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Modification of mechanical properties of Kevlar fibre by polymer infiltration

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While high-performance organic fibres such as poly (*para* phenylene benzobisthiazole) and Kevlar possess excellent mechanical properties under axial tension, their strength under compression is generally poor. This study focuses on a polymer infiltration approach to modify the mechanical properties of the Kevlar 49 fibre in tension as well as compression, in which various polymeric resins are infiltrated in an opened fibrillar network of Kevlar single filaments. Opening was achieved using concentrated sulfuric acid, which resulted in a strength loss at high acid concentrations. However, compared to the acid-treated fibre, both the tensile strength and strain-to-failure of the fibres were found to increase after infiltration with epoxy resins and bismaleimide polymers. Polymer infiltration also resulted in a significant improvement in the compressive strength of the Kevlar fibre, with the bismaleimide performing better than the epoxy resins. Plasma modification using ammonia was also used to enhance interfibrillar adhesion by incorporating reactive amine groups on the fibril surface.

1. Introduction

With the advent of high-performance fibres such as aramids, carbon, and polyethylene, the scope and diversity of the fibre composite industry has increased manifold. More recently, attention has been focused on developing strong, high modulus organic fibres such as Kevlar, Technora, poly (*para* phenylene benzobisthiazole) (PBZT) and polybenzimidazole (PBI). The outstanding mechanical properties of these fibres have been achieved by utilizing the ability of their constituent polymers to form liquid crystals in solution. In Kevlar fibre, the extended chain structure of poly (*para* phenylene terephthalamide) (PPTA) molecules along the fibre axis, together with the aromatic rings in the polymer chain, are responsible for its high modulus, strength and chemical and thermal stability [1]. These fibre properties have been utilized in a large variety of end-uses ranging from ropes and cables to protective clothing and from sporting goods to filament-wound pressure vessels and aerospace composites. While these fibres possess extremely strong properties in tension, their properties under compression leave a lot to be desired [2–4]. The compressive strength of Kevlar has been found to be 20% of the tensile strength, while the axial shear modulus is only 2% of the axial tensile modulus [2].

The high material anisotropy in Kevlar fibres is a result of covalent bonds along its axis as compared to the much weaker hydrogen bonds and Van der Waals attraction in the transverse direction. As a result, the transverse properties in both tension and compression are relatively poor. Substantial lateral compressive stresses due to bending and twisting may be imposed on these fibres, both during fibre and composite manufacture and subsequent end-use applications. These compressive stresses lead to fibre damage through buckling and kink-band formation, ultimately leading to failure. Owing to this early compressive failure, the high longitudinal strength potential of the fibres may not be fully realized.

The fibrillar nature of Kevlar is another important feature responsible for its poor lateral and compressive properties. Sawyer and Jaffe [5] have investigated the hierarchical structure of Kevlar and similar fibres. From X-ray diffraction patterns and electron photomicrographs, they showed that Kevlar fibre consists of crystallites with average dimensions of about 7 nm in the transverse direction. Several such crystallites combine to form micro-fibrils approximately 0.05 μm in diameter. Micro-fibrils combine together to form fibrils which are 0.5 μm in diameter. These fibrils further combine to form macro-fibrils which ultimately result in a 12 μm diameter fibre. In reality, however, this hierarchy may not be so well defined.

While the fibrillar structure is well developed, these fibres possess very little inter-fibrillar adhesion. Failure of these fibres in tension involves splitting or separation of the fibrils that individually fail over a large length, generally 20–70 fibre diameters [6, 7]. Fig. 1 shows a typical photomicrograph of a Kevlar 49 filament fractured in a simple tension test where the fibril separation is clearly evident. Fibrillation in Kevlar is further enhanced by poor lateral packing within the fibre and the presence of impurities or micro-voids in the fibre [6]. Micro-voids in Kevlar have been shown to affect both lateral and longitudinal strengths

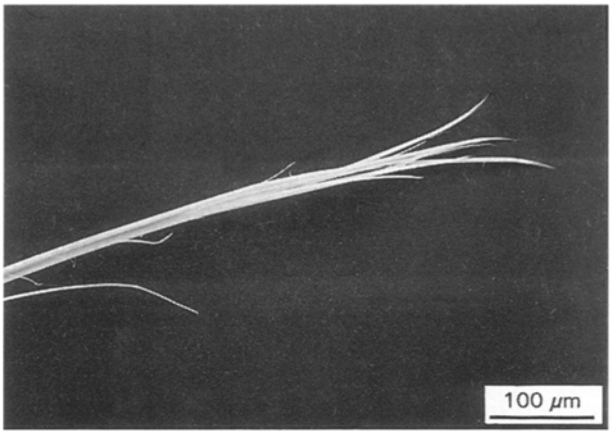

Figure 1 Scanning electron micrograph of the fibrillated end of a Kevlar fibre after tensile fracture.

of the fibre and that appropriate infilling is capable of improving the mechanical performance of the fibre [8].

Apart from their fibrillar nature, aramid fibres also exhibit a skin/core structure. The outer skin is highly oriented compared to the core and may be weak in the transverse direction [9]. This poses additional problems in composites when loaded in the transverse direction, because the bonding between the fibres and the matrix is preferentially at the surface.

