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Bonding of Amines to Carbon Fiber Surfaces to Improve and Control Adhesion: A New Paradigm for Adhesion in Carbon Fiber/Epoxy Composite Materials

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Abstract - We describe the immobilization of amines at the surfaces of high-modulus, pitch-based carbon fibers via direct, thermal reaction of the amine with the carbon fiber. Fourier transform infrared attenuated total reflectance spectroscopy (FTIR-ATR) and electrochemical measurements are used to demonstrate the immobilization. The influence of these reactions on the interfacial adhesion in carbon fiber-epoxy composite materials is investigated by using these fibers to fabricate composite test specimens with EPON-828 epoxy, and then using an embedded single fiber test to measure the interfacial shear strength between fiber and matrix for fibers that had been derivatized with didecylamine, dodecylamine, 1,9-diaminononane or 1,6-diaminohexane. A rational dependence of interfacial adhesion on the molecular structure of the immobilized amine is revealed. Further, by examining the interfacial shear strength in composites made from carbon fibers that had been derivatized with a mixture of amines, we demonstrate that by judicious choice of the relative amounts of these adhesion-controlling reagents in the derivatization mixture, it is possible to control the interfacial composition, thereby controlling the interfacial adhesion.

Key Words - Carbon fiber, composite, spectroscopy, cyclic voltammetry, dodecylamine, didecylamine, 1,9-diaminononane, 1,6-diaminohexane, embedded single fiber test, and polarized light observation.

1. INTRODUCTION

The development of strong and stiff carbon fibers (CF's) and their use as the reinforcing element in light weight composite materials is one of the major technological achievements of the past few decades. As the usage of the various CF types in these applications increased, so did the understanding of those materials properties that are needed for good composite performance. One property that has a very strong influence on this performance is the strength of the adhesion between the fiber and matrix. Since epoxy matrices are so commonly used, much of the work in this area has focused on the behavior of CF-epoxy composite materials. In particular, there has been a great deal of work on methods to enhance the interfacial adhesion in these materials. This contribution describes a new type of interfacial derivatization reaction for immobilizing amines at carbon fiber surfaces that can be used to manipulate the adhesion in CF-epoxy composite

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materials. The details of this immobilization process have been previously described [1]. Here we examine the results of this immobilization process on the adhesion in CF-epoxy composite materials using traditional mechanical testing methods. As will be discussed further below, these results provide a new paradigm for understanding the adhesive mechanism in these materials.

When used without any surface treatments, carbon fibers produce composites with very low interlaminar shear strength (ILSS). Many observations of this type led to the development of a number of surface treatments that could improve the fiber-matrix interfacial bonding. Several research groups [2-9] have studied various surface treatments toward this end, including both oxidative and nonoxidative methods. These techniques attempt to promote adhesion by increasing the mechanical interlocking between fiber and matrix by increasing the CF surface roughness or by increasing the reactivity of the interfacial region by producing surface functional groups that can enter into chemical bond formation with functional groups in the resin matrix. The latter notion has been a frequent topic of investigation. For example, Kozlowski and Sherwood [7] used X-ray photoelectron spectroscopy (XPS) to study the interfacial functional groups produced after the oxidation of carbon fibers. They concluded that there are two main types of functional groups produced on carbon fiber surfaces: the keto-enol or alcohol, and carboxyl/ester types. One reactive group present in many thermosetting resin is the epoxide group. Thus, they proposed a possible chemical reaction between these two types of interfacial functional groups and epoxides in the matrix as a means of promoting adhesion in CF-epoxy composites. This proposal is consistent with a large body of experimental evidence that shows good correlation between the presence of interfacial oxygen-containing functionalities and enhanced adhesion. Fitzer et al. [10] and Waltersson [11] also proposed reactions that might occur between functional groups present on the fiber surface and the amine groups of diamine compounds (present as the hardener) of the resin. These authors suggested that, in a first coupling step, chemical bonds are formed between interfacial carboxyl or hydroxyl groups and the diamines. Then, in a second coupling step, a diepoxide in the matrix is bonded to the amino groups. Pinson et al. [12] also demonstrated improvement in the adhesion of carbon fiber-epoxy composites by electrochemically oxidizing ω-diamines at CF surfaces with the hope that one amine group would react with the carbon fiber surface and that the other would remain free, being able to react later on with the epoxy groups of the resin. Thus, there is considrable precedent in the literature to support the notion that chemical bonding at the interface can influence the adhesion in these materials.

An alternative view of the origin of adhesion in CF-epoxy composite materials is one in which mechanical interlocking between roughness features on the CF surface and the matrix plays a prominant role. The key experiments that have been taken to support this view are those of Mimeault and Mckee [13] and Drzal [13]. Both groups used high vacuum, heat treatments to remove oxygen-containing functionalities from CF surfaces prior to composite fabrication. Based on their observations that adhesion was not significantly degraded when these functionalities were removed, both groups reached the same conclusion that the oxygen-containing functionalities do not play a pivotal role in producing interfacial adhesion in CF-epoxy composites. These results have been widely interpreted as suggesting that mechanical interlocking, and not interfacial chemical bonding, is the predominant mechanism by which adhesion is achieved in these materials [15,16]. However, these results actually only show that interfacial chemical bonding *that directly involves oxygen-containing functionalities* is not important in adhesion. As will be seen below, another possible interpretation of those results is that some other type of interfacial reaction (that does *not* necessarily involve oxygen-containing functionalities) may be influencing interfacial adhesion in these systems.

Based on these previous studies of interfacial adhesion and our recent demonstration of amine immobilization at CF surfaces via direct thermal reaction [1], we propose that a possible mechanism for producing good adhesion in these materials may involve the attack of amine reagents from the hardener directly at *non-oxygen-containing* reactive sites on the CF surface. Specifically, we propose that amines may add directly to vinylic C=C bonds at CF surfaces in a Michael-like reaction in which the C=C groups functions as an electrophile and the amine functions as a nucleophile. Figure 1 shows an illustration of such a reaction. In support of this proposal, we present data that speak directly to the contributions of interfacial chemical bonding to adhesion. First, we demonstrate (using FTIR-ATR and electrochemical measurements) that the direct, thermal reaction of amines with the carbon fiber surface can be used to attach adhesion-controlling reagents to the surface. Second, we demonstrate that, by judicious choice of these adhesion-controlling reagents, it is possible to control the interfacial composition, thereby controlling the interfacial adhesion.

