Characterization of Carbon Microfibers as a Reinforcement for Epoxy Resins

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Carbon microfibers produced by metal particle catalysis processes are microns in length and only hundreds of angstroms in diameter and possess a graphitic shell. Recent versions of this unique material are described, characterized, and then employed herein for polymer composite preparation, especially the fabrication of high-performance resin matrix composites. The resin used was diglycidyl ether of bisphenol A (DGEBA) epoxy. Three kinds of curing agents were used: diethylenetriamine (DETA); difurfuraldiamine (DFDA); and dimethylbenzylamine (DMBA). Differential scanning calorimetry measurements (DSC) were taken to determine the interaction between resin, curing agents, and carbon fillers. Carbon black was also used as a filler to compare with the carbon microfibers. Some chemical treatments such as ozone and pyridine were employed to alter the surface chemistry of the carbon fillers. X-ray photoelectron spectroscopy (ESCA) was applied to determine the resulting surface chemistry. In particular, a relatively new form of ESCA, designated as ESCALOSS, proved to be very useful in determining the surface graphitic character and oxidation states of carbon. It was found that the reactivity of curing agents has the order DETA > DFDA > DMBA. DMBA might be helpful in cocatalyst of the reaction in the presence of the other curing agents. It was also found that the incorporation of small amounts of carbon fillers could retard the curing reaction while large amounts of carbon fillers could enhance the curing reaction. It was reported that there was a significant difference between the carbon black and carbon microfibers in the manner and the magnitude of how the carbon fillers affect the curing reactions. The above-mentioned surface chemical treatments may further enhance those differences.

Introduction

Catalytically grown carbon microfibers (CMF) are produced by the interaction of hydrocarbons with metal surfaces. Numerous studies have shown that the ferromagnetic metals, iron, cobalt, and nickel are the most active catalysts for the formation of this type of carbon.[1] In this process the hydrocarbon is adsorbed on certain faces of the metal particle followed by subsequent formation of a relatively strong metal–carbon bond and the eventual rupture of a carbon–carbon bond in the molecule. A fraction of the carbon species produced in this fashion will dissolve, diffuse through, and eventually precipitate at the rear faces of the metal particle to form the fibrous material. The structural characteristics of the carbon microfibers are found to be a strong function of the nature of the catalyst particle from which they are produced. The degree of ordering of the fiber structure is governed by the interfacial energy of the respective catalyst particle faces in contact with the carbon surface. It has been suggested that metals which readily wet graphite will produce highly crystalline fiber structures, and this relationship depends on a combination of a number of factors including temperature, crystallographic orientation of the metal particle, and hydrogen content of the reactant gas mixture.[2,3]

Several studies indicate that the microfibers can be produced in various conformations including branched, spiral, and multidirectional depending on the chemical nature of the catalyst particle. This finding has prompted an effort to examine the manner by which various additives to the catalyst modify the growth characteristics[4-8] and the production of the microfibers. We have found that relatively large amounts of carbon microfibers can be produced from the decomposition of ethylene catalyzed by copper:nickel alloys, the amount and conformation in which they are produced being dependent on both the reaction temperature and catalyst composition. Previous

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studies have tended to focus on methods inhibiting the growth of this form of carbon since it exerts a number of deleterious features when formed in hydrocarbon conversion processes. Characterization of such deposits suggests that carbon microfibers may possess some unique attributes for use in a number of areas, and this aspect has provided the impetus to examine properties of the material which are important for their potential application in reinforcement of various polymeric matrices.

Our recent discoveries with ESCA using X-ray photoelectron induced loss spectra (ESCALOSS) have been shown to be particularly revealing in questions related to the graphitic character of carbon materials.[9-11] The new feature in the C–O valence band region, recently discovered and developed by both Sherwood's and our group, also has been proved to be unique in carbon surface characterization.[12,13] Therefore we decided to utilize this C–O valence band spectrum in addition to the ESCALOSS approach to help evaluate the CMF and related surfaces.

To provide a basis for further studies, therefore, we include in this paper the results obtained from ESCA surface analysis of graphitic carbon black (CB) and CMF, which were exposed to ozone, pyridine, and ammonia treatments. Also described are results obtained by differential scanning calorimetry (DSC) analysis of mixtures of diglycidyl ether of bisphenol A (DGEBA) epoxy resin with various amounts of treated and untreated CB and CMF. Curing agents chosen for the epoxy were diethylenetriamine (DETA), difurfuryldiamine (DFDA), and dimethylbenzylamine (DMBA).