The fibrillar structure and the poor adhesion between the fibrils have been shown to be also responsible for the poor compressive strength of Kevlar and other fibres such as PBZT and poly (*para* phenylene benzobisoxazole (PBO)) that are fibrillar in nature [2, 10, 11]. The fibrils and micro-fibrils buckle under compressive loads leading to the formation of kinks and kink bands along the fibre. The relationship between various mechanical models and the buckling of a polymeric fibre with a substructural hierarchy (fibril, micro-fibril, individual molecular chain) has been analysed by Lee and Santosh [10]. The critical buckling strength has been found to be dependent on the element geometry and the strength of interaction with the neighbours. Buckling instability at the fibril level has been deemed as the predominant reason for the low compressive strength of Kevlar [11].

The poor interfibrillar adhesion suggests that the single fibre can be considered as a loose bundle of fibrils. This structure is expected to behave similarly to a loosely packed bundle of fibres. The strength of a loose bundle of fibres, with no interaction between them, is generally found to be 60%–70% of the mean fibre strength [12]. When a load is applied to a loose bundle of fibres, all the fibres share the load equally. As the load is increased, the weakest fibre fails first and the load carried by the failed fibre is then shared "equally" amongst all the remaining intact fibres. This model of load distribution is often termed the "equal load sharing" model. The load redistribution, however, changes significantly when the fibre-to-fibre interaction is increased within the bundle by impregnating it with a matrix material. In general, the bundle becomes stronger after matrix impregnation. The matrix serves two important functions, both of which mitigate the potentially catastrophic effect of broken fibres [13, 14]. First, the effect of the break is isolated longitudinally along the fibre as the shear stresses generated in the matrix allow the fibre stress to return to normal only a short axial distance, a few fibre diameters, away from the break [14]. Second, the matrix shear causes the load to be transferred laterally to only the neighbouring fibres over a short longitudinal distance. Because the overload due to the fibre break is distributed only "locally" on to the nearest surviving fibres, it is termed the "local load-sharing" model. The theoretical strength of composites has been shown to be higher than the mean fibre strength [14]. This has also been supported experimentally by some researchers [15], who showed that the impregnated Kevlar bundle strength increased to over 112% of the single fibre strength.

Analogously, the strength of a single fibre, considered to be a loose bundle of fibrils, is expected to be lower than the mean fibril strength. However, if the fibrils were bound together with a suitable matrix material, the same fibre would behave more like an impregnated fibril bundle, resulting in a much higher fibre strength. Interfibrillar adhesion would also prevent buckling and kinking and thus improve the compressive strength of the Kevlar fibre.

Various attempts have been made to bind the fibrils through covalent and hydrogen bonding transversely across the fibre [16–19]. However, because the separation of fibrils is likely to be larger than the bond distances, such molecular modifications were not very effective in improving the compressive strength of Kevlar. These results further indicate that the failure mechanism under compression is by buckling at the fibrillar level rather than at the chain level. In a recent study, McGarry and Moalli [20] applied a thin, high-modulus ceramic coating on the surface of PBO and Kevlar fibres. By restraining fibril buckling, they were able to improve the compressive strength of the PBO fibre.

Chemical modification of Kevlar is difficult because the wholly aromatic rigid nature of the polymer chain and the highly crystalline structure of the fibre severely restrict accessibility to the polar amide groups within the fibre. Researchers, however, have been successful in improving the interfacial adhesion between Kevlar and epoxy matrices by chemical treatments [21–23]. Various plasmas of gases such as ammonia, nitrogen, monomethyl amine and allylamine and other surface-limited chemical reactions have been used to incorporate polar and reactive functional groups on Kevlar fibre surface [24–27].

The present study focuses on improving interfibrillar adhesion by infiltrating a thin layer of polymeric material in an opened fibrillar network of Kevlar fibre. Various epoxy and novolac resins and bismaleimide polymers have been employed for this purpose. A micro-composite has thus been formed from Kevlar single filament, wherein the fibrils constitute the reinforcing phase and the infiltrated polymer serves as the matrix phase. Plasma modification using ammonia gas has also been used to enhance the bonding between the infiltrated polymer and the fibrils. While the effects of the polymer infiltration technique on the mechanical properties of Kevlar fibre have been studied, particular attention has been focused on improving the compressive strength of Kevlar fibre.

2. Experimental procedure
2.1. Materials
The fibres used in this study were extracted from a 380 denier, 267 filament Kevlar 49 spool, supplied by E. I. du Pont de Nemours and Co. Inc. The various polymers used in this study for infiltration were epoxy and phenolic resins and bismaleimide. The epoxy resins used in this study were bisphenol-A based epoxies, namely DER 331 and DER 332 and the phenolic resin was an epoxy novolac, namely DEN 438 novolac resin, all of which were supplied by Dow Chemical Company. Both aliphatic as well as aromatic amines were used as hardeners to cure these epoxies. The aliphatic amines, DEH 26 and DEH 20, were supplied by Dow Chemical Company, while the aromatic amine, *meta* phenylene diamine (MPDA), was supplied by Du Pont Chemicals. The bismaleimide polymer was supplied by Aldrich Chemicals.

2.2. Fibre opening
Opening of the fibre into a fibrillar network was initially attempted by both lateral compression of the fibres and by solvent swelling. Lateral compression was achieved by compressing the single fibre between two platens, one fixed and the other moving. This technique, however, gave inconsistent results due to the small diameter (12 μm) of the fibre and the surface unevenness of the platens. Solvent swelling, on the other hand, was found to be quick and effective as well as reproducible.