This means of manipulating adhesion is depicted in Fig. 2. Reaction A shows the result of interfacial immobilization of simple N-alkylamines. In this case, if the amine immobilization process consumes most of the reactive sites at the CF surface, then the interfacial layer will not present the proper functionalities to the matrix material to produce good adhesion. Thus, direct chemical bonding between the surface and matrix is thwarted, and the interfacial shear strength in this case should be poor. Reaction B shows an example of interfacial immobilization of a reagent which <u>does</u> present the proper functionalities to produce good adhesion. In this case, direct chemical bonding between the surface and the matrix should be successfully mediated by the adhesion-controlling reagent, and adhesion is predicted to be improved relative to the case for Reaction A. Figure 3 shows the specific types of interfacial structures that were prepared to test these notions. In the sections below, we will present data that verify the general features of this idea and show how interfacial adhesion can be *rationally* manipulated using such an approach.

The success of this approach to engineering the interfacial molecular architecture to control interfacial adhesion is evaluated with standard mechanical tests using established protocols. The interfacial shear strength between fiber and matrix is measured by an embedded single fiber tensile test. This test provides a useful method to quantify the fiber-matrix interfacial bond strength [17]. The most critical limitation of this method is the requirement that the resin be transparent and of sufficient ductility to allow the critical fiber length to be obtained. The test specimen, which is a single fiber embedded a small dogbone-shaped resin sample (along the long axis of the sample), is shown in Fig. 4 [17]. The specimen is placed under an axial tensile stress in order to produce an axial strain of between one and three percent. The fiber will break into fragments when tensile stress of this magnitude is applied to the specimen. As the stress is increased, the fiber will continue to break until a critical length (l_c) is reached. The apparent fiber-matrix interfacial shear strength (τ_y) for a given sample can be estimated from the following equation [17]:

$$\tau_y = \sigma_f^u \ d / 2l_c \qquad (1)$$

where l_c is the fiber critical length, σ_f^u is the fiber ultimate tensile strength (4.4 GPa for Tonen HMU fiber), and d is the diameter of the carbon fiber (10 microns for Tonen HM fiber). The results of tests of this type on several composite samples that were fabricated using amine-derivatized CF's will be presented below. These will be seen to support the idea that interfacial adhesion can be rationally manipulated via amine immobilization reactions.

2. EXPERIMENTAL

A. Chemicals and Reactions. The chemical compounds used in this project, dodecylamine, didecylamine, 1,9-diaminononane and 1,6-diaminohexane (Aldrich), were distilled prior to use. Structures I-IV as shown in Fig. 3 were made by adding 0.02 mole each of dodecylamine (m.p.31°), didecylamine (m.p.38°), 1,9-diaminononane (m.p.37°) or 1,6-diaminohexane (m.p.43°) to a vessel containing Tonen HMU pitch-based (Tonen Corporation, Japan, HMU type, i.e., high-modulus surface untreated fiber) or HMS (surface treated with a proprietary oxidation process by Tonen Co.) carbon fibers in an amount sufficient to cover the fibers. These reactions were processed without solvent, under N_2, and at high temperature (150°C & 180°C) for different periods of time. Following reaction, the products were rinsed repeatedly with toluene and acetone and dried in a vacuum oven (100°C) for 8 hours. Extensive, prolonged exposure of these derivatized CF's to a variety solvents was used a means of excluding the possibility of adsorption or entrappment of the amine compounds onto or within cracks at the CF surface. Thus, the observations presented below of amine addition products at the surface of these CF's are definitely not due to these processes, rather, they are due to irreversible immobilization at the surface, presumably via covalent bond formation.

B. Instrumentation. FTIR-ATR was used to spectroscopically characterize some of the surface modification products. A Mattson CYGNUS 100 spectrometer with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector functioning in the range of 4000 -800 cm^{-1} was used. The spectrometer was continuously purged with nitrogen gas to minimize water vapor and atmospheric CO_2. Absorbance spectra were collected at a resolution of 4 cm^{-1} with 1024 scans. A SPECTRA-BENCH model ATR attachment and a germanium internal reflection element (SPECTRA-TECH Inc) with dimensions of 50 x 20 x 2 mm and with end face angle of 45° were used. Electrochemical experiments were done with a PAR 273 potentiostat and employed a conventional electrochemical cell, a platinum counter electrode, a saturated calomel electrode (SCE) as a reference electrode, and a 4 cm single carbon fiber used as the working electrode. The solutions were purged with argon prior to all experiments.

C. Embedded single fiber specimen preparation. A diglycidyl ether of bisphenol-A (EPON 828, Shell Chemical Company) cured with 14 parts per hundred by weight of meta-phenylenediamine (m-PDA, Aldrich) was chosen as the epoxy matrix. The structures of these materials are shown in Figure 5. The preparation of embedded single fiber specimens involves several steps. First of all, a single fiber was extended across a dogbone-shaped cavity in a mold made of RTV silicone rubber. After anchoring the fibers in the mold, the mold was heated in an oven at a temperature of 75°C. A syringe was used to inject the heated (75°C) and degassed resin into the cavities of the warm mold. The specimens were cured at 75°C for 2 hours and then 125°C for 3 hours. The critical length measurements employed a locally fabricated device for applying the tensile stress while the sample was observed using optical microscopy. The specimens were observed at a magnification of 75X using a Bausch & Lomb StereoZoom Model 4 Binocular Microscope. The fragment lengths were measured with an eyepiece containing a calibrated micrometer scale.

3. RESULTS AND DISCUSSION

A. FTIR-ATR and electrochemical characterization of alkylamine treated carbon fibers.

After carbon fibers are reacted with either didecylamine or 1,6-diaminohexane, the FTIR-ATR method can be used to characterize the interfacial products of this thermal reaction. FTIR-ATR has been shown to be a versatile technique that is very useful in the characterization of chemical functionalities and orientation of molecules at surfaces or in thin films [18]. This technique has been applied to the characterization of carbon fiber surfaces in several previous publications[18,19]. The asymmetrical (υ_{as}, CH2) and symmetrical (υ_{s}, CH_2) C-H stretches, near 2926 cm^{-1} and 2853 cm^{-1} [20], should be easily observed in FIR-ATR experiments due to the long alkyl chains of both compounds. Figure 6 shows the ATR spectra of pitch-based carbon fibers reacted with these two compounds, and also of a "bare" carbon fiber sample (i.e. one which has not been previously reacted with amines). These data give unambiguous evidence for the permanent, covalent immobilization of the amine-derived adducts at the CF surface following the reaction. However, they do not provide information on the type of linkage to the surface. Attempts to observe the C-N stretch of the adducts proposed in Figure 3 were unsuccessful due to interference from small amounts of atmospheric moisture in the spectrometer. Also, quantitative analysis of these data is not possible because the surface area probed in the FTIR-ATR sampling configuration is not known.

