

# The Effect of Carbon Surface Functionality on Tetrafunctional Epoxy Resin–Diaminodiphenylsulfone Cure Reactions

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## Synopsis

Acidic functionality on the surface of oxidized carbon blacks modifies the cure processes of the tetrafunctional epoxy resin MY720 (largely tetraglycidyl-diaminodiphenylmethane, TGDDM) crosslinked with diaminodiphenylsulfone (DDS). In the early stages of the cure (up to 60 min at 140°C), the rate of consumption of TGDDM and DDS and the rate of production of the 1 : 1 adduct are increased, together with an increase in the production of ether functionality. These chemical changes are associated with an increase in exotherm, an increase in gel fraction, and preferential adsorption of the amine curing agent on the carbon surface. During the middle stages of the cure (after 180 min at 140°C), the acidic carbon black has a slight retarding effect on the cure; but, on completion of the later stages of the cure, the effect of the carbon surface functionality diminishes, and, in contrast to earlier studies with difunctional epoxy resins, neither the total cure exotherm nor the final glass transition temperature is affected greatly. We attribute this difference to the greater ease of etherification reactions for the tetrafunctional resin compared to the difunctional case. Basic functionality on the surface of carbon black (induced by carbon dioxide treatment) has a slight retarding effect on TGDDM consumption in early stages of the cure. Less adsorption occurs on the basic carbon than on the acidic carbon, and the adsorbed material appears to be rich in resin. These results imply that treated carbon surfaces may advance or retard the local cure state of an MY720–DDS matrix, but will not affect markedly the final cure state.

## INTRODUCTION

The tetrafunctional epoxy resin system MY720 (Ciba Geigy), crosslinked with diaminodiphenylsulfone (DDS) forms the basis of several organic matrices for high performance composites.<sup>1–3</sup> The MY720 resin consists largely of the tetraglycidyl diaminodiphenylmethane (TGDDM), but contains appreciable (> 25%) amounts of oligomeric and lower functionality material. The crosslinking chemistry of this system has been studied widely, both with and without boron trifluoride–ethylamine catalysis.<sup>4–10</sup> This paper addresses the question of whether the surface functionality of the reinforcing fibers in composites modifies the local crosslinking chemistry of the matrix. If such a phenomenon were to occur, as has been demonstrated in other resin-reinforcement systems,<sup>11,12</sup> an interphase of modified composition and properties would be created around the fiber. Such an interphase would influence the mechanical and environmental stability of the composite.<sup>11–15</sup>

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We have demonstrated earlier that modified carbon black surfaces contain chemical functionality similar to that observed on modified carbon fiber surfaces, and have a qualitatively similar effect on the cure chemistry of difunctional epoxy matrices.<sup>11,12,16</sup> However, carbon blacks have the advantage of high surface area which allows interfacial effects to be observed with great sensitivity. We make no claim that carbon black is an adequate physical, morphological, or mechanical model for a carbon fiber surface. Modified carbon black and carbon fiber surfaces have been shown previously to retard the cure of epoxy-anhydride systems by adsorption of the tertiary amine catalyst, and to accelerate primary amine-epoxy reactions in a difunctional epoxy-amine system. In both cases, an interphase of reduced crosslink density was produced adjacent to the carbon surface, which resulted in modified mechanical properties and a decrease in the local glass transition temperature.<sup>11,12,16,17</sup>

## EXPERIMENTAL

The MY720 epoxy resin was supplied by Ciba Geigy (Batch #5083) and was stored in a freezer before use. The DDS was purchased from Aldrich and had a melting point of 176°C. A wide range of resin-curative ratios have been used with this system, and we selected a value of 50 phr (parts per hundred of resin) as being representative of the level used in uncatalyzed systems. The resin and curative were mixed as solutions in acetone. The acetone was removed at 60°C under vacuum. Such a procedure allowed less prereaction to occur between the resin and curing agent during the mixing step than when mixing took place by direct dissolution of the curative in the resin at > 120°C. When required, the carbon blacks were dispersed in the resin by stirring for 5 min at 105°C. The control specimen was put through an identical thermal cycle, but with no carbon, to compensate for the significant prereaction which might occur during this step.

The carbon blacks had similar surface treatments to those described in earlier publications, but because they were made from a different source material (Vulcan 7H, Cabot Corp.), their compositions differ from those described previously.<sup>11,12,16</sup> Surface areas, elemental analyses, infrared spectra, and pHs were determined as described previously.<sup>12</sup> The "basic" carbon black was heated to 1150°C under carbon dioxide for 30 min, and then cooled in a carbon dioxide atmosphere. The "nitric acid oxidized" carbon black was refluxed in concentrated nitric acid for 60 min, then washed repeatedly with distilled water, and dried in an air oven at 80°C for 3 weeks. A sample of the nitric acid oxidized carbon black was also reduced for 2 h at 500°C, and then cooled, in a flowing hydrogen atmosphere, with the aim of producing a very high area surface, but with little chemical functionality.

