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INFRARED SPECTROSCOPIC CHARACTERIZATION OF EPOXY MATRIX COMPOSITES

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ABSTRACT

Infrared spectroscopic characterization of composites is possible by many sampling techniques, including transmission, specular reflection, diffuse reflection, internal reflection, photoacoustic, and emission. The choice of technique depends on the physical form of the specimen and, in particular, on the scattering characteristics of the reinforcement. Examination of the interphase between the reinforcement and the matrix, in isolation from the rest of the composite, requires some sort of a model system involving either (a) an increased interfacial volume (e.g., use of a high-surface-area analog of the reinforcement), (b) spectroscopic labeling of the interphase, or (c) the use of a model for the reinforcement surface (e.g., a coated internal-reflection spectroscopy element). Several examples of category (a) and (c) are described here. It is demonstrated that the surfaces of commonly used reinforcements (e.g., metal oxides, aramids, carbon) modify the local crosslinking chemistry of epoxy matrices. In particular, the desorption of water from the reinforcement surface and preferential adsorption of polar components of the matrix precursor reduce the local crosslink density and modify the chemical properties of the polymer in the interphase.

INTRODUCTION

The type of technique best suited for the infrared (IR) spectroscopic characterization of epoxy matrix composites depends on the nature of the information required. IR spectroscopy has been applied successfully to problems of quality control [1-5], to studies of degradation [6-10], and to curing mechanisms [11, 12], but most of the emphasis has been placed on studies of reinforcement surfaces, coupling agents, and the interphase between the reinforcement and the epoxy matrix [13-20]. No attempt is made here to review the entire field because of its extreme diversity. Instead, selected examples are presented to illustrate the value of the IR spectroscopic technique, with particular emphasis on the author's application of internal reflection spectroscopy (IRS) to study the interfacial reactions in epoxy matrix composites.

A. IR SPECTROSCOPIC TECHNIQUES

Epoxy matrix composites are rarely in a physical form amenable to conventional spectroscopic analysis. They are insoluble, infusible, difficult to section, and often of complex shape. Furthermore, most commonly used reinforcements are highly scattering to IR radiation. Therefore, unless the situation permits the preparation of special thin or flat specimens, IR analysis is best accomplished by techniques such as diffuse reflection (acronym DRIFT) or photoacoustic spectroscopy (acronym PAS) since no specimen preparation is required and irregularly shaped specimens are permissible.

An example of a DRIFT spectrum of a carbon fiber/epoxy composite (Narmco Rigidite 5208/WC3000 prepreg cured into a test panel) is shown in Fig. 1. With use of modern FT-IR instrumentation, an adequate signal-to-noise ratio is readily attainable [1, 2, 21], but the value of the spectrum in a quantitative sense is limited by deviations from Beer's law, which result from an unknown contribution of specular reflectance from the front surface. The contribution of the specular reflectance component may be varied by placing a layer of powdered KBr on the composite material [22], and this technique also appears to enhance the surface specificity of the DRIFT technique [18, 22], but careful internal calibration is necessary if DRIFT is to be used with intact composite specimens for purposes other than identification or semiquantitative comparison. When the specimens are available in powdered form or when only single-component specimens are being examined (e.g., mineral fillers or reinforcements), DRIFT has a much firmer

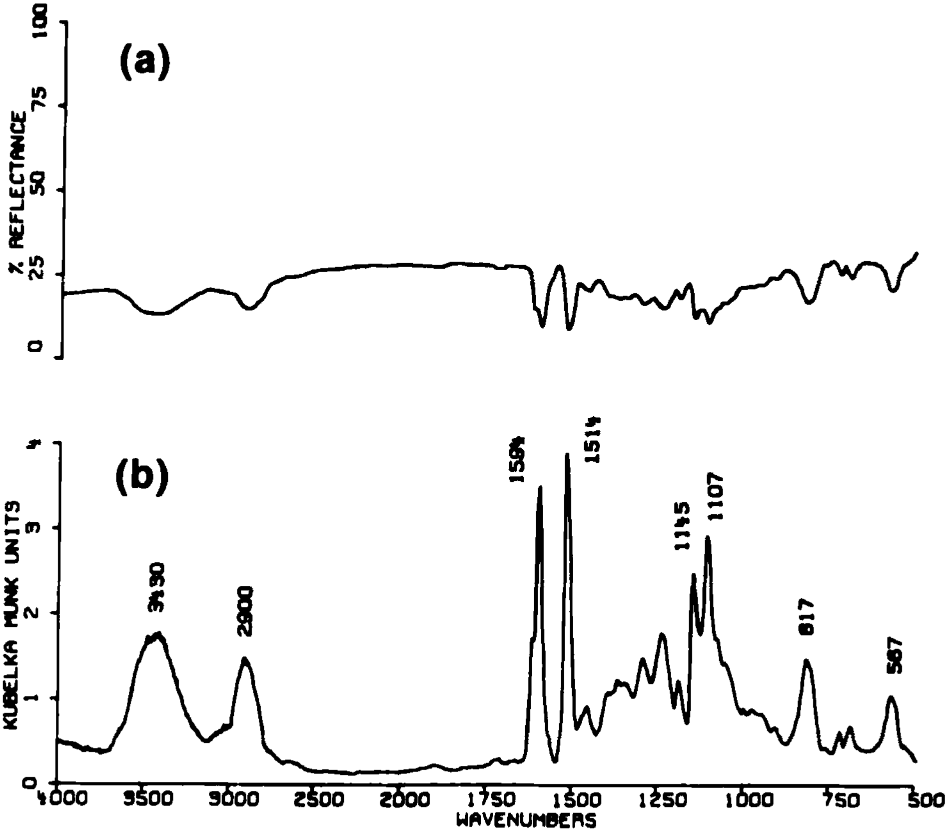


FIG. 1. DRIFT spectrum of Narmco 5208/WC3000; (a) as recorded and (b) after conversion to Kubelka-Munk units followed by baseline correction (reproduced from Ref. 1 with permission).

quantitative basis, but it then loses one of its main advantages, which is the ability to examine intact specimens.