Because of our inability to determine the amine surface coverage from the FTIR-ATR spectral data, an electrochemical method was developed to assay the yield of amines immobilized at the surface in these reactions. The details of this method were presented in another publication [1]. Briefly, the method involved protonation of the amines in solutions of relatively low pH (i.e. pH = 1), followed by electrostatic binding of an anionically charged redox probe (such as $Fe(CN)_6^{3-}$) to the cationically charged amine groups. Then, electrochemical measurements are used to determine the amount of the redox probe at the surface, from which the amount of immobilized amine is inferred (based on the charge stoichiometry). Analysis of the results of such experiments for these samples reveals that the surface coverage of the amines is ca. 5×10^{-11} mol cm^{-2}. Thus, the surface coverages achieved in these reactions are quite high, representing between 5% and 25% of a monolayer.

The attachment of didecylamine and 1,6-diaminohexane at the CF surface can also be qualitatively demonstrated by comparing their double layer charging currents with that of a bare carbon fiber. The double layer charging current is proportional to the differential capacity of the double layer at the CF surface (i.e., $i_c = C_{DL} \times \nu$, where ν is the scan rate) [21]. The differential capacity of a carbon fiber whose surface has been modified with long alkyl chains, C_{DL}', should be smaller than that of a bare carbon fiber, C_{DL}, so the double layer charging current of a carbon fiber with long chains should be less than that of a bare carbon fiber [21]. This is because the differential capacitance is inversely related to the thickness, d, of any dielectric layer that intervenes between the electrode surface (i.e. the fiber surface) and the solution [21], according to the following relationship between the differential capacitance and the thickness of the dielectric layer:

$$C = \varepsilon\varepsilon_o/d \qquad (2)$$

where d is the thickness of dielectric layer, ε is the dielectric constant of the layer, and ε_o is the permittivity of the free space [21]. As Fig. 7 shows, the double layer charging current of carbon fiber that has been treated with didecylamine is only about 1/3 of that of a bare carbon fiber, or about 2.3 $\mu F/cm^2$. Also, the cyclic voltammogram of this carbon fiber looks more featureless than that of a bare CF. On the other hand, for a carbon fiber derivatized with 1,6-diaminohexane, the double layer charging current is not significantly different than that observed for the bare fiber, as shown in Fig. 7C. This may be due to the reduced chain length, a smaller surface coverage, or a larger dielectric constant for the amine layer for this case compared to the didecylamine case. These qualitative changes in C_{DL} for the amine-derivatized CF's are consistent with the immobilization of amines at the CF surface. However, they do not provide a quantitative measure of the extent of immobilization. Thus, we interpret these comparisons simply as an indication that low to moderate surface coverages of these amine derivatives can be produced on carbon fiber surfaces, an interpretation that is consistent with our model of Michael-like addition chemistry, but certainly not exclusively so.

B. Embedded single fiber tests of N-alkylamine treated Tonen HM fiber/EPON 828-mPDA composites.

1. di-N-alkylamine and N-alkylamine individual specimens.

The results of embedded single fiber tests for the didecylamine and 1,6-diaminohexane treated Tonen HMU pitch-carbon fiber/EPON-mPDA specimens are shown in Table 1. The apparent fiber-matrix interfacial shear strength, τ_y, was measured at 42, 20 and 26 MPa (megaPascal) for Tonen HMU + 1,6-diaminohexane, Tonen HMU + didecylamine, and Tonen HMU, respectively. As expected, the interfacial strength of the 1,6-diaminohexane sample shows a 60% improvement over the control sample, presumably due to the chemical bonding between the free end of the immobilized amine and the epoxy groups in the resin. For the didecylamine sample, we speculate that the long alkyl chains of didecylamine blocked some of the resin molecules from reacting with the carbon fiber, leading to a poor interfacial shear strength, 22% less than that of the HMU control experiment.

The values in the table show a fairly large standard deviation. This large variation of the values obtained from this particular test is commonly observed because the tensile stress reaches a maximum at a distance $l_c/2$ from the ends. Therefore, the ultimate lengths of the fiber fragments will ideally range from $l_c/2 \leq l \leq l_c$. In consequence, a distribution of critical lengths is usually measured [22]. Narkis, et al. [23] indicated that, based on these considerations, coefficients of variation exceeding 50 percent are expected. In reality, the coefficients of variation are typically in the range of 10 to 30 percent, as reported by Bascom and Jensen [22]. Thus, coefficients of variation of the magnitude observed in Tables 1-3 are quite acceptable.

A weak boundary layer exists on most carbon fibers after the carbonization and graphitization manufacturing processes [24]. This is another factor that must be considered to gain a full understanding of adhesion. One approach to evaluate the importance of this weak boundary layer to the interfacial adhesion in these systems is to test the adhesion before and after removal of the weak boundary layer. Typically, the boundary layer is removed electrochemically, as part of the normal surface treatment. However, we chose not to use this approach because these treatments also change the numbers and types of surface functional groups on the fiber. Thus, we attempted to use sonication as a way to remove the weak boundary layer. Sonication is known to lead to cavitation (i.e. bubble formation) at surfaces [25], as do the electrochemical treatments. Since this is a likely mechanism by which the weak boundary layer is dislodged in the electrochemical treatments [26], sonication would seem to be a reasonable approach to achieve this end. Thus, a set of reactions was run under otherwise identical conditions as described above, but the bare carbon fibers were sonicated in distilled water at room temperature for two hours before reaction. The results of embedded single fiber tests are shown in Table 1B for these three samples, Tonen HMU + 1,6-diaminohexane, Tonen HMU + didecylamine, and Tonen HMU are 45, 25 and 30 MPa, respectively. Little change is observed.

Reaction temperature may play an important role in influencing the quantity of amine immobilized via these thermal reactions. To test this, we systematically varied the reaction temperature and examined the resulting interfacial adhesion. Toward this end, another set of reactions was done with Tonen HMU pitch-based carbon fibers at a higher temperature (180°C) for 15 hours. Before reaction, the bare carbon fibers were heated at 200°C in vacuum (<0.01 torr) for 24 hours to eliminate desorbable impurities on the CF surface. The embedded single fiber testing results are shown in

Table 2. These results are similar to those in Table 1. However, the reaction with 1,6-diaminohexane clearly shows adhesion that is much superior to the values in Table 1. In fact, in this case, the interfacial shear strength of the 1,6-diaminohexane sample (59 MPa) shows a 100% improvement over the control sample (28 MPa).

In addition to 1,6-diaminohexane and didecylamine, various other alkylamines were reacted with Tonen HMS and HMU pitch-carbon fibers at 180° C for 17 hours. Table 3 shows the results of embedded single fiber tests on these samples. There are two salient features of these data. First of all, the large interfacial shear strengths of 1,9-diaminononane (83 MPa) and 1,6-diaminohexane (59 MPa) treated Tonen HMS carbon fibers reveal that the enhancement of adhesion in these carbon fiber-epoxy composites from the diamine treatment approach is quite promising. In fact, the value of 83 MPa is the highest interfacial shear strength reported to date for Tonen HM-type fiber composites [15], and is comparable to the performance of the Hercules AS-4/EPON 828 composite system, which is a benchmark for adhesion measurements [14,15]. However, it is unclear at this point why the length of alkyl chains of diamines affects the interfacial shear strength of carbon fiber/epoxy composites. Further investigations will be necessary to better understand how the structure of an di-N-alkylamine influences the adhesion in carbon fiber/epoxy composites.