Cure exotherms and glass transition temperatures were determined with a Du Pont 910 differential scanning calorimeter (DSC). In order to reduce sampling errors, at least three and usually more specimens were analyzed by DSC. Exotherms were determined initially in isothermal measurements at selected cure temperatures. This provided valuable qualitative comparison of cure kinetics, but the difficulty in setting a baseline and performing integration under such conditions led us to use a 10°C/min temperature ramp for most of the quantitative experiments. Some data are presented in terms of "residual ex-

otherm," i.e., the magnitude of the exotherm produced in a temperature ramp experiment after the specimen had experienced a defined portion of the cure cycle. This parameter is therefore a measure of the amount of reaction which has not yet occurred at that point in the cure cycle.

Chemical changes during the early stages of the cure cycle (up to 2 h at 140°C) could be followed by immersion of partially cured specimens in acetonitrile and separation of the soluble components. The acetonitrile-soluble component was examined by liquid chromatography (LC, Varian 5000 with Model 7126 injector) using a water-acetonitrile (35 : 65) solvent mixture, a reverse-phase column (IBM #8635308, 250 × 4.5 mm, 5 μm C-18 packing) and an ultraviolet (UV, 254 nm) detector. The LC peak of DDS was identified by injection of the pure material. A specimen of pure TGDDM was provided by Dr. Gary Hagnauer of the U.S. Army (MTL, Watertown, MA), and this material was used to calibrate the LC peak of TGDDM in the partially cured specimens of MY720-DDS. Individual LC peaks were cut from the elutant and examined by FT-IR spectroscopy after evaporation of the water-acetonitrile solvent and redissolution in acetone. This solution, containing nanogram quantities of solute, was then dropped on to a 20 × 5 mm KRS-5 internal reflection spectroscopy (IRS) element for FT-IR analysis after evaporation of the acetone.<sup>18</sup>

The acetonitrile-insoluble component was examined by FT-IR spectroscopy after dispersion in a potassium bromide disc. An estimate was also made of the weight fraction of insoluble material by thermogravimetric analysis (TGA, DuPont 951), which involved heating the mixture of carbon and insoluble polymer in a flowing nitrogen atmosphere at 10°C/min to 800°C.

FT-IR spectra of the entire MY720/DDS/carbon system were obtained at various stages of the cure cycle by pressing the uncured mixture against a germanium IRS element, and following the cure process *in situ*. We have described this technique in detail previously,<sup>12,16,19</sup> and it has the advantage of providing good quality IR spectra for highly scattering samples such as these. The epoxide absorption at 905 cm<sup>-1</sup> was quantified using a pseudobaseline from 875 to 920 cm<sup>-1</sup>. An index of ether production was obtained from the difference spectra "cured-uncured," after scaling the 1517 cm<sup>-1</sup> absorption to zero to compensate for changes in the "effective thickness"<sup>20</sup> of the IRS spectrum. Ether was quantified as the 1037 cm<sup>-1</sup> absorption in the difference spectrum relative to a 1007 cm<sup>-1</sup> pseudobaseline. This indirect method was necessary because the strong spectral overlap in this region prevents direct quantification of the ether C—O group absorption from the original spectrum. The difference spectrum was also used to obtain an index of primary amine loss through the "negative absorption" at 1625 cm<sup>-1</sup>, as we have described previously.<sup>11</sup>

## RESULTS

The characteristics of the carbon blacks are summarized in Table I. All surface treatments produced some increase in surface area. The nitric acid treatment produced the highest incorporation of oxygenated functionality and gave a highly acidic surface. Note that the level of nitrogen in the nitric-acid-treated carbon black is only marginally higher than the other samples, which implies that excess nitric acid had been successfully washed from the carbon.

TABLE I  
Characteristics of Carbon Blacks

History	Surface area (m <sup>2</sup> /g)	pH	% C	% H	% S	% O	% N
Untreated	108	6.2	93.8	.3	1.1	4.7	.1
Nitric acid oxid	157	3.1	83.9	.3	0.8	14.6	.3
Hydrogen reduced	382	6.7	97.0	.5	0.8	1.4	.2
CO <sub>2</sub> -treated	145	9.2	98.1	.1	1.0	0.7	.0

Carbon dioxide treatment removes most of the oxygen from the carbon black, and gives a basic surface, as expected.<sup>12</sup> The hydrogen reduction was successful in producing an essentially neutral surface of high area. Infrared spectra of the carbon blacks showed oxygenated functionality in the acidic carbons (acids, esters, lactones, phenols, etc.) qualitatively similar to those we have reported previously.<sup>11</sup>

Figure 1 shows the liquid chromatogram of the MY720 epoxy resin. Clearly, the resin is a multicomponent system, but we demonstrated that the major peak at 6.02 min corresponded to TGDDM, both by IR spectroscopy of the isolated fraction, and by calibration of the chromatograph with a specimen of pure TGDDM. If similar extinction coefficients at 254 nm are assumed for all components of the mixture, then the resin can be assumed to contain about 75% TGDDM. This analysis is consistent with other LC analyses of