One of the objectives of this study is to determine the influence that various surface conditions of finely divided carbon fillers, filler loading levels, and types of curing agents or catalysts may have upon the curing characteristics of epoxy resins. Significant filler loading of such high surface area carbon systems may alter the curing kinetics via chemical reactions and/or the adsorption of chemical species such as the curing agents and catalyst.

Experimental Section

Preparation of Carbn Microfibers. (*a*) *Catalyst.* Copper–nickel powder catalysts used in the present experiments were prepared by coprecipitation of the metal carbonates from mixed nitrate solutions using ammonium bicarbonate. The detailed procedure is well described by Sinfelt et al.[14] and Best and Russell.[15] The precipitate was dried overnight at 110 °C and then calcined in air for 4 h at 400 °C to convert the carbonate to mixed oxides, which were then reduced in hydrogen at 500 °C in a quartz tube for 20 h to form the copper–nickel catalysts. The composition of the bimetallic powders was checked using energy dispersive X-ray spectroscopy (EDS). BET surface area measurements were carried out using nitrogen adsorption at −196 °C. Values of 1.0 ± 0.1 m^2 g^{-1} were obtained indicating that the average particle size was about 1 μm.

Table I. Compositions of 40 wt %[a] Carbon Filler-Epoxy-Curing Agent Mixtures of Equal Molar Composition

	epoxy DGEBA (g)	carbon filler (g)	DFDA 1:2 (g)	DETA 1:4 (g)	DMBA catalyst (g)
carbon black	2.00	1.7–2.03	1.00	0.5	0.04
carbon microfiber	0.50	0.43–0.51	0.25	0.12	0.02

MW of DGEBA = 340 equiv wt (g) 340/4 = 85 g
MW of DETA = 103 equiv wt (g) 103/5 = 20.5 g
MW of DFDA = 162 equiv wt (g) 162/4 = 40.5 g

[a] Weight filler/weight of DGEBA + DFDA or DETA + DMBA + filler.

(*b*) *Preparation of Carbon Microfibers.* The preparation of the fibers was performed in a quartz flow reactor (40-mm i.d. and 90 cm long) located in a Lindberg horizontal tube furnace. Flow rates of gases were controlled with needle valves and measured with rotameters. Catalyst samples (100 mg) contained in ceramic boats were reduced in a 10% hydrogen/helium stream for 2 h at the reaction temperature (usually at 600 °C). Following this step a mixture of ethylene/hydrogen 4:1 at a constant flow rate of 100 sccm was introduced into the reactor. The amount of catalyst was consumed after 8 h of reaction when the maximum amount of product, 20 g of microfibers was obtained in laboratory scale experiment.[2]

Equipment. A du Pont Model 910 differential scanning calorimetry (DSC) with a 2100 thermoanalyzer was employed to monitor the curing thermal activity by measuring the maximum reaction temperature and the corresponding reaction heat. A VG ESCALAB system equipped with three different photon sources for ESCA (plus a 3000A Auger capability) was used to accomplish surface analysis. For these analyses we utilized Mg Kα radiation as the excitation source.

Resin Production and Analysis. The three previously mentioned curing agents, representing primary, secondary, and tertiary functional amines were used to optimize the curing process. These curing agents are symbolized as DETA, DFDA and DMBA respectively. Approximately 0.5-g mixtures of DGEBA and the carbon materials in question were first hand mixed thoroughly to achieve a uniform distribution. A preselected amount of curing agent was then added and also hand mixed into the blend of epoxy and carbon filler in about 3 min. Stoichiometric amounts of DETA and DFDA were employed, and various amounts of DMBA as a catalyst were also explored; see Table I. About 10 mg of this mixture was placed in a DSC analysis chamber and analyzed within 20 min after the addition of the curing agent. (For DETA, the most active curing agent, the DSC analysis must be started within 20 min.) To obtain a completely cured sample, the mixture was placed in an oven for an hour at 105 °C and postcured at 120 °C for 2 h. DSC scans from −10 to 200 °C at 10 °C/min were made with a N_2 purge. All three curing agents were used for both carbon black and carbon microfiber samples. DMBA, as an additional catalyst, also was added to DFDA or DETA and played an important role in these reactions, as will be discussed below. Different loading levels of carbon fillers (0, 20, and 40 wt %) were used to determine the function of the carbon fillers during the reaction (see Table I for carbon filler amounts).