PAS techniques have also achieved impressive success in obtaining IR spectra of intractable composite samples and, in particular, with carbon-containing samples such as reinforced elastomers [23, 24]. The dependence of the PAS spectrum on the nature of the gas in the PAS cell has also been exploited to characterize the surfaces of reinforcements [18]. However, the sensitivity of the PAS data to such a wide range of experimental variables [nature of gas, pressure of gas, mirror velocity (or chopper frequency), thermal conductivity of specimen, etc.] makes it difficult to use PAS on a routine quantitative basis. Poor spectrum signal-to-noise (or long scanning times) can also be a limitation of PAS data for some specimens although there are regular reports of "new" PAS cell designs that claim to alleviate this problem, at least for the chosen specimens.

If the spectroscopist has some control over the physical form of the specimens, good quality IR spectra can be obtained by a wide range of techniques. In the simplest case, the reinforcement and uncured epoxy resin are mixed and cured in the form of a thin film. Provided the reinforcement does not scatter or absorb radiation too highly, transmission IR spectra can then be obtained in a quantitative fashion. For example, Chiang and Koenig [13] describe the affects of silane-treated glass fibers on the curing of an epoxy-anhydride system. In the case of solid cured composites, conventional powdering and pressing into a pellet with KBr can give quantitative results. For highly scattering reinforcements (e.g., carbon black), internal reflection spectroscopy (IRS) can have advantages over transmission techniques [25, 26]. In this case the uncured epoxy/reinforcement mixture is spread over the surface of a germanium IRS element and cured *in situ*. Good quality spectra can be obtained in such a fashion from epoxy resins containing up to 60 wt% carbon black although it should be pointed out that the subsequent cleaning of the element, by burning off the resin in a muffle furnace, followed by repolishing with alumina, requires both skill and patience.

When IR spectroscopy is exploited to characterize the interphase between the reinforcement and the epoxy matrix, the development of some sort of model system is necessary. Typical reinforcements have surface areas of appreciably less than 1 m^2/g, and so the proportion of interfacial material (i.e., in the boundary region a few hundred to a few thousand Å thick) is small, and so the so-called "interface" characterization studies usually involve either reinforcement surface characterization or are concerned with systems where the proportion of interfacial material has been increased by some method (e.g., using a high-surface form of the reinforcement or optically sampling only the interfacial component).

Almost every conceivable IR sampling technique has been used to characterize reinforcement surfaces. DRIFT and PAS can be particularly useful because of their ability to examine rough surfaces and their, at least partial, surface specificity. For example, McKenzie et al. [22] describe the application of DRIFT to the analysis of monolayer levels of coupling agents on glass. If precautions are taken to ensure reproducibility in particle sizes, mixing of specimens, and packing in the DRIFT sampling cup, quantitative information can be obtained about the surface coverage and detailed surface chemical composition. IR-reflection absorption spectroscopy (IR-RAS) and related techniques of grazing incidence reflection and Greenler reflection have been used extensively to examine coupling agents or adsorbed species on polished surfaces [27, 28]. As well as having the sensitivity to detect monolayer coverage, IR-RAS absorptions are also sensitive to the plane of polarization of the IR beam, which allows measurement of the orientation of adsorbed species relative to the plane of the surface [27].

The range of applicability of IRS techniques has recently been reviewed by Mirabella and Harrick [29]. IRS may be selected either because of its well-known surface specificity in sampling, or because the IRS element itself may serve as a model for the reinforcement surface [15]. In the former case, IRS may be used to obtain information about surface coatings on reinforcing fibers [30]. If the element surface is chosen to model a reinforcement surface satisfactorily, the technique provides one of the few routes to examine the polymer-reinforcement intervace *in situ.* For example, a sapphire IRS element has been used to obtain information about the alumina-coupling agent-polymer interphase [20]. If the IRS element is coated with a thin layer of a material which resembles the surface of a reinforcement, the effect of this surface on the chemical composition of the adjacent 0.2-2 μm of polymer matrix may be examined. In such a way we have examined how oxides, aminosilane coupling agents, aramids, and carbonized poly(acrylonitrile) affect the chemical state of the adjacent amine- or anhydride-cured epoxy resins. Some aspects of this work, as well as the effect of modified carbon and graphite surfaces, on the interfacial epoxy composition and properties will be described in the next three sections.

B. IRS ANALYSIS OF OXIDE-EPOXY INTERPHASES

A schematic representation of the IRS interphase characterization technique is shown in Fig. 2. The surface coating on the IRS element surface is appreciably thinner than the "depth of penetration" of the IRS beam into the specimen, and so the surface layers of the adjacent polymer matrix are sampled (for a more detailed discussion of the meaning of the term "depth of penetration," see Mirabella and Harrick [29]). At mid-IR wavelengths, the sampling depth into the polymer can be as low as 200-300 nm if a high angle of incidence and a high refractive index element are used.

The resulting IR spectrum is obviously the sum of the IR absorptions of the oxide coating and those of the adjacent polymer matrix. Spectral sub-

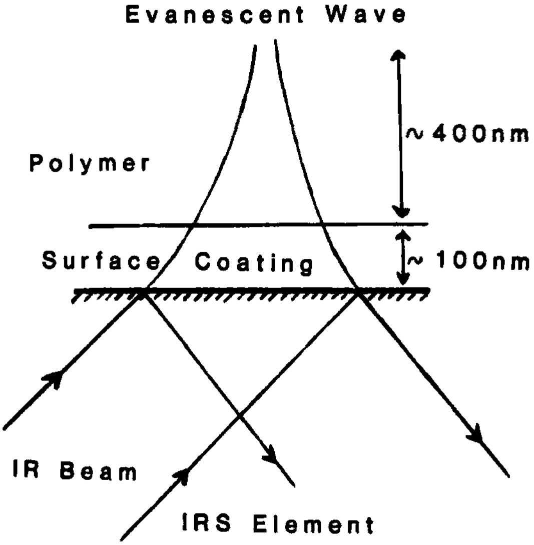
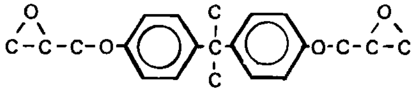


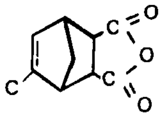
FIG. 2. A schematic representation of the IRS technique involving the use of a coated IRS element.

traction can be used to partially remove the oxide absorptions, but subtraction of IRS spectra is not always simple [15, 31], and in general it is better to restrict analysis to spectral regions where the oxide absorptions are neither strong nor rapidly changing. Fortunately, the relative simplicity of the IR spectra of most metal oxides means that this limitation is not too restrictive (see Fig. 3).