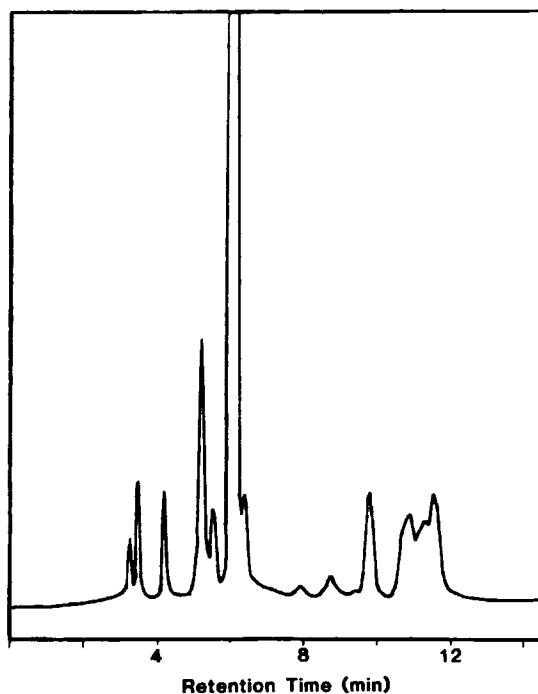


Fig. 1. Liquid chromatogram of MY720 resin. Peak at 6.02 min corresponds to TGDDM.

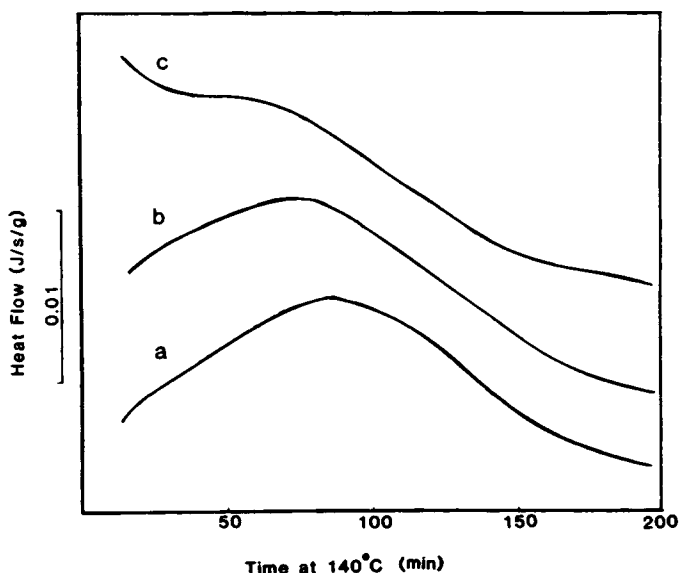


Fig. 2. DSC exotherms at 140°C. Thermograms displaced vertically for ease of comparison: (a) control; (b) containing 25 wt % basic carbon black; (c) containing 25 wt % nitric acid oxidized carbon black.

MY720<sup>2,3,6,8,21</sup> and we made no further effort to determine the identity of the minor components, which have been well characterized by others.<sup>2,6,8,21</sup>

The reaction exotherm measured in a 140°C isothermal DSC experiment provides a highly sensitive monitor of differences in reaction rates and mechanisms. It is clear from Figure 2 that the nitric-acid-oxidized carbon black produces acceleration in the early stages of the cure reactions. The effect of the basic carbon black is smaller. Uncertainties in the position of the baseline prevent accurate quantification of the exotherms involved, but for the control specimen the exotherm at 140°C is about 85 cal/g.

Temperature ramp experiments provide a more reliable way of determining the magnitude of the exotherm. Table II shows the residual exotherms after the isothermal cure steps, i.e., the magnitude of the exotherm in a temperature ramp experiment performed at the end of that stage of the cure. From the

TABLE II  
Exotherms by DSC

Specimen	Residual exotherm (50–300°C, 10°C/min)		
	Initial (cal/g)	200 min/140°C (cal/g)	60 min 180°C (cal/g)
Control	131.4 ± 1.0	37.9	16.5
Untreated cb	130.7 ± 1.2	—	—
Nit. acid ox. cb	135.8 ± 1.3	48.1	27.6
Basic cb	137.5 ± 2.4	40.6	21.9
Reduced cb	132.1	—	—

temperature ramp experiments performed directly after mixing, it is clear that the nitric acid oxidized carbon black and the basic carbon black produce a significant increase in the total cure exotherm (after correction to constant resin content), but the magnitude of the effect is very small (ca. 4%). The untreated and reduced carbons gave exotherms indistinguishable from the control. The initial acceleration in cure rate with the nitric acid oxidized carbon black (Fig. 2) is replaced by a significant retarding effect (Table II) in the middle portion of the cure cycle (i.e., higher residual exotherm). This "accelerating then retarding" effect is qualitatively similar to the behavior reported for a difunctional epoxy system,<sup>11</sup> although in that case the magnitude of the total exotherm was also decreased appreciably, contrary to what is observed here. The implication is that, although kinetic effects modify the chemical state in the early and middle part of the cure, the high temperatures associated with the final part of the cure overwhelm these kinetic effects and return the system to a similar final state. This implication is supported by the further observation that the  $T_g$  at the end of the temperature ramp experiment was greater than 200°C for all specimens and did not vary appreciably with the type of carbon black.