The second important point is that the N-alkylamine and di-N-alkylamine reagents are clearly seen to inhibit the development of strong interfacial adhesion in these composite samples. In fact, the interfacial shear strength of the didecylamine sample (21 MPa) is actually poorer than that of the HMU control sample (28 MPa). To further evaluate how the structure of the amine reagents influences interfacial adhesion, we tested several additional samples in which the amine reagent was either a simple N-alkylamine (such as dodecylamine) or a di-N-alkylamine (such as didecylamine). The embedded single fiber test results shown in Table 3 indicate that didecylamine (20 MPa) is considerably more effective at reducing adhesion in these composites than is dodecylamine (29 MPa), and that both give interfacial shear strengths considerably below the HMS control value (36 MPa). This effect is most likely due to the increased streric bulk of the two alkyl chains in didecylamine reducing the accessibility of the carbon fiber surface to the amine functional groups in the matrix material, thereby reducing the number of interfacial bonds formed between the surface and the matrix and depressing the interfacial adhesion.

These results suggest that it may be possible to control the adhesion in such systems in a relatively straightforward way by manipulating the interfacial composition of the amine adhesion-controlling reagents, a topic that is addressed in the next section. It is worth noting here that the control of interfacial adhesion is important in a wide variety of applications. For example, under conditions where the strength of the composite is of primary importance, one would desire to maximize the interfacial shear strength. On the other hand, under conditions where the impact resistance of the composite is more important than strength, one would chose to suppress the interfacial shear strength, since this typically gives better impact resistance due to termination of crack propagation at the fiber-matrix interface. An important point in this regard is that there are at present no rational approaches to manipulating interfacial shear strength with the type of fine control that is potentially offered with the methods described in the next section.

2. Mixtures of di-N-alkylamine and N-alkylamine specimens

The results discussed in the previous section demonstrate that it is possible to modify the interfacial shear strength of carbon fiber-epoxy composites through the use of alkylamine adhesion-controlling reagents. This suggests that it may be possible to *manipulate* the adhesion in these composites simply by controlling the interfacial composition of the adhesion-promoting and adhesion-depressing amine reagents. To test this notion, we reacted several mixtures of N-alkylamines and di-N-alkylamines with carbon fibers and examined the resulting single fiber test results. A basic premise of this experiment is that the composition of the reaction medium should influence the composition of the interfacial species, i.e. that the ratio of N-alkylamine to di-N-alkylamine in the reaction medium should influence the ratio of these two species at the surface, and therefore, influence the interfacial adhesion. The values shown in Table 3 clearly show that the results for these samples are intermediate with respect to those of the pure samples, in agreement with expectations.

These results can be most easily represented graphically in the form of a plot of the interfacial shear strength for a given series of reactions versus the ratio of the two types of amine reagents in the reaction medium. Such a plot is given in Fig. 8 for the case of 1,6-diaminohexane and didecylamine. This plot clearly shows the monotonic relationship between the interfacial shear strength and the ratio of amine reagents in the reaction medium. The fit to a direct, linear relationship is not perfect ($R^2 = 0.9557$), however, this is most likely due to the fact that the ratio of interfacial compositions of the two amines need not be the same as their ratio in the reaction medium. Nevertheless, this result is very encouraging because it represents the first successful demonstration of manipulation of interfacial adhesion in composites of this type using a rational approach based on direct knowledge of the chemical reactions from which the interfacial adhesion actually arises.

4. CONCLUSIONS

These results clearly show that amines can, indeed, be immobilized at carbon fiber surfaces, that this immobilization can be monitored in a straightforward way with FTIR-ATR and electrochemical measurements, and that it can be used to manipulate the interfacial adhesion in carbon fiber-epoxy composite materials produced from these derivatized fibers. It is especially significant that the adhesion results can be easily understood based on the molecular structures of the immobilized amines. These findings are consistent with our previous speculation that the amines are immobilized via nucleophilic attack at vinylic groups at the carbon fiber surface [1]. Interestingly, these ideas are also consistent with previous observations by others that adhesion in CF-epoxy composite materials can be correlated with the extent of surface oxidation of the carbon fibers during the oxidative pretreatments [7], because the electrophilic reactivity of a vinylic group would be considerably enhanced toward nucleophilic attack by an amine if it were conjugated with an electron withdrawing moiety, such as a carbonyl or carboxyl group [27,28]. Thus, the yield of chemical bonds between the

CF surface and the matrix (and, therefore, the interfacial adhesion) should depend on the extent of surface oxidation of the CF, not because of direct reaction between the oxygen-containing functionalities at the CF surface and nucleophilic species in the matrix, but because these oxygen-containing functionalities activate the *intrinsic* surface groups at the CF surface toward reaction with the nucleophiles in the matrix. These notions also are consistent with the previous results of Drzal [14] and Mimeault and Mckee [13], who demonstrated that removal of the oxygen-containing functionalities did not significantly reduce the interfacial adhesion in CF-epoxy composites. Thus, rather than taking their findings to imply that the adhesion is predominantly due to mechanical interlocking, we suggest that they imply that other interfacial coupling reactions can take place in the absence of oxygen-containing functionalities, namely the direct attack of amines at functional groups that are intrinsic to CF surfaces, such as vinylic groups.

There are several concluding remarks that can be made regarding the experimental results that have been described in the past sections. First, we believe these results require that we completely rethink our understanding of the adhesive mechanism in these composite materials. We interpret these findings as very suggestive that mechanical interlocking [15,16] does not play a significant role in adhesion in these systems. For example, if mechanical interlocking contributed the majority of the adhesive bonding in these systems, the results for the N-alkylamine and di-N-alkylamine samples should have been quite similar (i.e. manipulation of the surface chemistry should have had no effect), when in fact very different, and predictable, changes in adhesion in these samples were observed. Second, the results of the experimental study of the effect of mixtures of N-alkylamine and di-N-alkylamine adhesion-controlling reagents on the interfacial shear strength clearly show that it is possible to develop a predictive methodology for the composite material properties that will be produced using any given set of pretreatment conditions. This suggests that composite fabrication can be a much more precise and predictable science than it has been in the past.