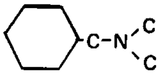
Curve a in Fig. 3 shows the IR-IRS spectrum of a germanium dioxide film on a germanium IRS element. Curve b in Fig. 3 is the summation of the spectrum of the oxide and an overlayer of anhydride-cured epoxy resin. The intense oxide absorption at 850 cm^{-1} does not interfere with interpretation of changes in the level of anhydride functionality (1780 cm^{-1}) and ester functionality (~ 1740 cm^{-1}). The epoxy resin was of the diglycidyl ether of Bisphenol A (DGEBA) type (Epon 828, Shell, Structure I) with Nadic methyl anhydride (NMA, redistilled, Structure II) and benzyldimethylamine (BDMA, redistilled, Structure III) catalyst. The initial epoxy anhydride composition was 100 parts DGEBA, 93 parts NMA, and 1 part BDMA, which were degassed and mixed in the conventional fashion [31, 32].



Structure I



Structure II



Structure III

The characteristic anhydride and ester absorptions were ratioed to an invariant aromatic absorption at 1509 cm^{-1} to obtain anhydride and ester indices so as to quantify the kinetics of the crosslinking reaction. The results are illustrated in Fig. 4, where the rate of reaction of anhydride curing agent is shown to depend on the nature of the surface to which it is adjacent. The

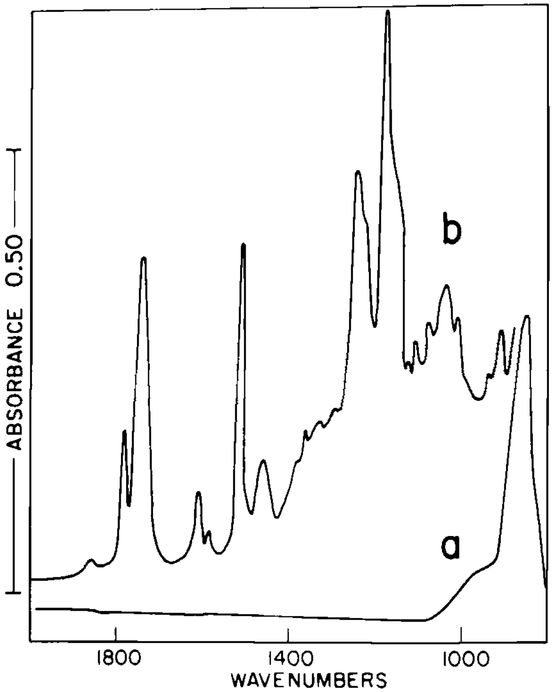


FIG. 3. IRS spectra of (a) a thin layer of germanium dioxide on a germanium IRS element (germanium absorptions subtracted), and (b) specimen (a) with an overlayer of epoxy resin/NMA, cured for 3 h at 100°C and 3 h at 150°C.

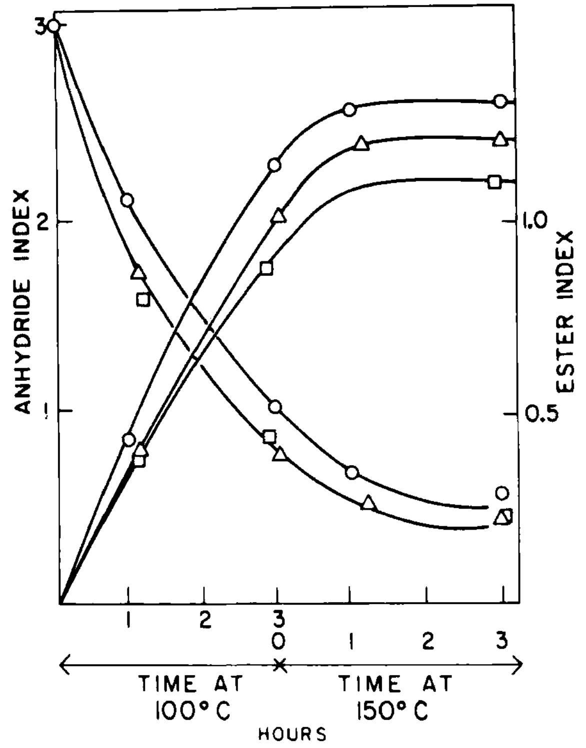
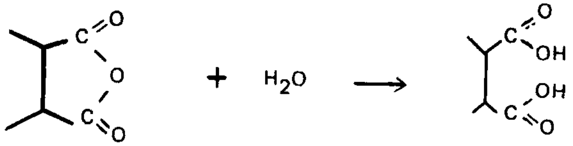


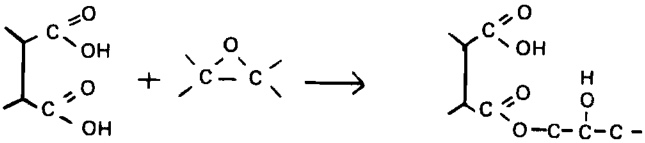
FIG. 4. A comparison of reaction kinetics for the curing of epoxy resin/NMA: (○) on freshly polished germanium, (△) on germanium dioxide coating, (□) on silicon dioxide coating.

rate of loss of anhydride functionality is in the order $SiO_2 > GeO_2 > Ge$, while the final yield of esters (the major crosslinking product, see below) is in the order $Ge > GeO_2 > SiO_2$. The reference system (Ge) corresponds to the crosslinking taking place adjacent to a dry, freshly polished germanium IRS element (60° incidence). We showed separately that the crosslinking kinetics adjacent to dry freshly polished germanium were little different from those in the bulk of the matrix (measured by transmission IR spectroscopy).

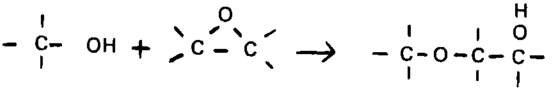
By varying the humidity history of the oxide surfaces, we demonstrated that the major factor in this interfacial effect was the release of adsorbed water from the oxide surface during the cure. Water reacts with the anhydride to produce a diacid, thus accelerating the consumption of anhydride


(1)

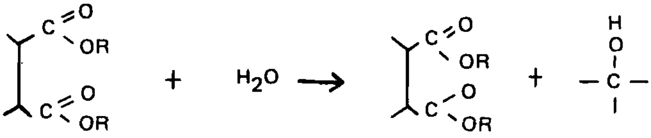
The diacid reacts with the epoxy functionality producing esters


(2)

However, the acid functionality also catalyzes hydroxy-epoxy reactions, thus reducing the overall yield of esters.