The most direct evidence of chemical reactions in the early stages of the cure comes from chromatographic separation of the reaction products. Figure 3 shows a typical chromatogram of the soluble component extracted from the MY720/DDS/carbon reaction mixture. The peaks due to TGDDM, DDS, and the 1 : 1 reaction product are marked. The nature of the product peak was confirmed by IR analysis of that fraction cut from the elutant (Fig. 4). A

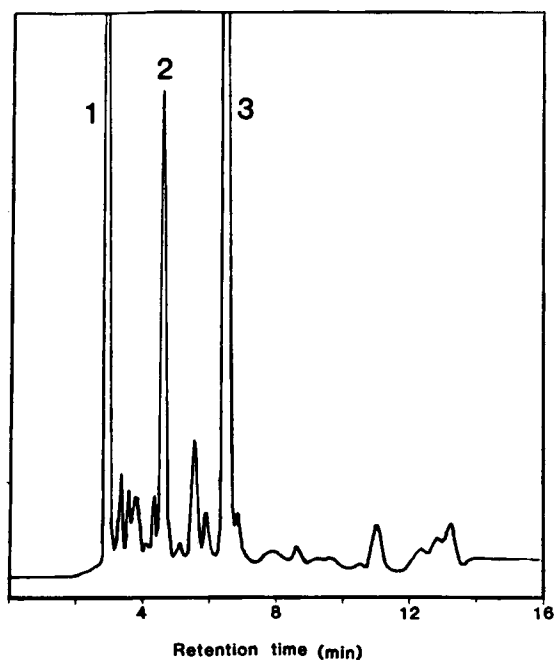


Fig. 3. Liquid chromatogram of MY720-DDS (soluble component) after 20 min at 140°C: (1) DDS, (2) 1 : 1 product; (3) TGDDM.

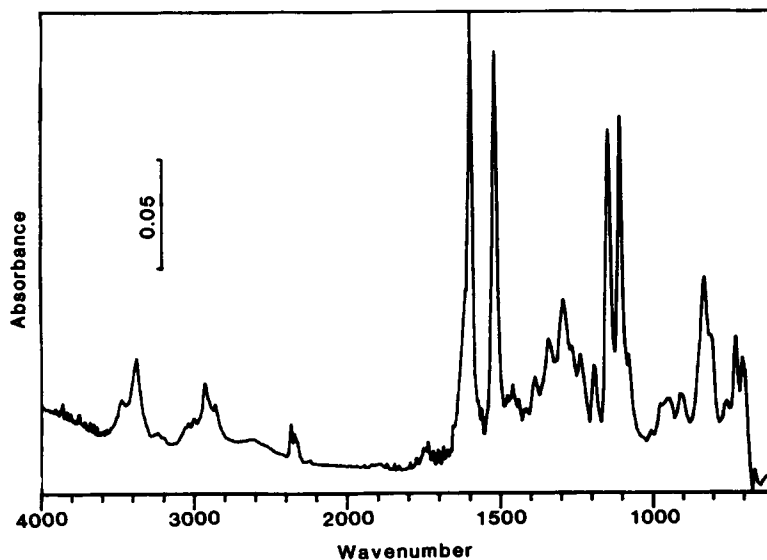


Fig. 4. IR spectrum of 1 : 1 reaction product.

comparison with the spectra of TGDDM and DDS and the use of spectral subtraction showed that the product contained about 75% of the epoxy functionality of TGDDM (from a ratio of the 906 and 1190  $\text{cm}^{-1}$  absorptions), and about 50% of the primary amine functionality of DDS (from a ratio of the 1625 and 1500  $\text{cm}^{-1}$  peaks in the difference spectrum "product-TGDDM").

The consumption of DDS appears relatively unaffected by the presence of the basic carbon black, while, for the nitric acid treated carbon black, appreciable reaction (or adsorption) of DDS occurs even during the mixing step (Fig. 5), and almost all the DDS is consumed during the 140°C stage of the cure cycle. The TGDDM shows similar qualitative behavior (Fig. 6). The yield of 1 : 1 product (Fig. 7) initially is highest for the nitric acid treated carbon black, as would be expected from the faster consumption of DDS, although interpretation of this parameter soon becomes complicated by the fact that secondary reactions (e.g., to produce the 1 : 2 product) will reduce the yield of the 1 : 1 product. In all cases the yield of 1 : 1 product decreases after 40 min at 140°C.