The solubility of the extended-chain liquid-crystalline PPTA polymer, from which Kevlar is derived, depends largely on the protonation or complexation of the chain backbone and is therefore restricted to strong protic or Lewis acids [1]. Suitable solvents for Kevlar are fuming sulfuric acid, chlorosulfonic and polyphosphoric acids. In the dry-jet wet-spinning operation of Kevlar fibre, the coagulation step, i.e. the phase separation of lyotropic liquid crystal polymers from a 99.9% sulfuric acid solution under certain conditions, yields a swollen network of micro-fibrils of around 5–10 nm in diameter [28]. The fibrillar hierarchy becomes developed as these micro-fibrils are dried and processed through subsequent operations. In order to infiltrate this micro-fibrillar network, two approaches could be adopted. In one approach, the matrix material could be infiltrated during the spinning operation itself when the fibre is still in the wet, swollen state [28]. Here, the micro-fibrillar mesh is not dried after emerging from the coagulation bath, but is treated with the matrix material while in the wet state. Farris *et al.* [29] have successfully used this technique to infiltrate PBZT fibres with selected matrix materials.

The other approach, which has been used in this study, is post-fibre manufacture where the fibre is immersed in the sulfuric acid bath of a much lower concentration than that of the spinning bath, so as to cause only swelling and not dissolution of the crystallites in the fibre. Ten to fifteen single fibres were extracted from the spool and mounted on a specially designed glass frame. The frame consisted of two tiers; fibres in the upper tier were used to study the effects of acid alone on the fibres, while those in the lower tier were used to study the effects of polymer infiltration after acid treatment. The frame was immersed in a sulfuric acid solution of a particular concentration for a predetermined period of time. Following the acid treatment, the fibres were kept in a tray and immediately washed in running water to remove any residual sulfuric acid. Removal of acid was confirmed by using pH paper. After washing for 10 min, the fibres were dried in air for 5 min before polymer infiltration. Acid concentrations and immersion times had to be optimized in order to achieve a reasonable amount of opening with minimal property losses due to the acid treatment. The effects of immersing the fibres for 15 s in acid concentrations ranging from 70%–85% on the mechanical properties of Kevlar fibre are reported.

2.3. Polymer infiltration
Three different types of thermosetting polymers were employed to infiltrate the opened fibrillar network. These included epoxy resins, phenolic (novolac) resins and polyimides. The epoxy resins used were DER 331 and DER 332, which are bisphenol-A-based liquid resins having two epoxide functionalities. Upon curing with various hardeners through the epoxide groups, these resin/hardener systems result in highly cross-linked thermoset polymers. The phenolic resin used in this study was DEN 438, which is an epoxy novolac resin having an average epoxide functionality of 3.6. This multifunctionality leads to an increased cross-link density which results in better physical and mechanical properties at elevated temperatures and improved chemical resistance as compared to the bisphenol-A-based resins.

The epoxy resins were polymerized in stoichiometric ratios with two different types of hardeners. Two aliphatic primary amines, DEH 20 (diethylene triamine) and DEH 26 (tetraethylene pentamine), and one aromatic amine (metaphenylene diamine, MPDA) were used for the purpose. The amines react with the epoxy group through the active amine hydrogens, and therefore, in theory, each primary amine group is capable of reacting with two epoxide groups. While the aliphatic amines are general purpose room-temperature curing agents (or can be cured faster at 100 °C for 2 h), the aromatic diamine is incorporated in the resin by melting at elevated temperatures. In general, the aromatic amines impart higher thermal and chemical resistance as compared to the aliphatic amines. The high-temperature stability of Kevlar has found increasing use in high-temperature composite applications. This requires a thermally compatible matrix which would be stable at high processing temperatures and subsequent applications. This is particularly true if Kevlar fibres are used with thermoplastic resins, e.g. poly (ether ether ketone), poly(phenylene sulfide) (PPS).

The third type of thermosetting polymer used as infiltrating matrix material was a methylene dianiline-based bismaleimide. Bismaleimides belong to a high-temperature-resistant class of thermosetting polyimides which are becoming increasingly popular in structural and electrical applications. They are low molecular weight, low-viscosity oligomers with an activated double bond as part of the five membered imide ring. These structures are highly reactive due to the two carbonyl groups that flank the double bond and can homopolymerize or react with other co-reactants through the double-bond end groups. The bismaleimide used in this study was cured at 230 °C for 3 h to obtain a highly cross-linked network. The resultant polymers possess higher temperature capabilities up to 225 °C compared to 175 °C for the epoxies. They also exhibit higher glass transition temperatures and have improved mechanical and electrical properties than epoxies. Further, their properties can be tailored by varying the chemistry of the backbone and end-groups. Bismaleimides have been shown to undergo a Michael addition reaction with aromatic amines [30] which suggests the possibility of a covalent bond formation with the amine end groups in Kevlar. It is understood, however, that a very few of these amine end groups would be present in the fibre.

These polymers were infiltrated in the opened fibrillar network by immersing the acid-treated, opened fibres in an acetone solution containing the resin/hardener or bismaleimide. The infiltration process was optimized for resin pick up by varying resin concentrations for a fixed immersion time of 10 min and by varying the immersion times for a 10% concentrated solution of resin/hardener in acetone. The infiltrated fibres were then heated in an oven to cure the resin and subsequently tested for their mechanical properties.