Carbon Filler Surface Treatments. Some samples were prepared by using the carbon fillers following different surface treatments, e.g., ozone, pyridine and ammonia (see Table II for various treatment procedures).

Results and Discussion

Characterization of Carbon Microfibers. (*a*) *Scanning Electron Microscopy.* The physical characteristics of the carbon microfibers were determined by examination in a JEOL JSM 840 scanning electron microscope. An example of the various types of micro-fibers produced in these experiments is shown in Figure 1, where at least three different conformations can be distinguished: (A) coiled, (B) twisted, and (C) straight. The diameters of the fibers range from 10 to 125 nm and lengths of up to 10 μm from, which it is possible to estimate an aspect ratio of about 150. On the basis of the relative sizes of the microfibers and that of the starting catalyst powders, it

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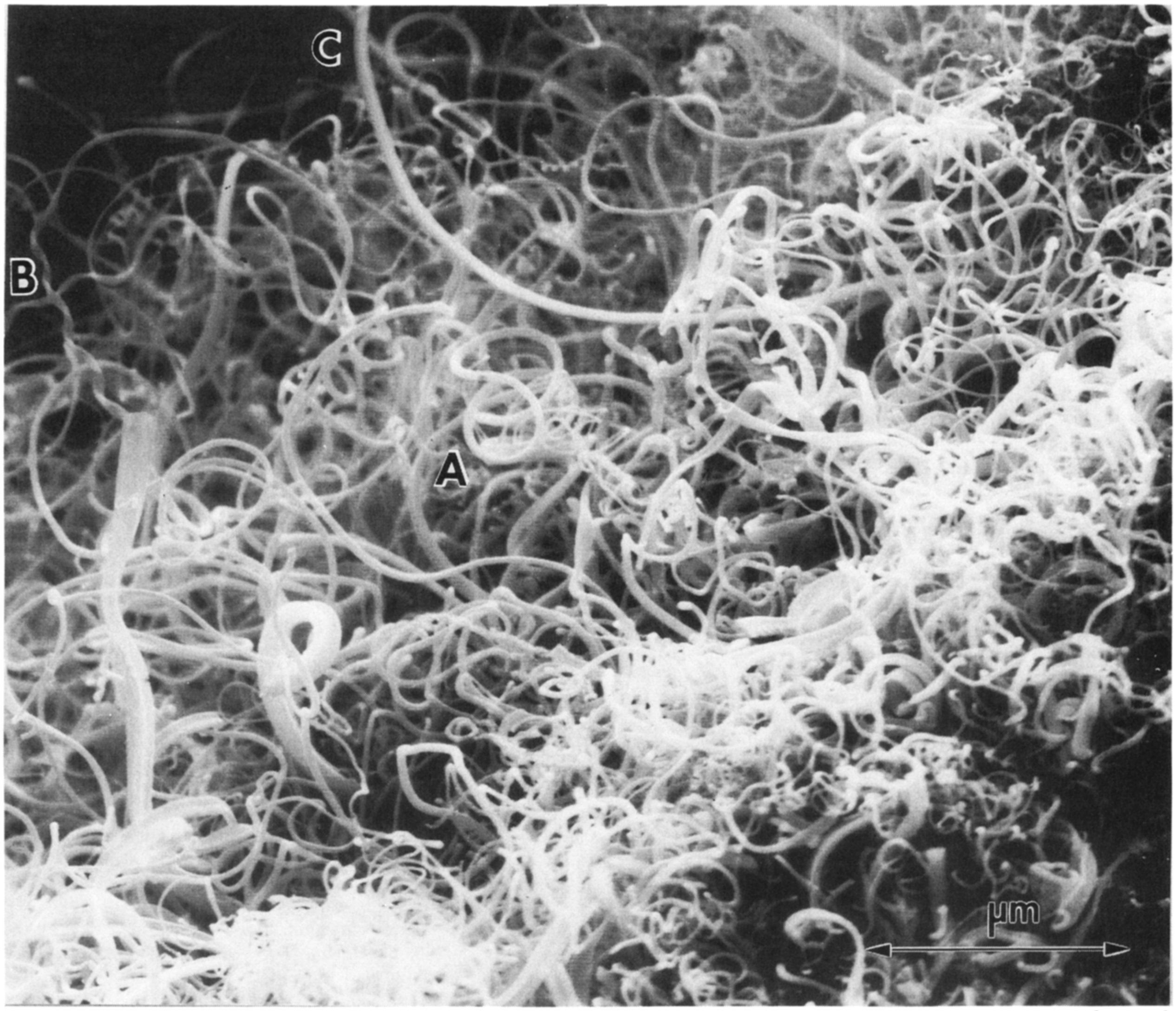