The insoluble component of the reaction mixture was characterized by FT-IR spectroscopy and TGA. Table III shows the TGA data for the acetonitrile-insoluble component of the reaction mixture, i.e., the carbon and the polymer gel. The data are expressed in terms of the difference in thermal mass loss between the partially cured specimen after extraction, and the uncured mixture after extraction, and therefore represent a semiquantitative index of the gel fraction. Gel fractions were not determined in the classical gravimetric fashion because of difficulties in reliably filtering, drying, and weighing the carbon blacks. At short cure times, the index of gel fraction is higher for the nitric acid oxidized carbon black than for the basic carbon black, but at longer times the data converge.

The IR spectra of the insoluble component (Fig. 8) show that the nitric acid oxidized carbon black adsorbs an appreciable amount of material from the

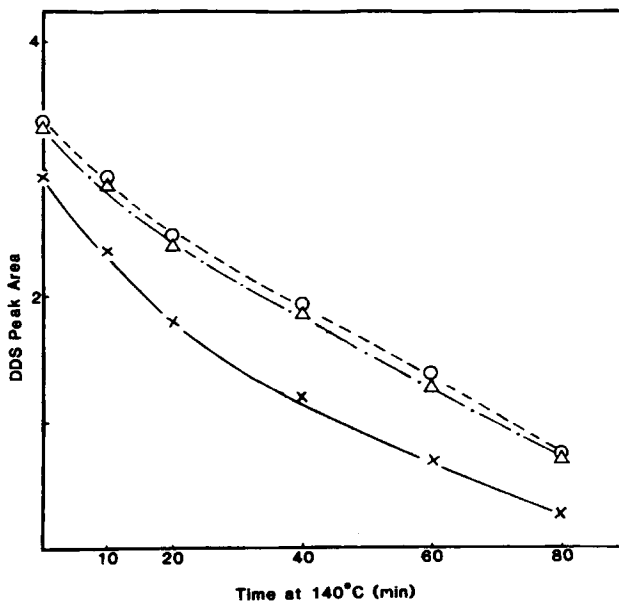


Fig. 5. DDS concentration in soluble component of reaction mixture. Data in Figures 5-7 refer to a constant injection volume: (O---O) control; ( $\Delta$ --- $\Delta$ ) containing 25% basic cb; (X---X) containing 25% nitric acid oxidized cb.

MY720/DDS reaction mixture. A comparison with the spectra of the resin and the curing agent (Fig. 9) shows that the adsorbed material is relatively "rich" in DDS. This observation may be quantified by ratioing the absorption at  $1517\text{ cm}^{-1}$  (which is characteristic of aromatic functionality within TGDDM) to the

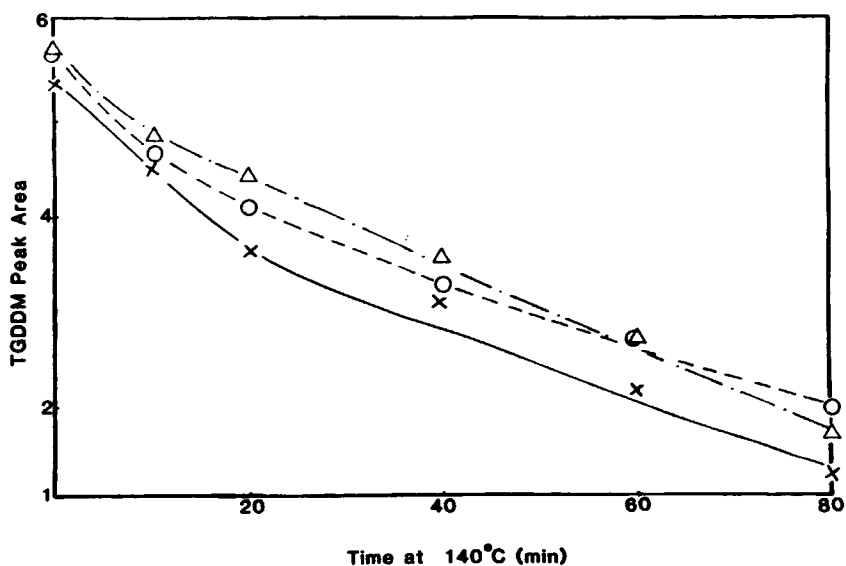


Fig. 6. TGDDM concentration in soluble component of reaction mixture symbols as in Figure 5.