2.4. Plasma treatment

Ammonia plasma treatments were carried out in a plasma chamber, model PDC-32G made by Harrick Scientific Corporation. Ten to fifteen fibres were mounted on each tier of the glass frame, as described earlier, opened up in sulfuric acid, washed in running water, dried in air for 5 min and then inserted in the plasma chamber. The plasma was generated by a 13.56 MHz capacitively coupled discharge system which was pumped down to a vacuum of 2 torr (1 torr = 133.322 pa) prior to the admission of ammonia. The effects of different power levels, flow rates and treatment times on the mechanical properties of the fibre have been previously studied [31]. It was observed that above power levels of 60 W, the UV generated in the plasma chamber causes significant mechanical strength degradation of the fibres. In this study, a flow rate of 40 $cm^3 min^{-1}$ for 2 min at a power input of 60 W was selected as the optimal conditions for plasma treatment in this system. After plasma treatment, the fibre samples were flushed with ammonia for an additional 3 min to allow any residual surface radicals to combine with ammonia to form amine groups. The plasma-treated fibres were then infiltrated with the polymer resin in the same manner as described in the previous section.

2.5. Control of variability

Kevlar 49, like most brittle fibres, shows considerable variability in failure strength with coefficients of variation ranging up to 25%. This is attributed to the presence of flaws and surface irregularities along the fibre. Although the nominal diameter of these fibres was 12 μm, there was a significant diameter variability between different fibres extracted from the same spool. The effect of these variabilities on fibre strength has been studied by Schwartz *et al.* [32].

To minimize effects of variability on the mechanical properties of the fibre before and after treatment, each extracted fibre was divided into three parts. The first part was used to measure properties of the untreated (control) sample, the second part was mounted on the upper tier of the glass frame for determining the fibre properties after acid treatment alone, while the third part was mounted on the lower tier of the frame in which the polymer was infiltrated after acid treatment.

The fibre was subdivided into six parts when results of polymer infiltration with and without plasma treatment were to be compared. The three additional parts were used to determine the effect of plasma alone on the fibre; the effect of ammonia plasma on the acid-treated fibre; and the effect of polymer infiltration on the fibres which were treated with acid followed by ammonia plasma. These parts were mounted on another glass frame which had three tiers. Therefore, when the effects of polymer infiltration with and without plasma treatment were to be compared, two frames were used simultaneously. While one frame was treated with acid followed by polymer infiltration, the second frame was treated first with acid under the same conditions, treated with ammonia plasma, and finally infiltrated with the same polymer solution under identical conditions. The two frames were then kept in the oven for the curing operation and subsequently prepared for mechanical testing.

2.6. Mechanical property testing

As mentioned above, each single fibre was divided into three or more parts. Each part was further subdivided into two parts. One part was used to measure the linear density of the fibre using the vibroscope method according to ASTM D1577. The linear density is the mass per unit length of the fibre and is proportional to its cross-sectional area. The other part of the fibre was used to measure the tensile and compressive failure loads of the fibre. The failure loads and the areas of cross-section together were used to determine the failure stresses of each fibre. For tensile testing, the fibre was mounted on construction-paper tabs, following a modified version of ASTM D3379 [33]. Tensile testing of the fibres was carried out on the Instron Universal Testing Machine (model = 1122), interfaced with an IBM-AT computer. A gauge length of 20 mm and a strain rate of 2.5% were used.

Compressive testing of fibres was performed using the single-fibre recoil test using similar specimen-tabbing preparation and parameters outlined above [34]. In this test, the single fibre was loaded to a predetermined stress level and fibre recoil was initiated by cutting the fibre at its midpoint using surgical scissors. The scissors were supported on a fixed platform to enable steady, precise cutting. Both halves of the cut fibre were inspected under the optical microscope for kinks. Initially, the stress levels were low and showed no evidence of fibre kinking. The stress levels were then increased incrementally until kinking was observed, which marked the onset of compressive failure. This stress level was noted as the compressive strength of the fibre.

3. Results and discussion

Table I compares the mechanical properties reported in the literature for Kevlar 49 fibres with those obtained in this study at a gauge length of 20 mm [1].

3.1. Effects of acid treatment

Sulfuric acid concentrations ranging from 75%–85% were used to swell the Kevlar fibre and enable separation of fibrils for subsequent polymer infiltration. Figs 2–4 show the scanning electron micrographs of the Kevlar fibres opened using different acid concentrations. The fibrillar morphology of the Kevlar fibre is also revealed, with the fibrils running parallel to the fibre axis. Closer inspection of these micrographs suggest that the fibrils are not completely separated or split but overlap with each other at junctions along the fibre, indicating the formation of an interconnected network of fibrils. This structure is similar to that formed during the coagulation stage of the spinning process of Kevlar [28] and PBZT fibres [35].

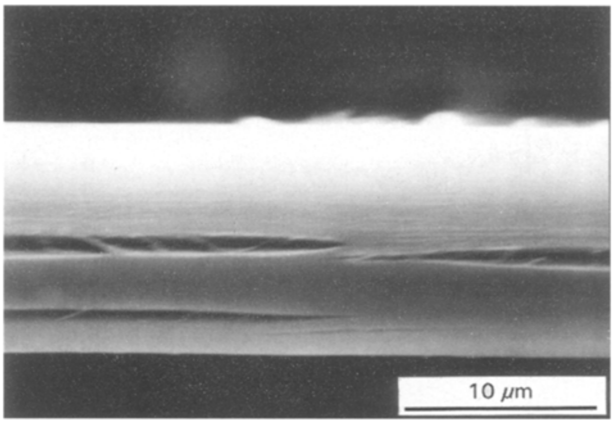

Figure 2 Scanning electron micrograph of a Kevlar fibre opened by 75% concentrated acid, 15 s.

