to the mode of delamination (for a ratio of loading span to depth equal to 8).[26] It is also evident that specimens made of original fibers start to fail at relatively low deflections, although they do not break catastrophically. However, in composites containing plasma-treated fibers, the load continued to increase until catastrophic failure took place.

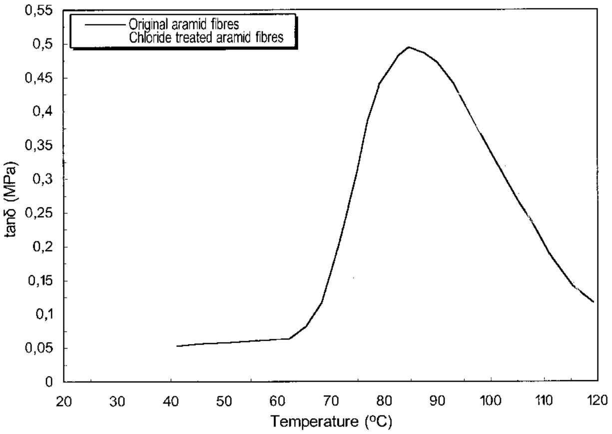


Figure 12 tan δ versus temperature for composites containing 40% fibers.

From the results of ultimate flexural strength versus V_f (Fig. 10), it can be seen that the specimens reinforced with chloride-treated aramid fibers have improved properties, especially at lower V_f. For $V_f = 0.45$, the specimens reinforced with treated and original fibers have the same behavior. The improvement of the flexural properties at a low V_f is explained by the enhanced interfacial properties of the chloride-treated fibers due to the surface roughening after treatment. This is not valid for higher V_f, probably due to the lack of enough resin, as discussed above. The interactions between the fibers and the epoxy matrix result in changes in the failure mechanisms of the composite specimens. According to Jang,[27] the increased flexural strength of composites reinforced with plasma-treated fibers can be attributed to a lower degree of compressive fiber buckling due to enhanced interfacial bonding.

The flexural modulus values were calculated from the slopes of the linear elastic portions of the load–deflection curves. From these results presented in Figure 11, a marked increase especially in the area of low V_f is evident. Some researchers confirm that the flexural modulus is controlled by the tensile and compressive properties of the fiber and matrix rather than by interfacial properties.[28]

However, it is reported that in cases of a very low ratio of loading span to depth, the beam deflection may contain shear and bending components, which give an apparent flexural modulus lower than the true flexural modulus.[1]

The study of the ILSS does not reveal any differences between the two series of specimens, as is presented in Table VI. Also, the loss tangent versus temperature plot, as derived from the DMA experiments, is presented in Figure 12. Since a poor fiber–matrix adhesion will promote interfacial friction, this will be reflected by a higher value of the loss tangent.[27] Energy is expected to be dissipated at the fiber–matrix interface when the specimen is subjected to continuous cyclic loading. The amount of internal energy dissipated at the interface depends upon the degree of adhesion. A weaker bond is expected to result in more energy loss, which should correspond to a higher damping coefficient. Thus, it is possible to determine the amount of energy dissipation due to poor interfacial adhesion by any vibrational technique. Based on the above, Figure 12 gives a qualitative indication that treated aramids should display an improved interfacial behavior with the epoxy matrix.

CONCLUSIONS

From the above results, the following conclusions can be drawn. Treatment of the aramid fibers with methacryloyl chloride seems to be an interesting modification for the subsequent use of those fibers as reinforcement in epoxy matrices. The obvious effect on the fiber surface is a change in morphology. However, changes in chemical consistency have not been identified by the analytical technique employed in this study. Due to the etching of the fiber, its tensile properties are declined, and the same is observed for the tensile strength of composites made of treated aramids. Despite the above results, the flexural properties of composite specimens are improved when treated aramids are used as reinforcement, which clearly suggests that the adhesive bonding between fiber and epoxy matrix becomes stronger. We could speculate various adhesion mechanisms generated by the chloride treatment of aramid fibers. These include (1) an enhanced degree of mechanical keying between the fiber and matrix because of the increased fiber surface roughness, which is more likely to happen; (2) possible removal of the weak boundary layer, which provides better fiber–matrix contact and contributes to a stronger interface; (3) an increased surface energy and therefore more efficient wetting of the fiber by the epoxy; and (4) chemical grafting of methacrylic groups on the surface of the fiber or coating of the fiber by species deriving from the hydrolysis of methacryloyl chloride. No evidence for this latter possibility has been found in this work nor in similar research with other matrices conducted in the past.

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