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(A)

Thermal reaction at 150° C for 28 hours	Interfacial shear strength
Tonen HMU + 1,6-diaminohexane	42 ± 14 MPa
Tonen HMU + didecylamine	20 ± 5 MPa
Tonen HMU pitch fiber (control)	26 ± 6 MPa

(B)

Thermal reaction at 150° C for 18 hours (fiber was sonicated in water 2 hours before reaction)	Interfacial shear strength
Tonen HMU + 1,6-diaminohexane	45 ± 16 MPa
Tonen HMU + didecylamine	25 ± 6 MPa
Tonen HMU pitch fiber (sonication)	30 ± 9 MPa
Tonen HMU pitch fiber (non-sonication)	29 ± 8 MPa

T2

Thermal reaction at 180° C for 15 hours	Interfacial shear strength
Tonen HMU + 1,6-diaminohexane	59 ± 20 MPa
Tonen HMU + didecylamine	21 ± 7 MPa
Tonen HMU pitch fiber (control)	28 ± 8 MPa
Tonen HMU + 1,6-diaminohexane (2/3) + didecylamine (1/3) mixture	47 ± 22 MPa

Thermal reaction at 180° C for 17 hours	Interfacial shear strength
Tonen HMS pitch fiber (control)	36 ± 12 MPa
Tonen HMS + 1,6-diaminohexane	59 ± 19 MPa
Tonen HMS + 1,9-diaminononane	83 ± 33 MPa
Tonen HMS + dodecylamine	29 ± 7 MPa
Tonen HMS + didecylamine	20 ± 5 MPa
Tonen HMS + 1,6-diaminohexane (1/4) + didecylamine (3/4) mixture	25 ± 8 MPa
Tonen HMS + 1,6-diaminohexane (1/2) + didecylamine (1/2) mixture	36 ± 10 MPa
Tonen HMS + 1,6-diaminohexane (3/4) + didecylamine (1/4) mixture	47 ± 19 MPa
Tonen HMS + 1,9-diaminononane (1/2) + didecylamine (1/2) mixture	48 ± 14 MPa

Tonen HMS : commercially surface treated by Tonen Co.

Figure Captions

Fig. 1. A possible mechanism for attack of amine reagents at vinylic groups at CF surfaces.

Fig. 2. Illustration of the use of adhesion-controlling reagents to manipulate interfacial adhesion in CF-epoxy composites.

Fig. 3. Specimen geometry used for critical length tests.

Fig. 4. Structures of the proposed interfacial adducts formed from the amine immobilization reactions.

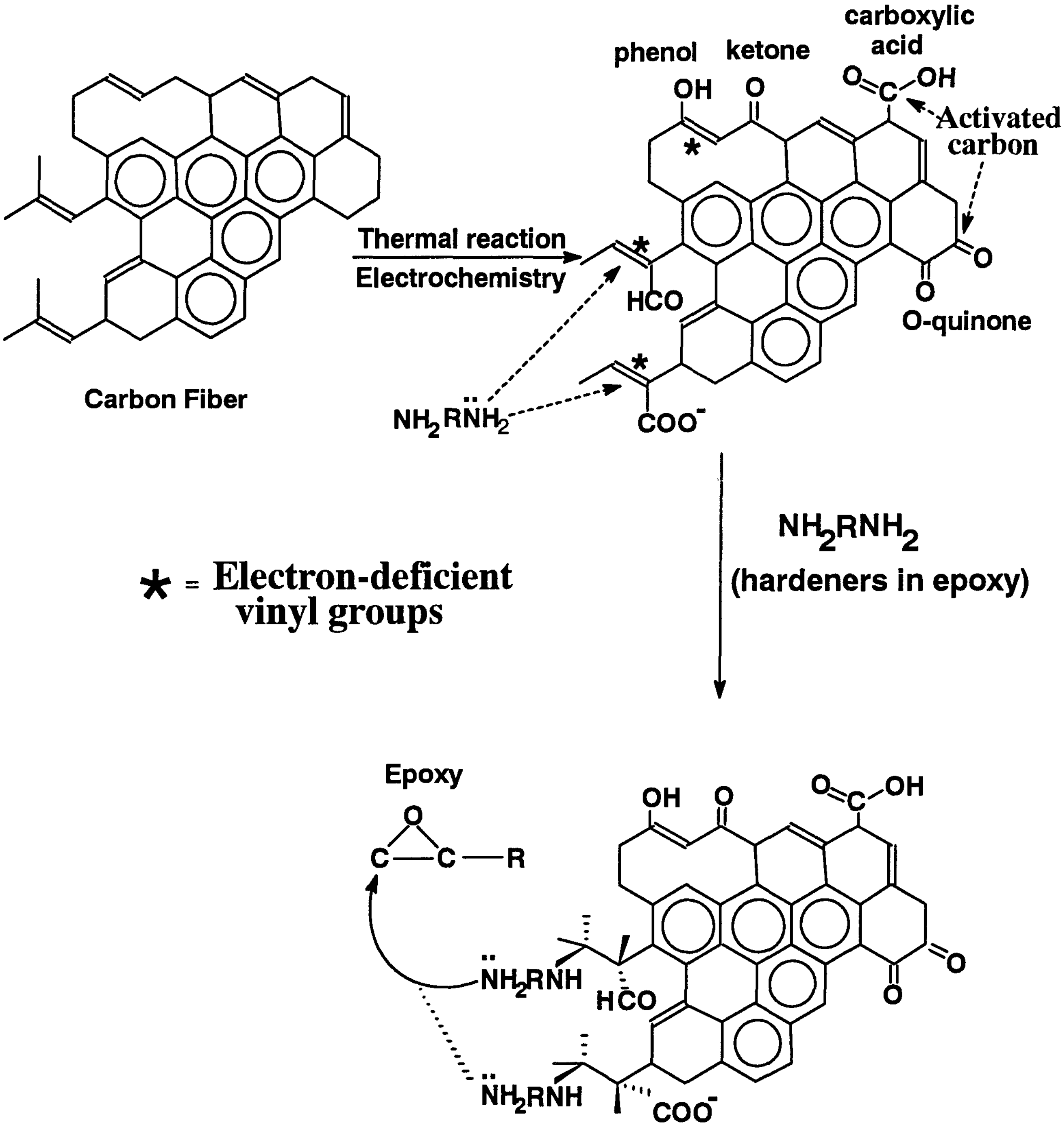
Fig. 5. Structures of the resin components used to produce the composites.

Fig. 6. FTIR-ATR spectra of CF's after reaction with A) didecylamine, and B) 1,6-diaminohexane. C) Spectrum of a bare CF sample.