Figure 1. Scanning electron micrograph of carbon microfibers produced from the interaction of a copper:nickel (3:7) powder catalyst with ethylene at 600 °C, showing (A) coiled, (B) twisted and (C) straight morphologies.

is clear that during the reaction, fragmentation of the starting material occurs prior to fiber formation. Examination of carbon microfibers produced from various catalyst formulations indicated that the average size of these structures was independent of the starting alloy composition. This phenomenon of catalyst fragmentation has been observed directly with controlled-atmosphere electron microscopy when metal particles were reacted in acetylene,[8] and other workers[16] have invoked this process to account for the nucleation and growth of carbon microfibers from metal foils.

(*b*) *Transmission Electron Microscopy.* The detailed structural features of individual carbon micro-fibers was determined from high resolution transmission electron microscopy examination performed in a JEOL 200CX electron microscope. The specimens for these examinations were prepared by ultrasonic dispersion of a mass of the deposit in isobutyl alcohol and a drop of the suspension was applied to a carbon support film. Figure 2 is an electron micrograph showing both whiskerlike (A) and helical (B) microfibers and the respective locations of copper–nickel catalyst particles in these structures. From close inspection of fiber A it is also possible to discern the appearance and direction of stacking of graphite platelets in the material.

(*c*) *Surface Area Measurements.* In the interaction of solids with solvents or in this case matrices, the determination of the surface area is of extreme importance. In the present work measurement of this property was carried out by two independent methods.

(i) N_2 adsorption at −196 °C was performed in an Omnisorb 360. The isotherm obtained corresponds to the Type II typical of a nonporous solid. Measurements of the surface areas of various batches of carbon microfibers showed a strong dependence on the composition of the catalyst used in their preparation; a maximum value of 270 m^2/g being obtained for microfibers produced from a copper–nickel (20:80) catalyst and a minimum value of about 10 m^2/g for a catalyst containing 85 wt % copper, Figure 3.

(ii) I_2 adsorption at 25 °C was carried out to evaluate the adsorption properties of the solid in an aqueous solution. The procedure for the determination of surface area using the Dubinin–Raduschkevich equation is reported elsewhere.[17] Using this method, surface areas were somewhat higher than those determined by gas adsorption

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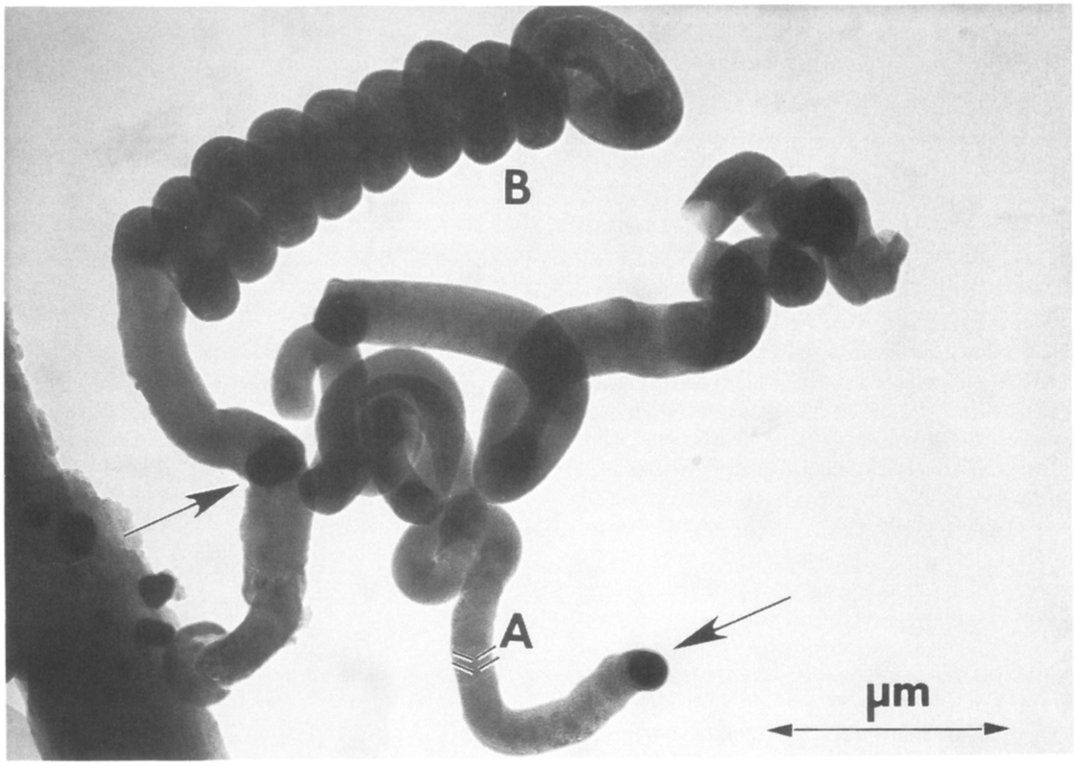