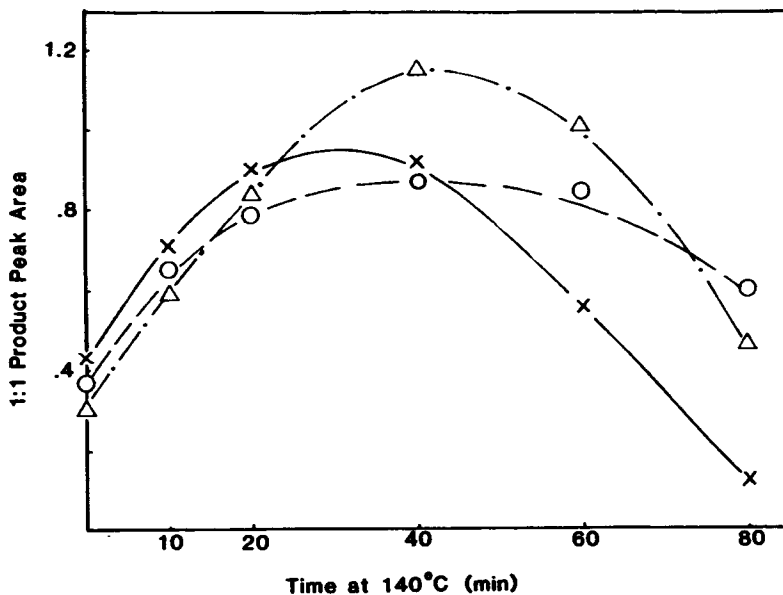


Fig. 7. 1 : 1 product concentration in soluble component of reaction mixture symbols as in Figure 5.

absorption at  $1594\text{ cm}^{-1}$  (which is characteristic of aromatic functionality within DDS). The ratio is close to zero in Figure 8(a), compared to about 1.2 in the carbon-free control [Fig. 9(c)]. After 60 min at  $140^\circ\text{C}$ , the insoluble component [Fig. 8(b), absorbance  $1517/1594$  about 1.1] is very similar to the bulk matrix [Fig. 9(c)]. With the basic carbon black, the amount of material adsorbed from the uncured MY720/DDS was appreciably less, and so the infrared absorptions corresponding to Figure 8(a) were weaker by a factor of about 3. However, despite this relatively poor spectral quality, we could estimate the ratio of the  $1517$  and  $1594\text{ cm}^{-1}$  absorbances to be  $> 2$ , which indicates that the adsorbed material was "resin-rich" compared to the bulk material. After 60 min at  $140^\circ\text{C}$ , the acetonitrile-insoluble component of the basic carbon-black-containing specimen was indistinguishable from the acidic carbon specimen [Fig. 8(b)] and the bulk matrix [Fig. 9(c)].

In a separate experiment, DDS alone was deposited on to the nitric acid oxidized carbon black. The resultant spectrum was similar to that shown in

TABLE III  
Mass Loss Characteristics of Insoluble Fraction by TGA

Cure history	Difference in mass loss 50–800°C (see text)	
	+25% nit. acid oxid. cb	+25% basic cb
0 min at $140^\circ\text{C}$	—	—
20 min at $140^\circ\text{C}$	3.7%	2.7%
40 min at $140^\circ\text{C}$	12.0%	8.5%
60 min at $140^\circ\text{C}$	26.3%	26.9%

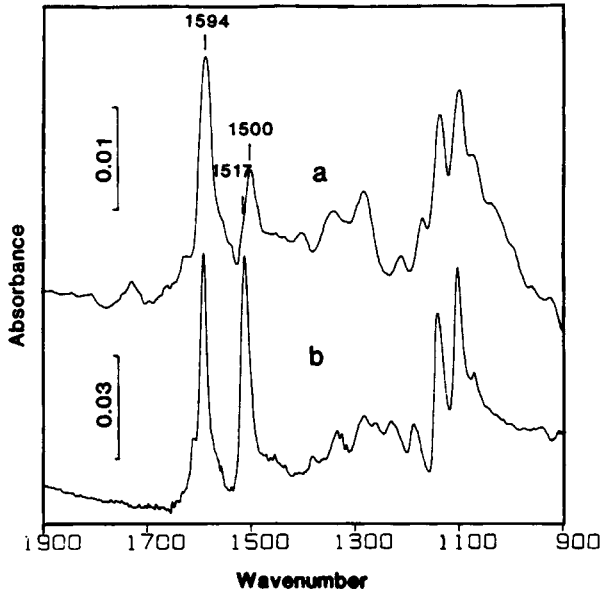


Fig. 8. Transmission IR spectra of insoluble components: (a) MY720/DDS/nitric acid cb, after mixing step only; (b) MY720/DDS/nitric acid cb, after 60 min at 140°C.

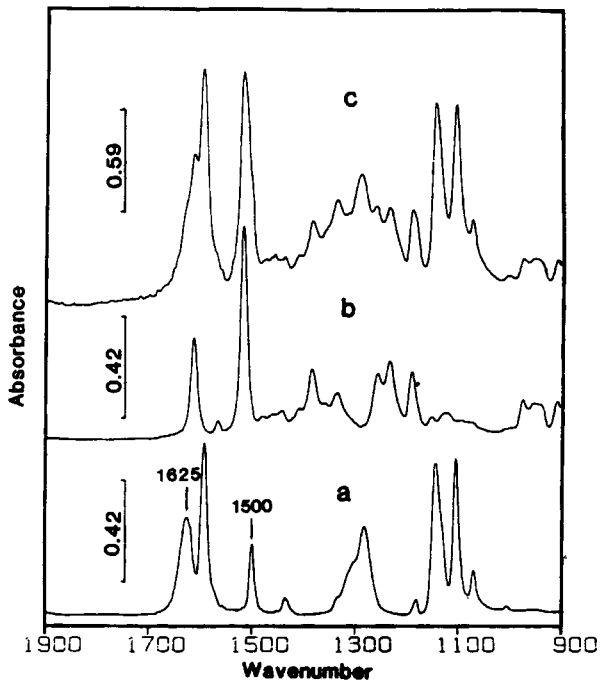


Fig. 9. Transmission IR spectra of (a) DDS, (b) MY720, and (c) MY720/DDS after 60 min at 140°C.