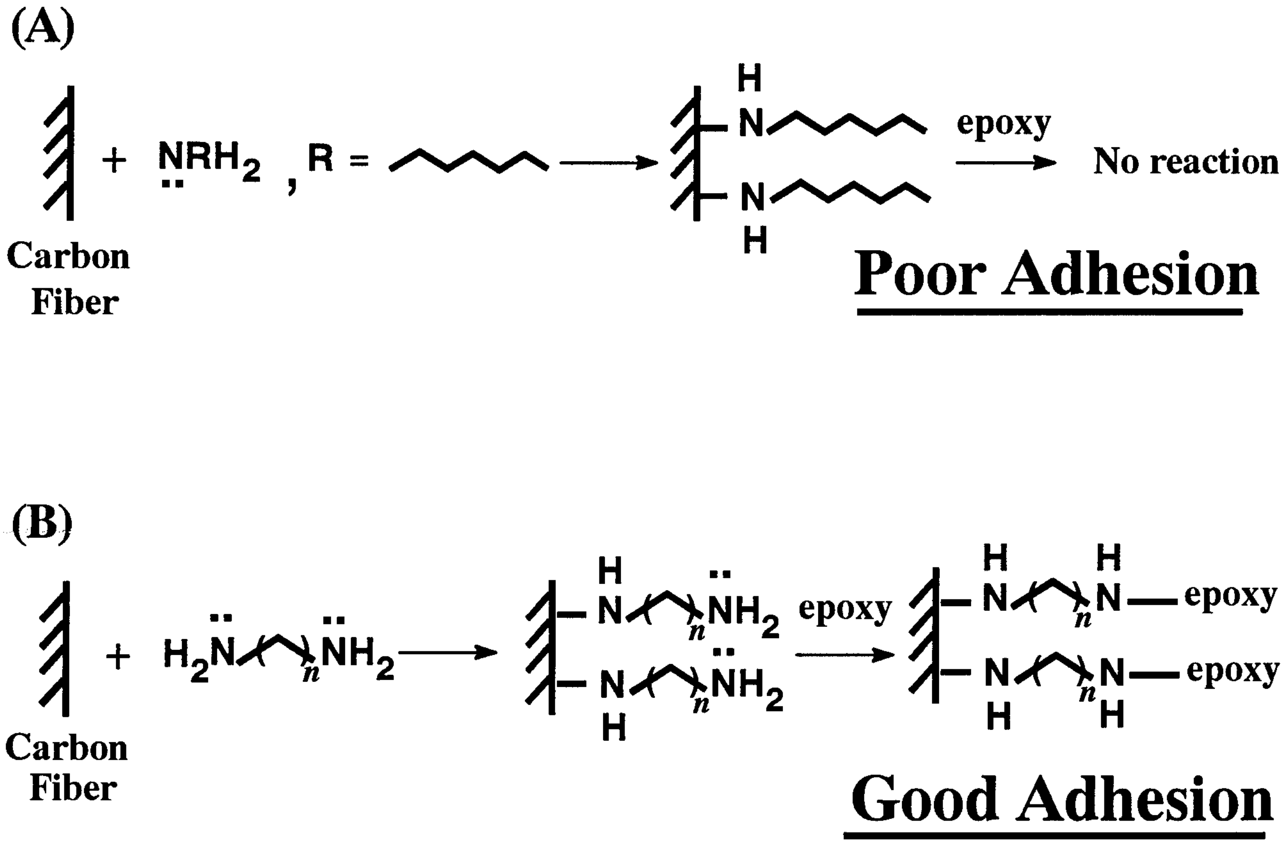
Fig. 7. Cyclic voltammograms of individual, 4 cm length carbon fibers. Supporting electrolyte: 0.1 M H_2SO_4, scan rate: 100 mV/s. A) didecylamine-derivatized CF, B) 1,6-diaminohexane-derivatized CF, C) bare CF.

Fig. 8. Plot of interfacial shear strength (from critical length tests) versus mole fraction of 1,6-diaminohexane in five reaction mixtures composed of 1,6-diaminohexane and didecylamine.

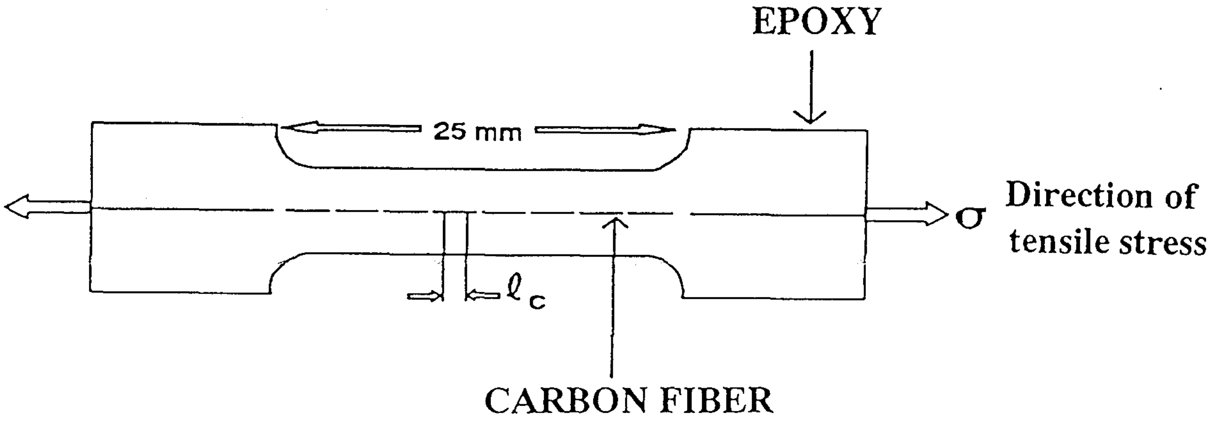
F1


Carbon Fiber
Thermal reaction
Electrochemistry
phenol
ketone
carboxylic acid
OH
O
O
C
OH
Activated carbon
HCO
O
O
O-quinone
$NH_2R\ddot{N}H_2$
COO⁻
*
NH_2RNH_2
(hardeners in epoxy)
* = Electron-deficient vinyl groups
Epoxy
O
C—C—R
$\ddot{N}H_2RNH$
HCO
$\ddot{N}H_2RNH$
COO⁻
OH
O
O
C
OH
O
O

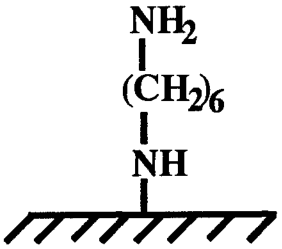
F2


(A)
Carbon Fiber
+ NRH2 , R =
H N
N H
epoxy
No reaction
Poor Adhesion
(B)
Carbon Fiber
+ H2N n NH2
H N n NH2
N H n NH2
epoxy
H N n N — epoxy
H N n N H — epoxy
Good Adhesion