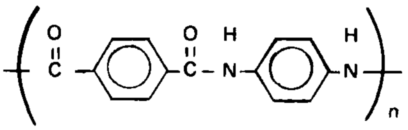

(3)

There is also the possibility of reversible hydrolysis of ester functionality occuring at the interface:


(4)

C. IRS ANALYSIS OF ARAMID-EPOXY INTERPHASES

Aramid reinforcements such as Kevlar (Du Pont, Structure IV) are widely used in applications where high tensile strength and good impact resistance are required [33].



Structure IV

A germanium IRS element was coated with a thin layer of aramid by dipping into a sulfuric acid solution of Kevlar, then coagulating the film by immersion in water, with subsequent washing [34, 35]. The resultant coating spectrum is much more complex than the oxide case (Fig. 5), but it is still possible to extract anhydride and ester indices from the adjacent epoxy layer. In this case the effect on the crosslinking kinetics was appreciably greater than

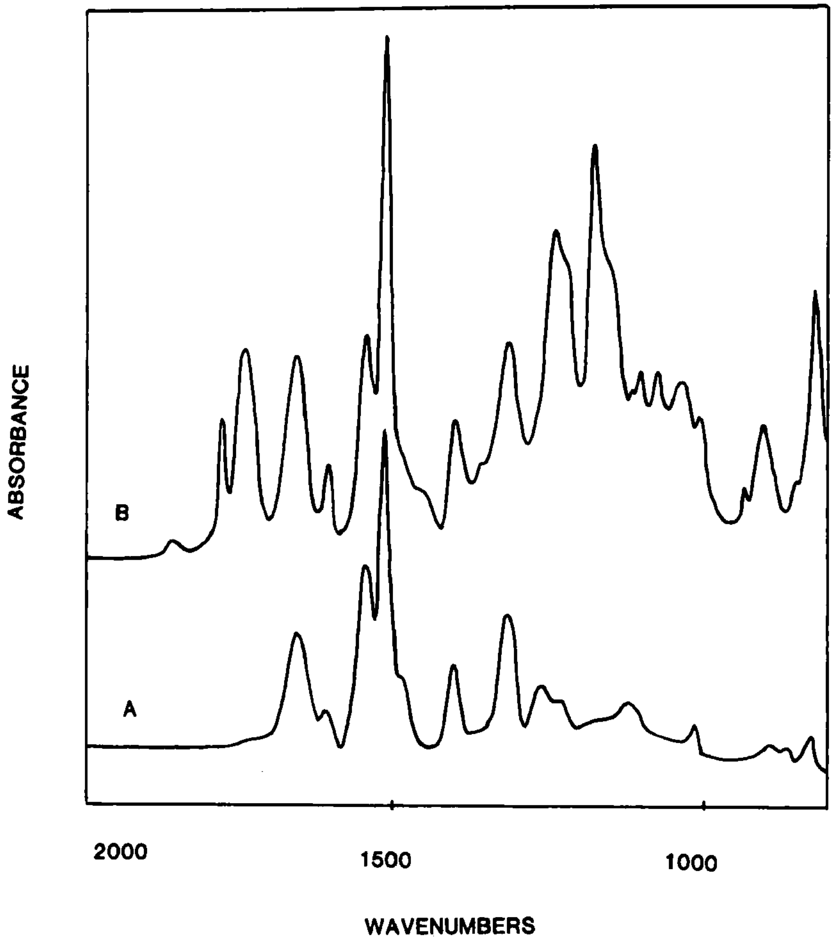


FIG 5. IRS spectra of (A) thin layer of Kevlar on a germanium IRS element, and (B) specimen (A) with an overlayer of cured epoxy/NMA.

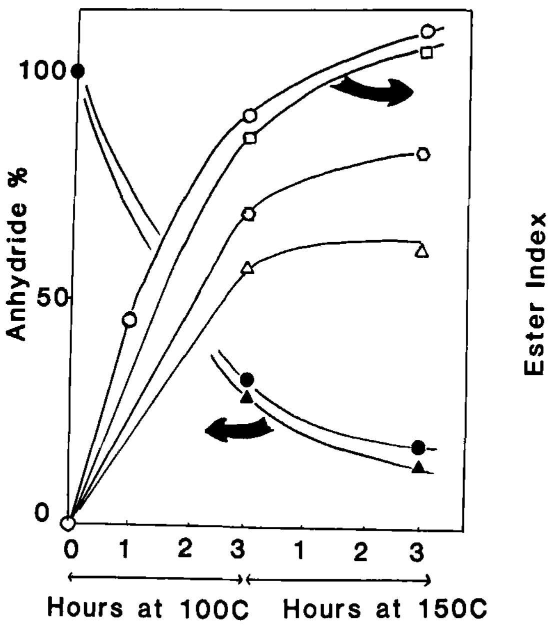
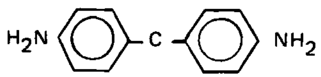


FIG. 6. Consumption of anhydride and production of esters during crosslinking processes, (○, ●) adjacent to clean germanium, (□) adjacent to vacuum-dried aramid coating, (o) adjacent to humid aged aramid coating, and (△, ▲) adjacent to incompletely dried aramid coating (see Ref. 35).

with the oxide (Fig. 6). Aramids adsorb more than 5% water, and so varying the humidity of the doating has a marked effect on the local crosslinking chemistry. The chemical effects were again explained on the basis of the above reaction scheme. Interestingly, when an amide curing agent was used (diaminodiphenylmethane, Structure V), no effect due to the aramid coating was observed on the crosslinking kinetics (as measured by epoxy indices). For example, the control epoxy/amine specimen (adjacent to clean germanium) had a residual epoxide level of 10% at the end of the cure cycle, while adjacent to the aramid coating the residual epoxy level was 9% with a standard deviation of 2% [35]. This is entirely consistent with the insensitivity of the amine cure process to water [32]