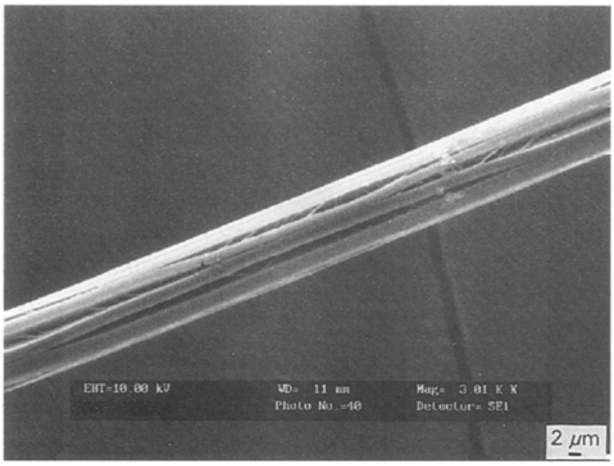

Figure 3 Scanning electron micrograph of a Kevlar fibre opened by 78% concentrated acid, 15 s.

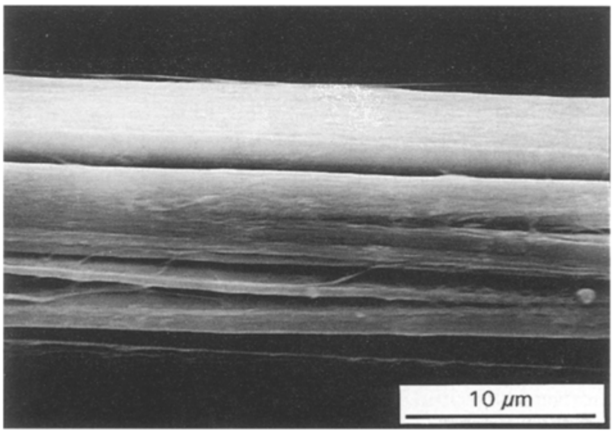

Figure 4 Scanning electron micrograph of a Kevlar fibre opened by 85% concentrated acid, 15 s.

While increasing the acid concentration increases the extent of opening of the fibre, it also affects the tensile strength as expected. The effect of increasing acid concentration on the fibre strength is shown in Fig. 5. A 25% loss in tensile strength was observed when the fibres were immersed for 15 s in an acid bath of 80% concentration, while at 85% acid concentration, the loss in strength was around 35%. While strength losses were not observed for acid concentrations below 75%, the extent of opening at low concentrations was almost negligible for effective polymer infiltration. This loss in strength at lower concentrations could be attributed mainly to the breakage of the weak hydrogen bonds between the polymer chains. However, at higher concentrations, acid-catalysed hydrolysis is possible, leading to chain scissioning and a greater strength loss. Degradation of Kevlar fibres

TABLE I Typical values of untreated Kevlar 49 fibre

	Tensile strength (GPa)	Tensile modulus (GPa)	Compressive strength (MPa)	Failure strain (%)
Reported	2.9	135	370[a]	2.8
Present study	3.7	107	374	3.5

[a] Obtained from tensile recoil tests [33].

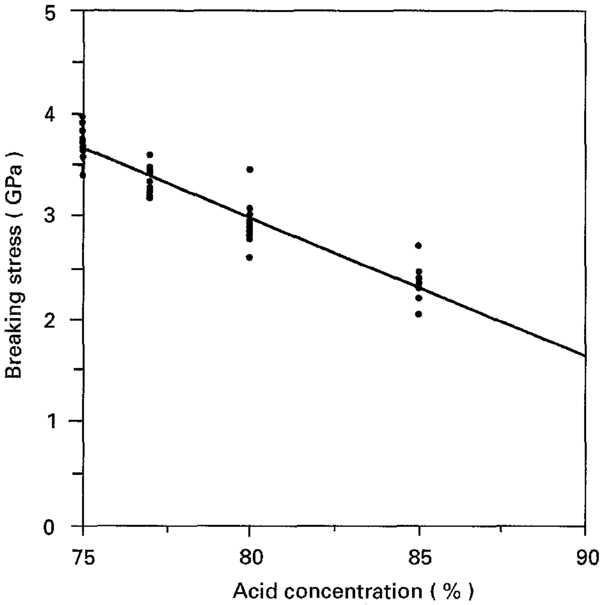

Figure 5 Effect of acid concentration on the tensile strength of Kevlar.

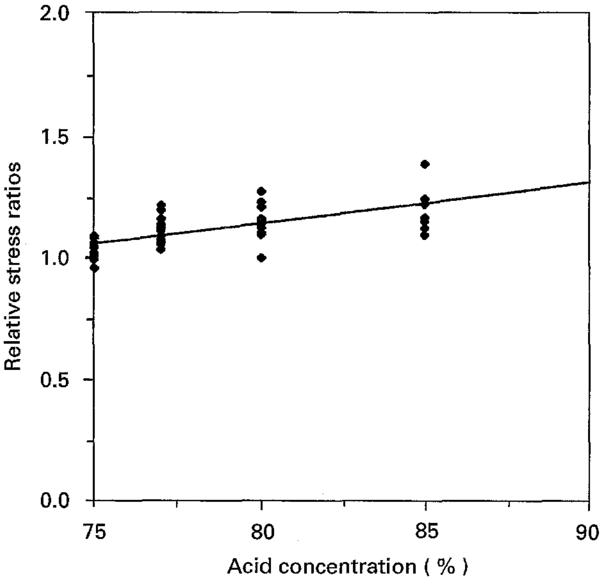

Figure 6 Relative comparison of stress ratios after (◆) acid and polymer infiltration.