Figure 8(a). In particular, the N—H bending mode at  $1625\text{ cm}^{-1}$  in the pure DDS [Fig. 9(a)] is broadened and shifted to lower frequency. Such behavior is consistent with a strong interaction between the acidic carbon black and the amine functionality.

An indication of the quality of the spectra obtainable from the carbon-filled specimens is given in Figure 10. When comparing this spectrum to the spectrum of the unfilled material [Fig. 9(c)], it should be recalled that Figure 10 is an IRS spectrum while Figure 9(c) is a transmission spectrum, and so the relative band intensities will differ, because of the wavelength-dependent “effective thickness” of the IRS spectrum.<sup>20</sup> These IRS data cannot be compared directly with the data in the remainder of the paper since they were obtained with a different batch of MY720 resin, but, qualitatively, the data support the LC observation that the oxidized carbon black accelerates DDS reaction. After 180 min at  $140^\circ\text{C}$ , about 89% of the primary amine functionality was consumed with the acidic carbon, while about 75% was consumed in the control specimen. Figure 11 shows the “ether production index” as a function of cure history. For the control specimen, little ether production takes place at  $140^\circ\text{C}$ , but occurs rapidly at  $180^\circ\text{C}$  and higher. With the nitric acid oxidized carbon black, significant etherization occurs at  $140^\circ\text{C}$ , although the final state is little different from the control.

## DISCUSSION

In the early stages of the cure, the effect of carbon surface functionality is qualitatively similar to the effect reported previously on difunctional epoxy-

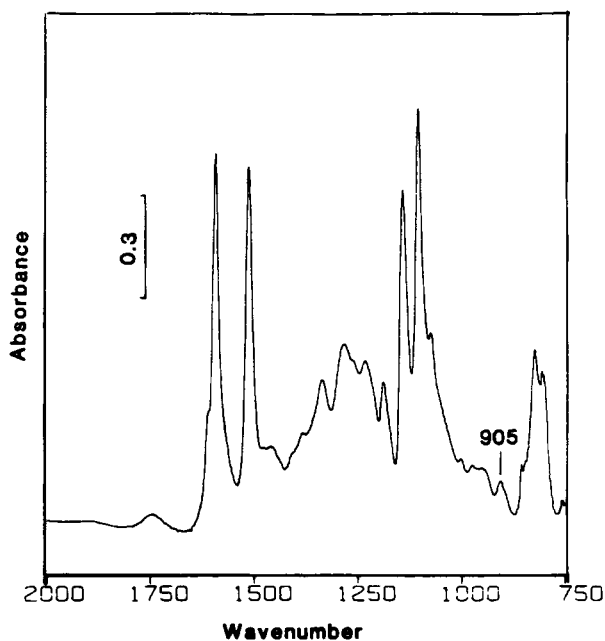


Fig. 10. IRS spectrum of MY720/DDS containing 25% nitric acid cb, after 160 min at  $140^\circ\text{C}$ .

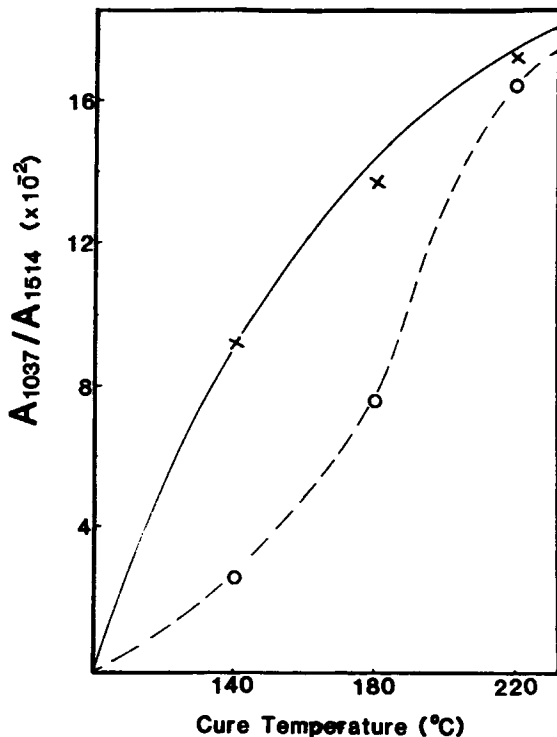
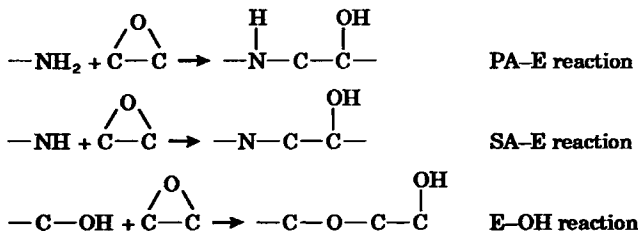


Fig. 11. Ether production index (see text) as a function of cure temperature: (O---O) control; (X---X) containing 25% nitric acid cb.