Structure V

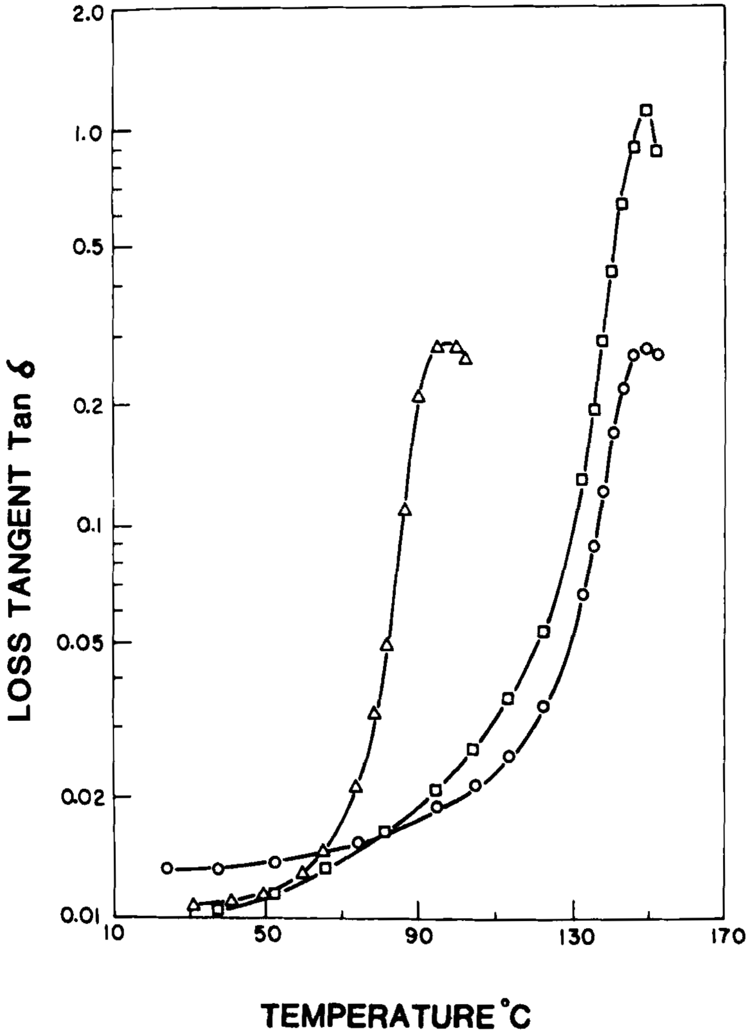


FIG. 7. Dynamic mechanical analysis (DMA) of Kevlar-epoxy composites (at 1 Hz, after cure of 4 h at 100°C and 8 h at 160°C): (□) unreinforced epoxy resin/NMA/BDMA, (○) composite prepared with vacuum-dried Kevlar fiber, and (△) composite made with conditioned Kevlar fiber.

The physical consequences of the modifications to the interfacial chemistry were demonstrated by making a series of epoxy-aramid composites with various fiber humidity histories prior to impregnation with the epoxy [34,35]. Their dynamic mechanical properties showed that modification of the cure chemistry by water lowered the matrix T_g (Fig. 7). This was an irreversible chemical effect, not a simple plasticization by water since, after completion of the cure cycle, the specimens were completely dry. Separate analysis by differential scanning calorimetry (DSC) of portions of the specimen not immediately adjacent to the reinforcement revealed that chemical modification was limited to regions in close contact with the humid-aged fiber. A simple fracture experiment (Fig. 8) showed that the modifications to the interphase chemistry resulted in a catastrophic decrease in the interfacial strength.

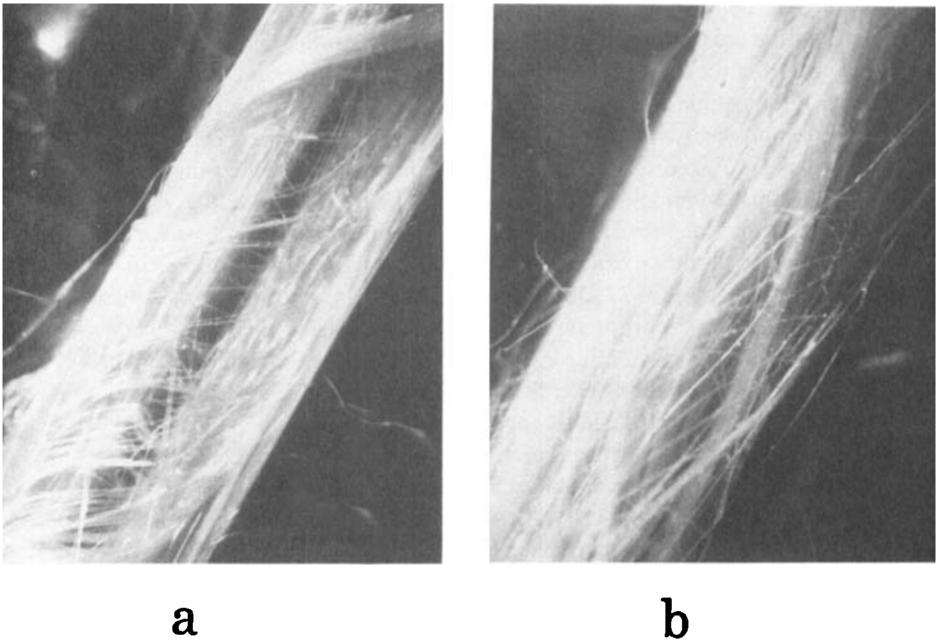


FIG. 8. Optical micrographs of fracture surfaces produced by flexure of composites. Matrix was epoxy resin/NMA/BDMA. (a) Composite made with vacuum-dried Kevlar fiber. (b) Composite made with conditioned Kevlar fiber.

Composites made with amine-cured epoxy matrices were relatively unaffected by the prior humid-aging of the fiber as might have been expected from the absence of effect on the interfacial chemistry [35].

D. IRS ANALYSIS OF CARBON-EPOXY INTERPHASES

The analysis of carbon and graphite-epoxy interphases took two paths. First, a layer of carbonized poly(acrylonitrile) (PAN) was produced on an IRS element to crudely simulate the surface of a PAN-based carbon fiber. This was achieved by solution coating a germanium IRS element with PAN, then subjecting the coated element to a carbonization history at least superficially similar to that involved in carbon fiber production [36]. The carbonized PAN film was sufficiently IR-transparent that anhydride, ester, and epoxy (for amine-cured systems) indices could be determined in the manner described in the previous section. The major effect of the carbonized PAN surface on the crosslinking chemistry was again due to the release of adsorbed water during the cure. The magnitude of the effect was not as pronounced as with the aramid films, because of the relatively lower affinity for water of the carbonized PAN, but the interfacial chemistry and interfacial properties (particularly T_g) correlated with the humidity history of the film and fibers (Fig. 9, Refs. 34 and 36).