F3

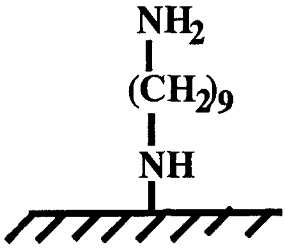

EPOXY
25 mm
σ
Direction of tensile stress
ℓ_c
CARBON FIBER

F4



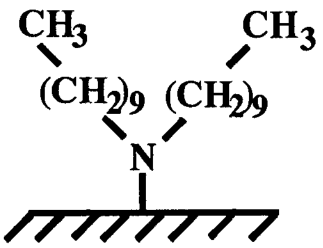
1,6-diaminohexane

I



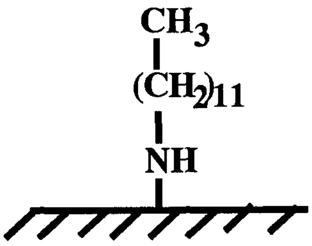
1,9-diaminononane

II



didecylamine

III

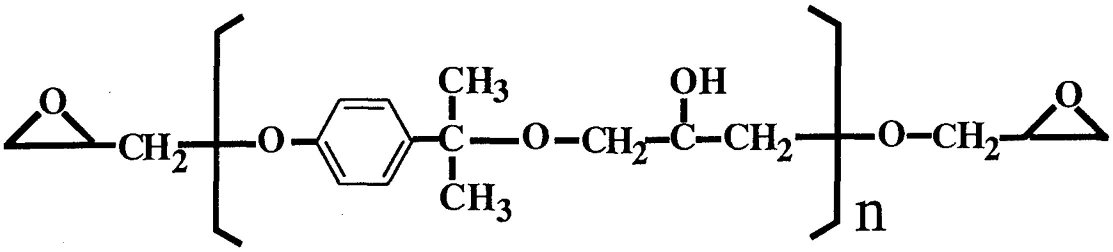


dodecylamine

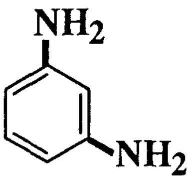
IV

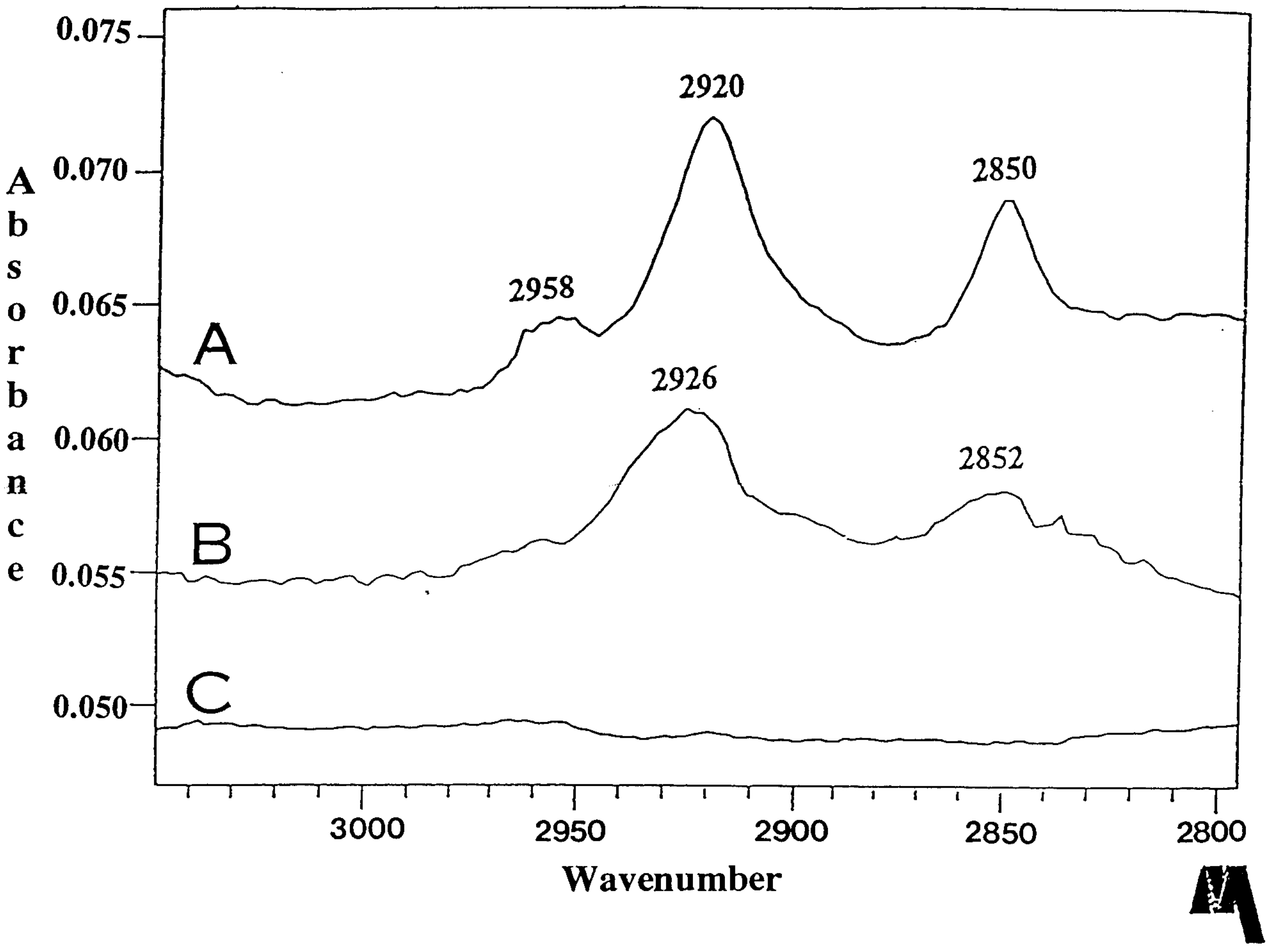
F5

EPON 828 epoxy