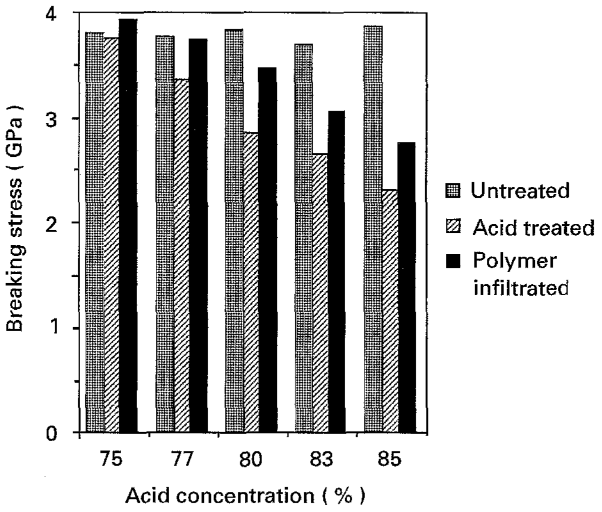

Figure 7 Changes in tensile strength after epoxy infiltration.

due to acid hydrolysis, has been observed by other researchers too in 100% sulfuric acid and other environments [36, 37]. Hydrolytic degradation can cause possible damage to the crystallites and fibrils resulting in breakage of the fibrillar network, thus contributing to a lower tensile strength.

3.2. Effects of polymer infiltration

3.2.1. Tensile properties

Interesting results were obtained when the acid-treated fibre was infiltrated with the epoxy resins and bismaleimide. Fig. 6 gives the ratio of the strength of epoxy infiltrated fibre to that of the acid-treated (opened) fibre as a function of acid concentration. For an acid solution of 77% concentration, the ratio of the strength of the epoxy infiltrated fibre to the acid-treated fibre is about 8%, which increases to 15% for an acid concentration of 80%, and 20% when an acid concentration of 85% is used. These results therefore demonstrate that polymer infiltration is possible, once the fibrillar network of Kevlar fibre is opened up. The increased strength with increased polymer infiltration confirms the earlier discussed theory of bundle strength. The theory applies to the present case where the load distribution changes from the "equal load-sharing" model for the untreated fibre, to "local load-sharing" after polymer infiltration.

Results of the changes observed in the tensile properties of the fibres at different stages of treatment, with epoxy as the infiltrating matrix, are shown in Figs 7–9. Fig. 7 shows the changes observed in the tensile strength as a function of acid concentration. It can be seen that at acid concentrations over 77%, although polymer infiltration helps the fibre recover some of its lost strength, it is still unable to attain its original untreated strength. However, at acid concentrations between 75% and 77%, the infiltrated fibre regains its original strength. It should be noted that 75% acid concentration appeared to be a lower limit for any significant swelling to occur. At this concentration, a marginal improvement in the tensile properties was observed. The presence of epoxy and bismaleimide polymers as matrix materials within the interfibrillar regions of the fibre is manifest in the higher failure strain values obtained after infiltration. This is indicated in the plot of failure strain versus acid concentration as shown in Fig. 8. Fig. 9 shows the effect of acid treatment and epoxy infiltration on the tensile modulus of the fibre. The tensile modulus of the fibre was also found to decrease with increasing acid concentration. This was expected because the modulus is primarily dependent on the chain rigidity, chain length and orientation along the fibre axis. Owing to chain scissioning, the tensile modulus is expected to decrease with increasing acid concentration. A similar trend in the tensile properties was observed when novolac resins and different epoxy/hardener combinations were used as the infiltrating polymers.

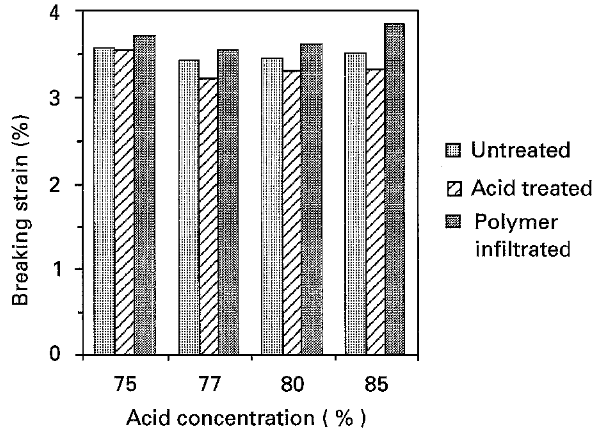

Figure 8 Changes in strain to break after epoxy infiltration.

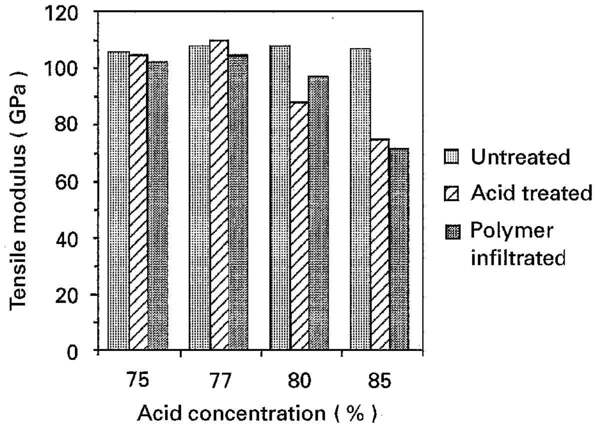

Figure 9 Changes in tensile modulus after epoxy infiltration.