Figure 2. Transmission electron micrograph showing the whiskerlike growth (A) and helical growth (B) of carbon microfibers produced from the interaction of copper–nickel (3:7) with ethylene/hydrogen (4:1) at 650 °C. The direction of the stacking of graphite platelets in growth (A) is indicated and also the location of catalyst particles in these structures.

Table II. Various Pretreatment Procedures

treatment	procedure	results	ESCA spectra
ozone	Griffin Technics ozone generator 5A, 8 psi, for 30 min	surface oxygen content increased by 10-fold	a strong peak emerged at 28.5 eV, O_{1s} principal peak narrowed
ammonia	immersed in concentrated NH_3 for 1 h, rinsed with deionized water	no significant change	no significant change in nitrogen spectra, surface oxygen increased
pyridine	immersed in aqueous pyridine for 1 h, rinsed with deionized water	surface nitrogen increased more than 10×	nitrogen has two peaks, corresponding to different oxidation states

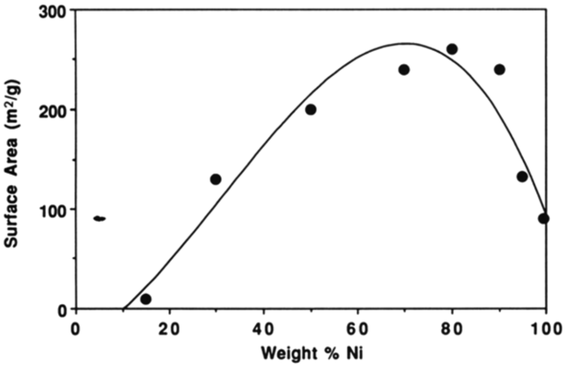

Figure 3. BET nitrogen surface area of carbon microfibers as a function of catalyst composition.

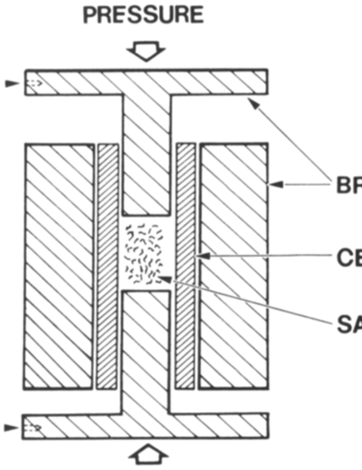

Figure 4. Schematic representation of the apparatus used to measure electrical resistivity of carbon microfibers.

for the fresh micro-fibers produced from a copper–nickel (3:7) catalyst, the values were 350 m^2/g.