The second manner of examining the carbon-epoxy interfacial chemistry was by using modified carbon blacks as high surface area analogs of the carbon fiber surface [17, 37, 38]. The surface of carbon blacks can be made acidic or basic by appropriate chemical treatments, and then they can be mixed with the epoxy curing agent at 20-50% loading to determine their effect on the crosslinking chemistry. Because of the highly scattering nature of carbon black, acceptable IR spectra could only be obtained when the carbon-filled prepolymer was spread on an IRS element and crosslinked *in situ*. Anhydride, ester, and epoxy indices were then determined as a function of cure conditions. The most dramatic effect of the carbon surface was with the anhydride-cured epoxy, where the tertiary-amine catalyst was selectively adsorbed and immobilized on the carbon surface, and the cure was almost totally inhibited.

Figures 10 and 11 show the effect of untreated, CO_2-treated, air-oxidized, and nitric acid-oxidized carbon blacks on the epoxy-anhydride cure. The acidic surfaces all adsorb the tertiary amine catalyst (Table 1) and retard the cure, particularly at the lower temperatures. The basic carbon, with its lower affinity for BDMA, had relatively little effect on the cure. The most obvious physical effect of the modified cure chemistry was on the interphase T_g

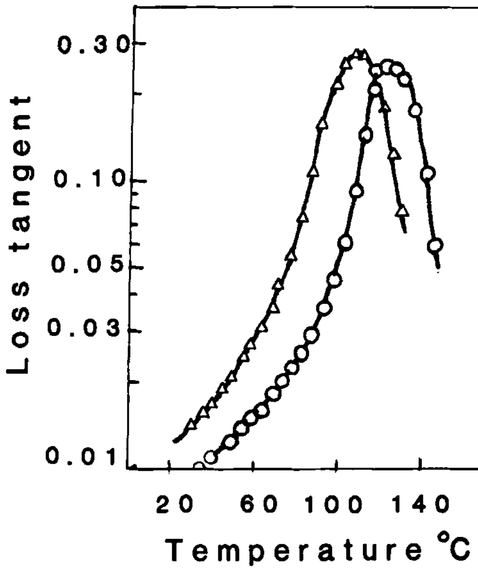


FIG. 9. Dynamic mechanical analysis at 10 Hz of carbon fiber-epoxy-NMA composites: (○) made with vacuum-dried fibers, and (△) made with conditioned fibers (see Ref. 34).

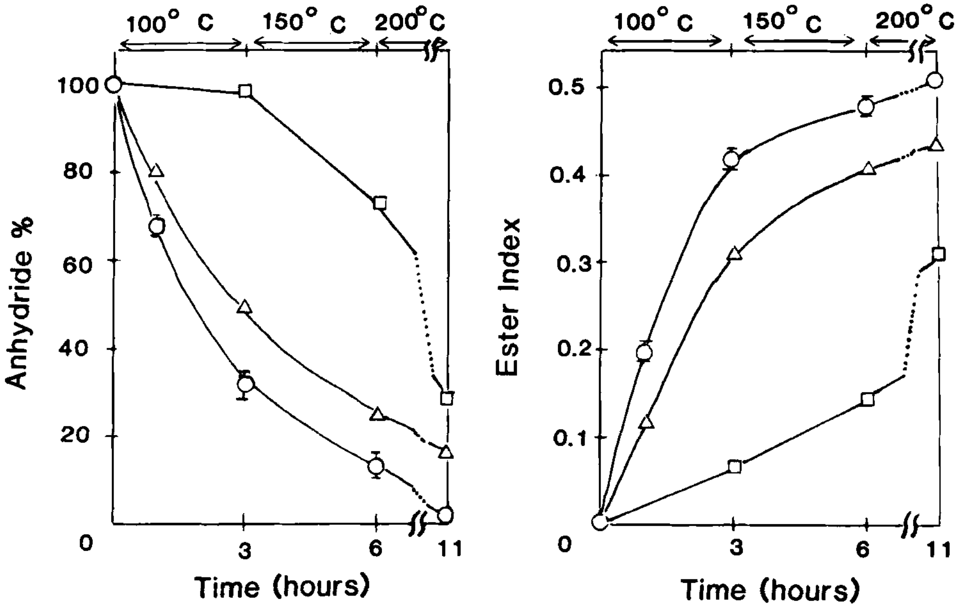


FIG. 10. Crosslinking kinetics of the Epon 828/NMA/BDMA system (○) no carbon, (△) containing 25 wt% carbon black, and (□) containing 25 wt% air-oxidized carbon black.

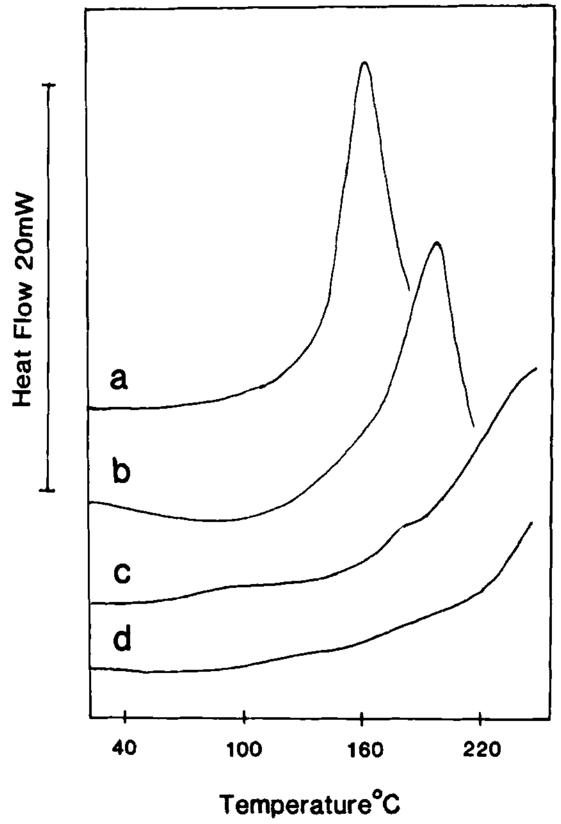


FIG. 11. Exotherms associated with the crosslinking of Epon 828/NMA/BDMA at 10°C/min heating rate: (a) control (no carbon), (b) 25% as-prepared carbon black, (c) 25% nitric acid ox carbon black, and (d) 25% air-oxidized carbon black.

(Table 2). In the case of the carbon-black-filled systems, the interfacial area is so large that the entire matrix component may be considered as being in intimate contact with the carbon surface, and hence typical of "interphase" material.