All of the results above indicate the formation of a micro-composite of a single Kevlar fibre after polymer infiltration. The properties of the micro-composite can be explained by applying the basic rule of mixtures to the polymer-infiltrated fibre. While the presence of the infiltrated polymer increases the fracture strain of the fibre, it also mitigates the effect of tensile fracture by forming a cross-linked network around it. Further, the low volume fraction of the epoxy, coupled with its relatively low modulus compared to the fibre, is not expected to decrease the modulus significantly.

The amount of infiltrated polymer was increased by increasing epoxy concentration and infiltration time. However, results showed that this merely led to epoxy deposition on the fibre surface, thus preventing any further infiltration. Also, several blank experiments were conducted in which the fibres were immersed in the polymer bath without opening with acid treatment. The absence of any significant change in the tensile properties confirmed the necessity and effectiveness of the opening step in our approach. Therefore, while the efficacy of the infiltration technique is clearly demonstrated, any significant gain in the tensile strength is limited by the strength loss due to the acid treatment. At first glance, these results show that an acid concentration of around 77% would be an optimal condition where the fibre strength is not sacrificed while obtaining a reasonable amount of opening.

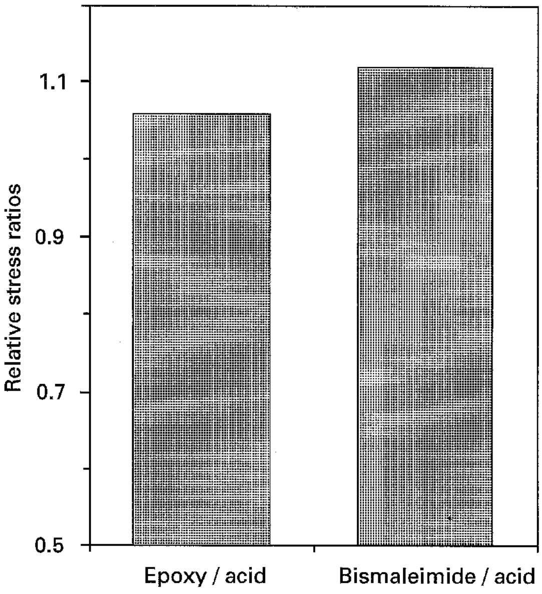

Figure 10 Comparison of epoxy and bismaleimide infiltration on the tensile strength of Kevlar fibre opened by 77% acid.

Infiltration using a 10% solution of bismaleimide was carried out after treating the fibre with 77% concentrated sulfuric acid. A comparison of the tensile strengths obtained using epoxy resin and bismaleimide after opening the fibre using 77% acid concentration is shown in Fig. 10. While the acid-treated fibre increased in tensile strength by 5%–6% after infiltrating with epoxy and novolac resin, infiltration by bismaleimide resulted in a strength increase of 12%. The higher strength could be due to the activated double bond in bismaleimide, which makes it more reactive than the epoxy resin. The increase in fracture strain and lower modulus values after bismaleimide infiltration follow a similar trend to those observed for the epoxy infiltrated fibre.

3.2.2. *Effects of plasma treatment on tensile properties*

The opened Kevlar fibre obtained by the acid treatment was also exposed to ammonia plasma to incorporate amine ($-NH_2$) groups on to the fibril surface before infiltrating the epoxy resin. Plasma exists as a cloud and can easily penetrate the crevices in the fibre and activate the fibril surface. While the bonding between the fibrils and the infiltrated resin without plasma treatment was more physical than chemical, treatment with ammonia plasma to incorporate amine groups is expected to form covalent bonds between them, thus binding the fibrils more strongly [24]. Ammonia plasma has been shown to increase the interfacial shear stress (IFSS) between Kevlar and epoxy [38].

As an index for the efficacy of the ammonia treatment, the interfacial shear strength (IFSS) of the unopened fibre was measured before and after plasma treatment. The IFSS was measured using the microbond technique, in which micro-drops of DER

TABLE II Effect of ammonia plasma treatment on Kevlar/epoxy IFSS

	Untreated	60 W	77 W
IFSS (MPa)	26.99	34.08	35.96

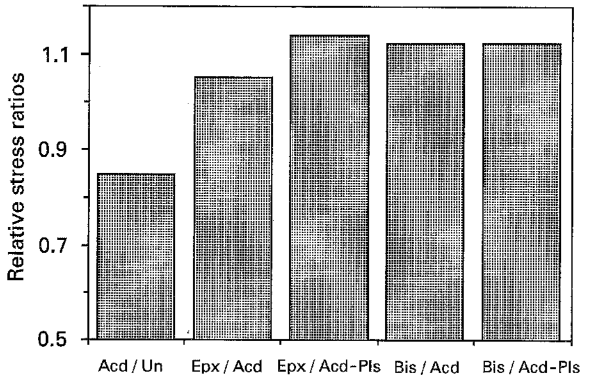

Figure 11 Effects of ammonia plasma on relative stress ratios of polymer infiltrated fibre. Acid/Un, acid treated versus Untreated; Epx/Acd, epoxy infiltrated versus acid treated; Epx/Acd-Pls, epoxy infiltrated after plasma treatment versus acid treated; Bis/Acd, bismaleimide treated versus acid treated; Bis/Acd-Pls, bismaleimide infiltrated after plasma treatment versus acid treated.

331/DEH 26 were cured at 100 °C for 2 h on the fibre surface [39, 40]. The micro-drops were sheared at a crosshead speed of 5 mm min^{-1} on the Instron using a microvice. The IFSS values obtained at two power input levels are shown in Table II. The values shown are an average of five replicates of the experiment. Results indicate a significant increase in the IFSS after treatment with ammonia plasma, confirming the earlier results [21, 24, 38]. A similar effect is anticipated at the fibrillar level, though the actual measurement of the IFSS at that level is difficult.