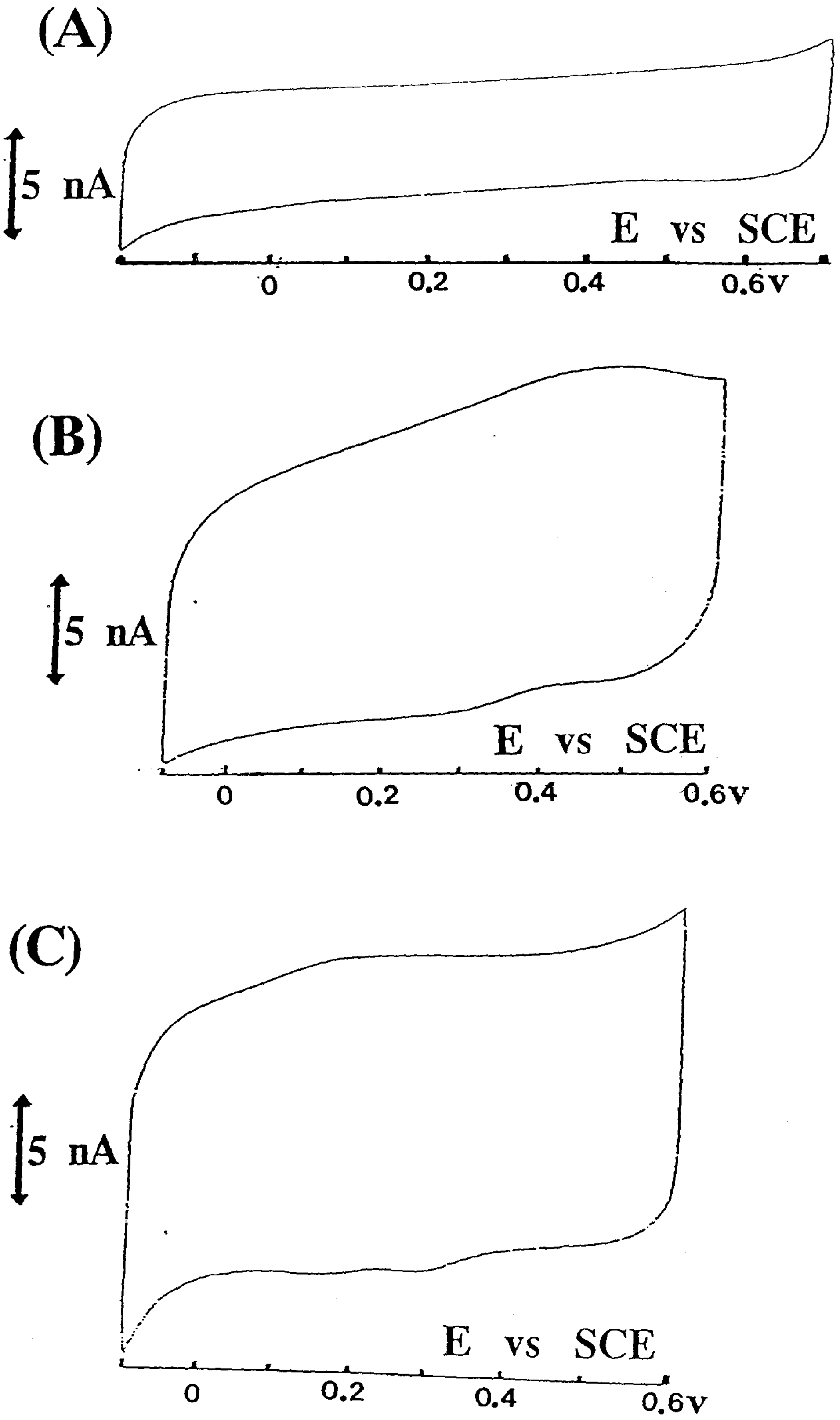


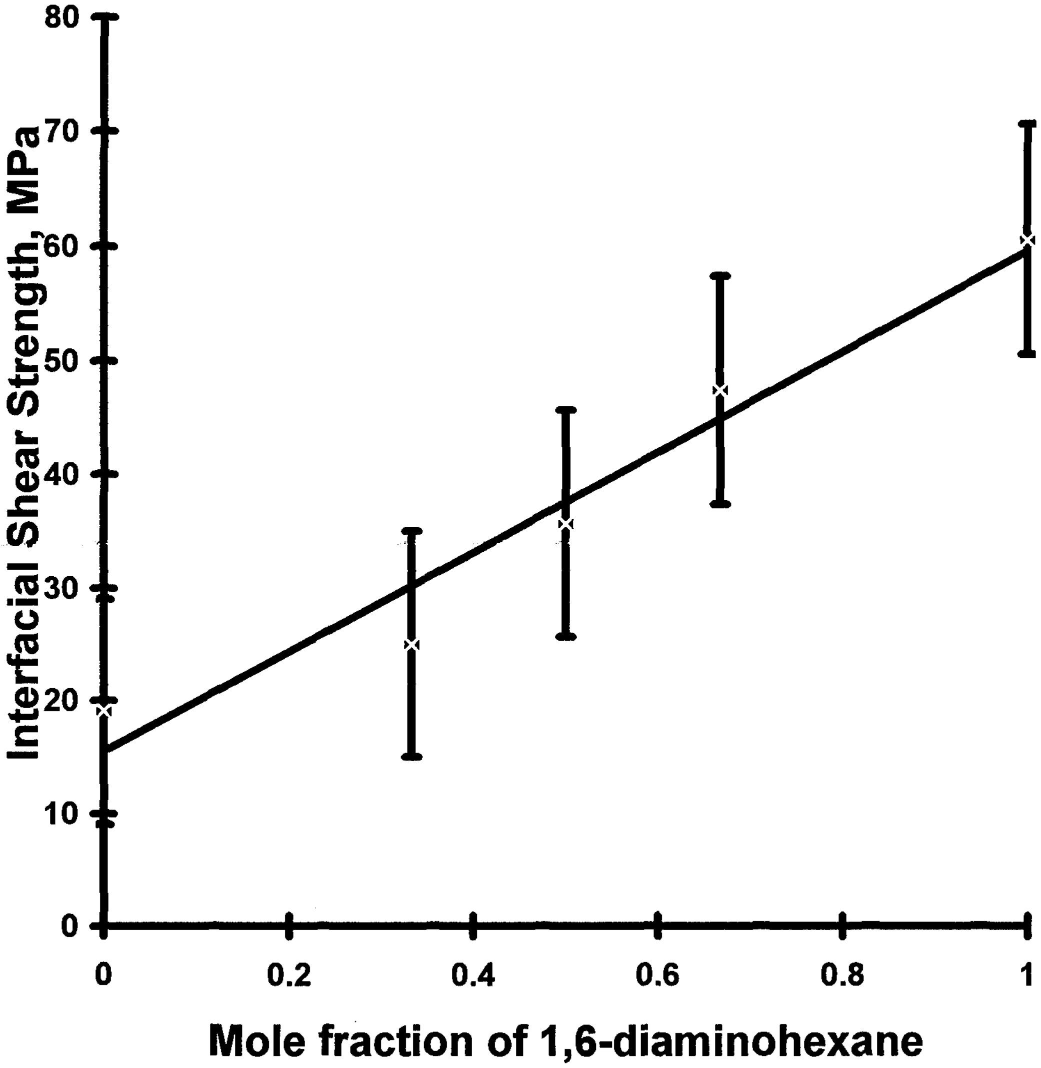
mPDA (curing agent in epoxy) ------>




0.075
0.070
0.065
0.060
0.055
0.050
Absorbance
2920
2850
2958
A
2926
2852
B
C
3000
2950
2900
2850
2800
Wavenumber

F7


(A)
5 nA
E vs SCE
0
0.2
0.4
0.6v
(B)
5 nA
E vs SCE
0
0.2
0.4
0.6v
(C)
5 nA
E vs SCE
0
0.2
0.4
0.6v


Interfacial Shear Strength, MPa
80
70
60
50
40
30
20
10
0
0
0.2
0.4
0.6
0.8
1
Mole fraction of 1,6-diaminohexane