(*d*) *Electrical Resistivity Measurements.* Because of the microscopic nature of carbon microfibers (~5 μm in length), it is not a simple task to perform conventional electrical resistivity measurements. To overcome the difficulty of working with powdered materials, a device was designed to determine the resistivity of this type of material while the sample was held under constant pressure. A schematic representation of the experimental arrangement used for these determinations is presented in Figure 4. A more detailed description of the operational procedures is described elsewhere.[18] The apparatus consists of a hollow brass cylinder containing a nonconducting ceramic sleeve, in which two brass pistons form a pressure chamber. The electrical resistance between the contact points of the two brass pistons was measured with a 3465B Hewlett-Packard digital multimeter while the sample in

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Table III. Dependence of the Electrical Resistivity of Carbon Microfibers with Catalyst Composition

catalyst composition Cu:Ni	resistivity Ω cm × 10^3	catalyst composition Cu:Ni	resistivity Ω cm × 10^3
0:100	3.46	30:70	3.14
5:95	3.32	85:15	5.27
10:90	2.85	graphite[a]	1.375
20:80	2.55	active carbon[b]	2,547

[a] SP1 graphite used as reference. [b] Darco KB.

the chamber was maintained at a pressure of 9000 psi. The height of the sample bed at a constant cross-sectional area was measured using a micrometer and the apparatus calibrated using standard carbon materials with known electrical resistivity. The values obtained for the relative resistivities of carbon microfibers produced from various catalysts are shown in Table III along with data obtained for other forms of carbon using the same experimental approach.

Characterization of Reactions of Carbon Fillers and Epoxy Resins. General DSC results showed that the exothermic curing reactivity for the three types of curing agents has the following descending order: DETA > DFDA > DMBA based upon the maximum observed curing temperatures and the evolved exothermic heat. Small amounts (less than 20%) of CB and CMF fillers increased the maximum curing temperature when the least reactive curing catalyst (DMBA) was used (see Table IV). Higher filler loadings lowered the maximum curing temperature. This indicated that the curing reactions were enhanced by the presence of larger amounts of carbon fillers. We also noticed that a filler subjected to a different surface treatment had a different impact on the thermal curing behavior. Table IV and Figures 5–7 show typical DSC analyses of epoxy and the carbon fillers.

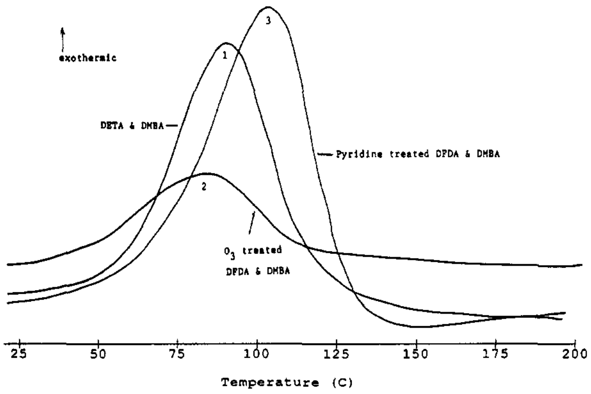

Figure 5. DSC results: (1) Epoxy with 40 wt % carbon microfiber, DETA as curing agent, DMBA as catalyst. (2) Epoxy with 40 wt % O_3-treated carbon microfiber, DFDA as curing agent, DMBA as catalyst. (3) Epoxy with 40 wt % pyridine-treated carbon microfiber, DFDA as curing agent, DMBA as catalyst.

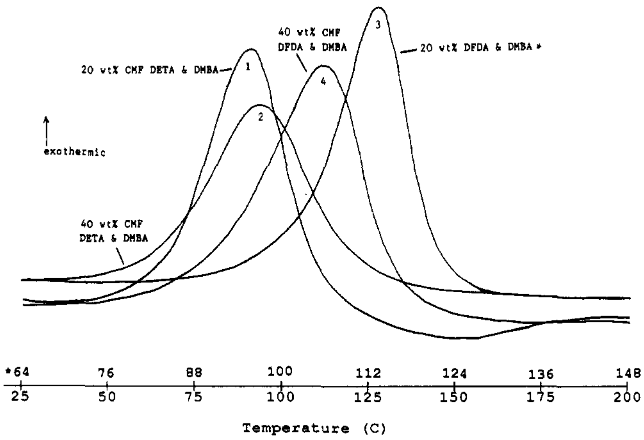

Figure 6. DSC results: (1) Epoxy with 20 wt % carbon microfiber, DETA as curing agent, DMBA as catalyst. (2) Epoxy with 40 wt % carbon microfiber, DETA as curing agent, DMBA as catalyst. (3) Epoxy with 20 wt % carbon microfiber, DFDA as curing agent, DMBA as catalyst (note ★ temperature scale). (4) Epoxy with 40 wt % carbon microfiber, DFDA as curing agent, DMBA as catalyst.