The effect of ammonia plasma treatment on the tensile strength was studied by opening the fibres using acid solutions of 77% concentration, subjecting them to ammonia plasma and then infiltrating the fibres with polymer. Fig. 11 compares the tensile strength of the fibres infiltrated with epoxy after plasma treatment to those which were infiltrated without plasma. While the increase in strength of the epoxy-infiltrated fibres without plasma treatment was 5% with respect to the acid-treated fibre, the strength of fibres subjected to ammonia plasma prior to infiltration with epoxy increased to 14%. These results suggest that ammonia plasma was effective in enhancing the bonding between the epoxy and fibrils, as expected, and therefore imposing greater resistance to shear between the fibrils. As mentioned earlier, cross-linking of epoxy around the fibrillar network was effected by curing the epoxy with primary amine hardeners. Apart from providing covalent bonding between the epoxy and Kevlar, the ammonia plasma incorporates primary and secondary groups, which could have resulted in improved cross-linking of the infiltrated epoxy. While the advantages of using ammonia plasma are evident from our results, care must be taken in optimizing the plasma conditions, so that the strength loss due to UV photodegradation, is minimal.

In contrast, no further improvement in the tensile strength was observed when bismaleimide was used as the infiltrating polymer after the plasma treatment. The results of this treatment are also shown in Fig. 11. Bismaleimide is a self cross-linking polymer and therefore incorporation of amine groups is not expected to increase the cross-linking any further. Cross-linking of bismaleimide is primarily due to the presence of carbonyl groups which cause homopolymerization of the imide ring.

3.3. Compressive properties

Compressive strength of Kevlar fibres was measured for fibres treated with 77% acid concentration followed by infiltration by bismaleimide and epoxy resin/hardener combinations described earlier. Results obtained from the tensile recoil tests are shown in Table III.

The compressive strength of 374 MPa obtained for the untreated Kevlar fibre compares fairly well with that obtained using the same technique by other researchers [20, 34]. Interestingly, the compressive strength of the fibre after acid treatment was almost the same as that of the untreated fibre. While breakage of hydrogen bonds and chain scission due to acid treatment decrease the tensile strength of the fibre, the compressive strength remains relatively unaffected. This suggests that the mode of failure of the fibre under compression is different from that under tension. As stated earlier, the critical elements governing

TABLE III Compressive strength of Kevlar fibre after polymer infiltration

	Untreated	Acid treated (77% conc.)	Epoxy resin/hardener Infiltration				Bismaleimide infiltration	
			DER 331 DEH 26		DEN 438 MPDA	Others^a		
			Without plasma	With plasma	Without plasma	Without plasma	Without plasma	With plasma
Compressive strength (MPa)	374	371	406	412	413	402	424	436

^{a}Others include DEN 438/DEH 26 and DER 331/MPDA resin hardener combinations.

the compressive failure of the fibre are the fibrils. In this study, we have assumed the Kevlar fibre to be a loose assemblage of fibrils, with only a small interaction between them. An acid treatment of 77% concentration merely results in breakage of the hydrogen bonds while separating the fibrils further for ease in polymer infiltration. Because the integrity of the individual fibrils within the fibre is still maintained with little or no interaction between them, the compressive strength of the fibre would be expected to be the same after acid treatment.

Promising results were obtained, however, when the fibres were infiltrated with polymer. An increase of about 8%–10% in the compressive strength is obtained when the fibre is infiltrated using the aliphatic epoxy/aliphatic hardener combinations. Infiltration by novolac resin also resulted in a similar increase in the compressive strength of Kevlar fibre. Further, ammonia plasma treatment prior to epoxy infiltration resulted in a marginal increase in the compressive strength of the fibre.

Infiltration using bismaleimide proved better than the epoxies, and resulted in over 13% increase in the fibre compressive strength. Plasma treatment with ammonia before bismaleimide infiltration resulted in about 17% increase in the compressive strength of the fibre.

The increase in compressive strength after polymer infiltration is primarily due to the cross-linked polymer network which serves the purpose of restraining the fibrils against buckling and kink-band initiation. Further, due to the increased fibril–fibril binding, the fibrils tend to buckle as a group as compared to the buckling of the individual fibrils occurring before polymer infiltration. Plasma treatment with ammonia, as seen earlier, increases the interfibrillar interactions thus resulting in an even higher compressive strength.

4. Conclusion

A new technique to modify the tensile and compressive properties of Kevlar 49 fibre by infiltrating a polymeric material into an opened fibrillar network has been investigated. Fibre opening was achieved by swelling the fibre in sulfuric acid with concentrations ranging between 75% and 85%. Although a strength loss was observed with increasing concentrations of acid, results suggested that the tensile properties are not sacrificed if the concentrations are kept around 75%–77%. Various commercial epoxy resin/hardener combinations and bismaleimide were used as the matrix material. While a significant improvement in the tensile strength of the polymer-infiltrated fibre was achieved in comparison with the acid-treated fibre, it was offset by the strength reduction by the acid treatment. The compressive strength of the fibre, however, showed a marked increase after infiltration with the polymers, with the bismaleimide performing better than the epoxy resins. Plasma treatment of the opened fibre further improved the binding between the fibrils, resulting in an increase in both the tensile strength as well as the compressive strength of Kevlar.

The polymer infiltration technique shows much potential in tailoring the fibre properties for selective end-use applications by a judicial combination of acid concentration and the matrix materials. This approach can be applied to other fibres as well, which are fibrillar in nature.

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