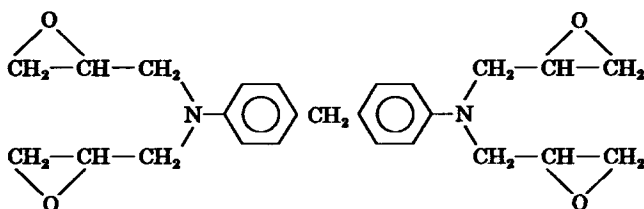
amine systems.<sup>11</sup> Acidic carbon functionality catalyzes primary amine-epoxy (PA-E) reactions, as is well known for many organic acids.<sup>11,22,23</sup> Adsorption of the amine curing agent on to the acidic carbon surfaces also modifies the local stoichiometry, producing a DDS-rich region at the polymer-carbon interface, and in consequence a DDS-poor interphase which has been depleted by the adsorption phenomenon. Neutral or basic carbon surfaces have a much less pronounced effect on the cure. The effect appears to be related primarily to chemical functionality rather than surface area of the carbon, since the hydrogen-reduced carbon, with its very high surface area, had little effect on the cure.



In the middle portion of the cure (e.g., 60–180 min at 140°C) the acidic carbon black produces significant retardation in the cure, as was also found

(although to a greater degree) in the difunctional epoxy-amine systems. We attributed this behavior previously to hindrance of the secondary amine-epoxy (SA-E) reactions by the stoichiometric imbalance and by the reduction in mobility caused by adsorption.<sup>11</sup> The lesser magnitude of the effect in MY720-DDS is entirely consistent with mechanistic studies on this system which indicate the SA-E reactions play a relatively small role in the overall cure mechanism.<sup>1,4,5,9,24</sup>

It is in the later stages of the cure (at 180°C and above) that MY720-DDS differs most from the difunctional system. The effects of the carbon surface functionalities in the earlier stages of the cure diminish, until, at > 200°C, the cure states are similar in terms of total exotherm,  $T_g$ , and IR spectrum. The difunctional epoxy resin system studied previously exhibited a marked reduction in total exotherm and in  $T_g$  in the presence of acidic carbon blacks and carbon fibers.<sup>11</sup> It should be noted, however, that temperature ramp experiments were only performed up to a maximum of 240°C, because of concerns over the thermal stability of the difunctional system. The difference in behavior presumably results from the differing importance of epoxy-hydroxy (E-OH) reactions in the two systems. E-OH reactions are reported to play a major role in the cross-linking of MY720-DDS.<sup>1,4,5,9,24</sup> For example, Morgan and Mones<sup>1</sup> report that 52% of the epoxy groups in a catalyzed TGDDM-DDS system were consumed by E-OH reactions. The previously mentioned mechanistic studies, together with the study of model systems<sup>25</sup> imply that this facile etherization results in part from the tertiary amine functionality present within the TGDDM structure, and in part from the opportunity for intramolecular E-OH reaction provided by the higher functionality of TGDDM. Etherization therefore provides the system with a mechanism for bypassing the hindrance of SA-E reactions by the carbon surface functionality.



TGDDM Structure I

Acidic carbon surface functionality appears to catalyze E-OH reactions (Fig. 11), although this may be due in part to the catalysis of PA-E reactions which lead to increased hydroxyl content (the E-OH reaction is autocatalytic). Such behavior is typical of organic acids, and in extreme cases can provide a mechanism for rapid curing of epoxy resins.<sup>22,23</sup>

The importance of etherization in the cure of the MY720-DDS system also provides an explanation for its relative insensitivity to the concentration of curing agent. A difunctional epoxy system (e.g., Epon 828-metaphenylene diamine) will exhibit marked variations in modulus, strength, and particularly  $T_g$  when the curing agent is varied from 0.8 to 1.2 times the stoichiometric ratio.<sup>22</sup> However, Hagnauer et al.<sup>8</sup> report that, on varying the epoxy/amine ratio from 1.46 to 1.95, there was no significant effect on the mechanical prop-

erties of the cured matrix, and the  $T_g$ 's differed by only 10°C. Similarly, Barton<sup>9</sup> has reported the  $T_g$  of MY720-DDS to be little affected by amine concentration over a wide range. Such a behavior will minimize the effects of the acidic carbon functionality on the final cure state.

In technological terms, the implication of these data is that acidic carbon surface functionalities, as will be produced by for example acid treatment of carbon fibers, will advance the local cure state of MY720-DDS. This may lead to difficulties in the processing of stored prepreg materials (prepreg), and may necessitate some modification of the optimum cure cycle. However, the final cure state in the interphase between the matrix and the fiber surface will be affected less than with an equivalent difunctional epoxy-amine system.

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