For the amine-cured system, Epon 828-metaphenylenediamine (MPDA), the effect of the acidic carbon surface was initially to accelerate the epoxy-amine reactions but to inhibit the later stages of the reaction such that a higher proportion of the epoxy functionality was unreacted at the end of

TABLE 1. Characteristics of High-Surface-Area Carbons

	Surface area, m^2/g	pH	C, %	O, %	BDMA adsorbed,[a] %
Carbon blacks:					
As-prepared	167	3.1	94.78	4.65	1.4
Air-oxidized	442	3.5	86.21	13.25	8.8
Nitric acid oxidized	177	3.0	72.19	26.63	10.3
CO_2 treated	270	10.0	99.25	0.40	0.13
Carbon fibers:					
Nitrogen treated	–	6.7	–	–	–
CO_2 treated	12	7.0	95.24	<0.01	0
Air-oxidized	85	4.6	91.10	3.31	0.5
Nitric acid oxidized	11	3.8	90.24	4.47	0.2

[a] The term "BDMA adsorbed" refers to a selective adsorption experiment performed by passing a solution of BDMA in tetrahydrofuran through a column of the carbon.

TABLE 2. T_g of Carbon/Epoxy Composites[a]

Cure	Type of carbon	T_g, °C
Anhydride	Control	140
	25 wt% as-prepared CB	88
	25 wt% air-oxidized CB	~40
	25 wt% nitric acid-oxidized CB	~40
	40 wt% CO_2-treated CF	138
	40 wt% nitric acid-oxidiced CF	102
	40 wt% air-oxidized CF	68
Amine (MPDA)	Control	167
	25 wt% as-prepared CB	80
	25 wt% air-oxidized CB	115
	25 wt% nitric acid-oxidized CB	88
	25 wt% CO_2-treated CB	159

[a] CB, carbon black; CF, chopped carbon fibers.

the cure cycle (Figs. 12 and 13). The initial acceleration was attributed to the well-known stabilization of the transition state of the epoxy-amine reaction by carboxylic acid and hydroxy functionalities [32]. Following the initial acceleration, however, adsorption and immobilization of the amine curing agent limits further reaction resulting in an undercured interphase.

The data obtained from carbon black-epoxy specimens were also shown to be relevant to carbon fiber-epoxy composites. In these initial experiments, crushed and chopped carbon fibers were used to provide a suitably large interfacial area, so that the effects were detectable spectroscopically. In such a way we showed that carbon fibers with treatment history similar to the carbon blacks had a similar effect on the epoxy cure chemistry. This work is now being extended to continuous carbon fiber composites using new spectroscopic techniques [42]. Nonspectroscopic techniques, such as liquid-phase adsorption experiments, can also demonstrate the connection between the carbon black data and the more technologically relevant carbon fiber-epoxy composites. Figure 14 shows the UV spectra of the eluant when a dilute solu-

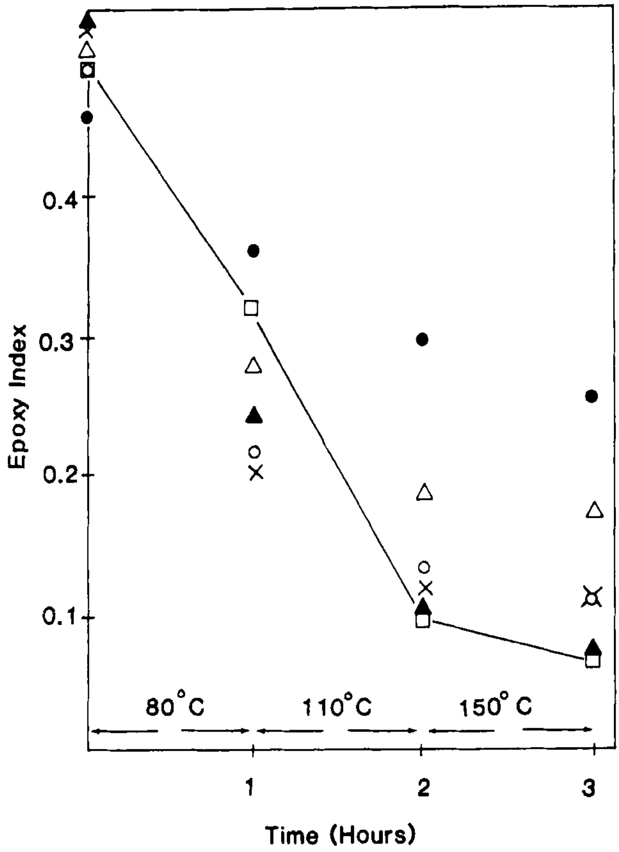


FIG. 12. Consumption of epoxy functionality during the crosslinking of Epon 828/MPDA: (□) no carbon, (X) 25 wt% untreated carbon black, (▲) 25 wt% CO_2-treated carbon black, (○) 25 wt% air-oxidized carbon black, (△) 25 wt% nitric acid-oxidized carbon black, and (●) 50 wt% nitric acid-oxidized carbon black.

tion of Epon 828-MPDA is passed through a column of oxidized carbon fibers. The amine curing agent is preferentially retained on the carbon fiber surfaces while the epoxy resin component is relatively unaffected [38].

A second epoxy-amine system which we are now examining in more detail consists of the tetrafunctional resin MY 720 (largely Structure VI) with diaminodiphenylsulfone (DDS, Structure VII) crosslinking agent. This sys-