(*a*) *Differences among Curing Agents.* A curing agent and/or catalyst was needed to cure the epoxy and its composites as seen in Table IV. DMBA catalyst is the least reactive for curing of the unfilled and filled epoxy. The epoxy curing reaction induced by the DMBA (stoichiometric amounts) had the highest maximum curing temperature and evolved the smallest amount of heat (see Table IV). However, the addition of a small amount of DMBA to the other two curing agents promotes the curing rate of filled epoxies as shown by the lower maximum

Table IV. Maximum Observed Curing Temperature (°C) and Exothermic Heat Evolved for Sample Studies by the DSC (J/g)[a]

	pretreatment	no curing agent	stoich DMBA	DMBA 1 wt % of total mass	DMBA 10 wt % of total mass	DFDA, no DMBA	DETA + DMBA	DFDA + DMBA
epoxy only		no reaction	108.3 °C, 55[b]					113.8 °C
epoxy, 20 wt % CB	none	no reaction	no reaction			110.6 °C, 206,[b] 391[c]	85.3 °C, 424,[b] 673[c]	106 °C, 388,[b] 737[c]
epoxy 40 wt % CB	none	no reaction	no reaction	no reaction	121.7 °C, 173,[b] 346[c]		76.8 °C, 195,[b] 406[c]	91.9 °C, 253,[b] 645[c]
	O_3 treated							109.6 °C, 121,[b] 309[c]
	pyridine treated						77.4 °C, 245,[b] 514[c]	
epoxy, 20 wt % CMF	none	no reaction	133.1 °C, 118,[b] 148[c]	little reaction			85.8 °C, 475,[b] 754[c]	113.7 °C, 435,[b] 826[c]
epoxy 40 wt % CMF	none	no reaction	125.3 °C, 118,[b] 197[c]	little reaction			88.5 °C, 557,[b] 1170[c]	106.7 °C, 462,[b] 1178[c]
	O_3 treated							84.3 °C, 378,[b] 964[c]
	pyridine treated							101.2 °C, 473,[b] 1206[c]

[a] Accuracy of measurements ±0.4 °C for maximum temperature and ±5% for exothermic heats. [b] Based on total mass basis. [c] Based on mass of epoxy only.

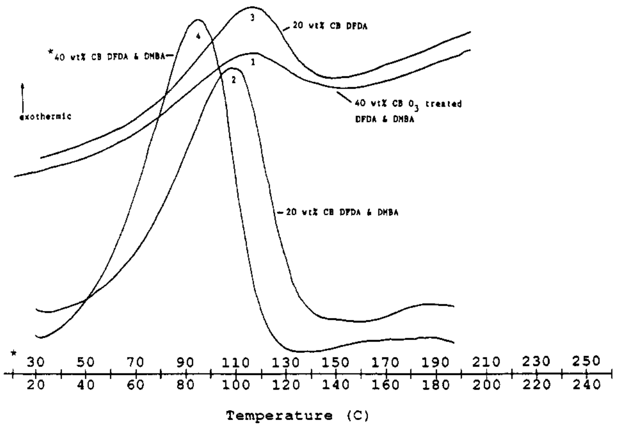

Figure 7. DSC results: (1) 109.6 C, epoxy with 40 wt % O_3-treated carbon black, DFDA as curing agent, DMBA as catalyst. (2) 106.0 °C, epoxy with 20 wt % carbon black, DFDA as curing agent, DMBA as catalyst. (3) 110.6 °C, epoxy with 20 wt % carbon black, DFDA as curing agent, no DMBA. (4) 91.9 C, epoxy with 40 wt % carbon black, DFDA as curing agent, DMBA as catalyst (note ★ temperature scale).

curing temperature and the greater heat of reaction compared to the curing reactions with DFDA or DETA alone. For example, see Figure 7 (2) DFDA with DMBA versus (3) for DFDA alone. This suggests a synergistic influence of DMBA with these curing agents. As expected, DETA (with DMBA as a cocatalyst) is the fastest curing agent, independent of carbon filler type and amount, because of its aliphatic primary amine nature, see Figures 5 (1) and 6 (1 and 2) and Table IV. DFDA (with DMBA) is a moderate curing system, Figure 5 (3).