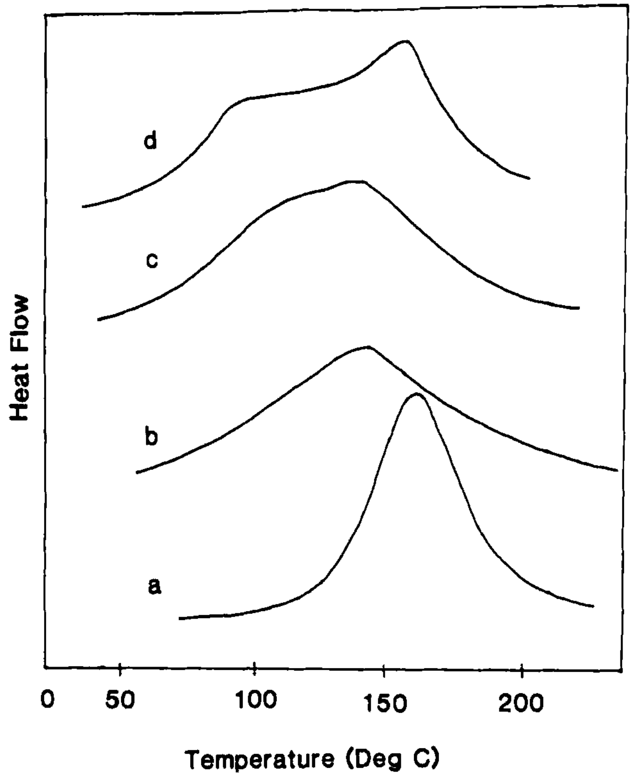
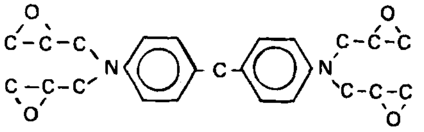
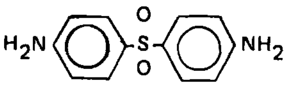


FIG. 13. DSC exotherms associated with the crosslinking of Epon 828/MPDA at 10°C/min heating rate: (a) no carbon, (b) 25 wt% as-prepared carbon black, (c) 25 wt% air-oxidized carbon black, and (d) 25 wt% nitric acid-oxidized carbon black.

tem has a T_g above 200°C and finds application in the areas of aerospace and electronics.



Structure VI



Structure VII

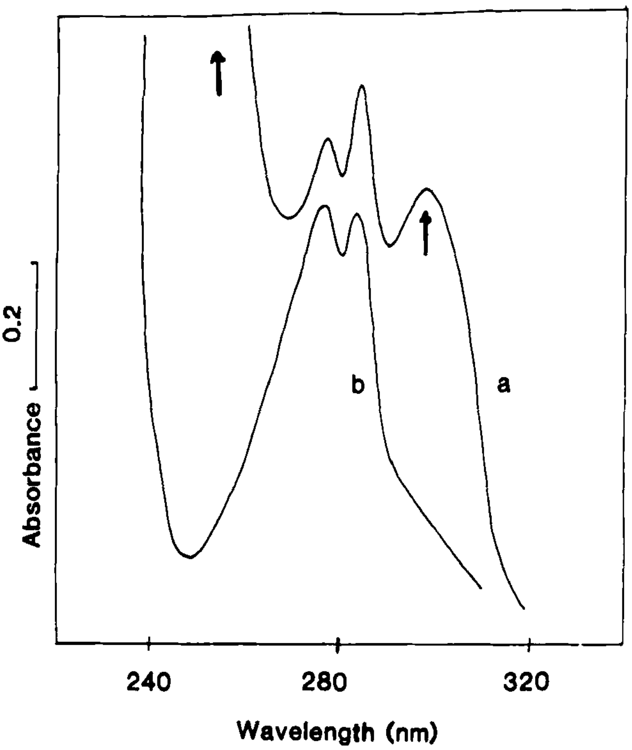


FIG. 14. UV spectra of epoxy/MPDA mixture in THF solution: (a) initial, and (b) after passage through a column of air-oxidized carbon fibers. Arrows denote absorptions characteristic of MPDA.

Our initial experiments show that the effects of functionalized carbon surfaces on this system are qualitatively similar to the Epon 828-MPDA case, in that acidic carbon surfaces initially accelerate then inhibit epoxy-amine reactions, but that much more severe cure conditions are required to drive the crosslinking reactions even close to completion. The effect of an acidic carbon surface is particularly pronounced if no other catalyst (such as BF_3) is present. In carbon fiber prepregs made with this resin system, the carbon surface functionality may have a complex effect in advancing the local cure state in the B-staged material, but reducing the interphase cure state in the fabricated part. We will describe these experiments in more detail elsewhere [39].

Figure 15 shows the initial DSC results for the MY 720-DDS system so as to illustrate the magnitude of the effect of functionalized carbon surfaces on the

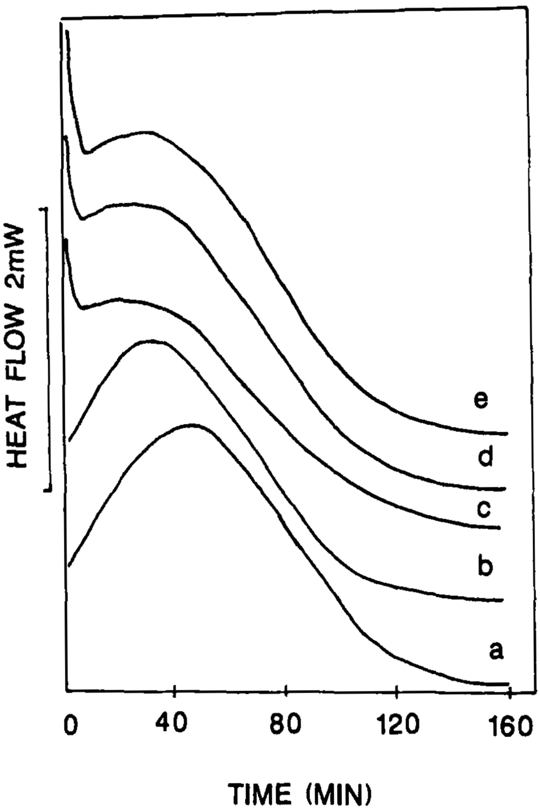


FIG. 15. DSC exotherms associated with isothermal cure of MY720/DDS at 140°C: (a) no carbon, (b) containing 25 wt% CO_2-treated carbon black, (c) containing 25 wt% as-prepared carbon black, (d) containing 25 wt% nitric acid-oxidized carbon black, and (e) containing 25 wt% air-oxidized carbon black.

cure chemistry. We caution, however, that the crosslinking reactions of this system are complex and only partially understood [12, 40, 41]. We are, therefore, examining the effect of a wide range of surface functionalities (amine, thiol, amide, among others) to obtain a more complete picture of the potential benefits of carbon-fiber surface functionalization in composite fabrication.

CONCLUSIONS

IR spectroscopy provides information on a molecular level about the chemical and physical state of epoxy matrix composites. The specimens usually are not in a form suitable for classical spectroscopic techniques, and so an innovative approach is required to sample preparation and spectral analysis. The spectroscopic information so obtained provides a link between a molecular interpretation of composite properties and the more widespread engineering approach to composite design and fabrication.

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