From Figures 6 and 7 and Table IV, it can be seen that when DFDA or DETA with DMBA is used as a system of curing agent plus catalyst, the epoxy composite with a higher percentage of carbon filler (40 wt %) shows nearly the same or a lower maximum curing temperature than the epoxy composite with lower percentage (20 wt %) carbon fillers (see for CMF Figure 6 (1) versus (2) and (3) versus (4), and for C.B., Figure 7 (2) versus (4)). In other words, the curing reaction seemed to be facilitated by further addition of carbon fillers in most instances.

(*b*) *Surface Chemical Function of Carbon Fillers.* The graphitic CB used here is approximately 6–10 times the surface area of the CMF (1500 m^2/gm or greater for CB vs 270 m^2/gm for CMF). The chemical reactivity of the CB surface should be enhanced over CMF due to its increased surface area. However, the chemical constitution of either carbon filler will produce specific interactions with the curing system and thus this specific activity of the filler will also play a role on curing kinetics. The curing reaction mechanisms of graphitic carbon filler-epoxy mixtures can be explained in terms of a dual function of these carbon surfaces which influence the curing reaction. First, as in most catalytic reactions, the activated carbon surfaces possess sites which could help form transition complexes with adsorbed chemical species and initiate chemical reactions. Second, when the interaction between the carbon surface and the reactant molecule becomes very strong, chemical reactions with other species are inhibited or prevented. For example, the aromatic structure of DMBA is much more likely to be compatible with the graphitic structure on these carbon surfaces than that of the other two curing agents, thus its ability to catalyze the epoxy is reduced. These active adsorption sites are apparently related to the presence of functional groups and chemical alterations.

Both of these features are generally present on the carbonaceous filler systems in inverse proportion to their graphitic nature. Carbon microfibers possess more ordered graphitic surfaces than the graphitic carbon black studied here as was discerned from ESCA results discussed later. Hence carbon microfibers are more inert or have less active surfaces and/or do not accommodate as many active adsorption sites. Thus considering the adsorption–inhibition function, the CB-epoxy composite material does not cure when only a small amount of DMBA is added, whereas a moderate reaction can be catalyzed for the CMF-epoxy composite materials with the identical amount of DMBA (see Table IV, 1 wt % DMBA). If, on the other hand, the amount of DMBA added exceeds the adsorption inhibition capacity of the CB, the reaction also occurs for CB composites (see Table IV, 10 wt % DMBA).

In the case of DFDA or DETA, the adsorption–inhibition function evidently is less, since their structures are dissimilar from that of the graphitic surfaces of the carbon fillers. Therefore, the catalytic function, which is related to the initiation of the curing reaction at the chemically active sites on the carbon surfaces, became more important.

When DFDA was used as a curing agent, with or without a small amount of DMBA, the maximum curing temperatures fell from 106 to 92 °C when the loading levels were changed from 20 to 40 wt % for the CB filler (Figure 7 (2) versus (4)). For the CMF filler, the maximum curing temperatures fell from 113.7 to 106.7 °C (Figure 6 (3) versus (4)). One may speculate that, for these curing systems, the interfacial area between epoxy and carbon fillers may provide the chemically active sites for the initiation of curing reactions. Since the graphitic CB has a more chemically reactive surface with these curing systems, its catalytic function was greater than that of the CMF as indicated by the lower maximum cure temperatures.

When a very active curing agent was used and was not significantly adsorbed, the catalytic function was less important although still observed for CB fillers. If DETA was used as the curing agent for the graphitic CB-epoxy composites, the maximum curing temperatures changed from 85.3 to 76.8 °C as the loading level changed from 20 to 40 wt % (see Table IV), whereas for the CMF-epoxy composites, the temperatures for comparable loading levels changed from 85.8 to 88.4 °C (Figure 6 (1) versus (2)). Hence, for this very active curing agent (DETA), the catalytic function of the filler is no longer important for the less reactive carbon filler (CMF).

In view of these features, we conclude that the incorporation of carbon fillers changes the curing mechanism of epoxy as a result of the action of two major functions. The relative importance of either function depends upon the relative reactivities of the carbon surface and curing agent. Correspondingly, it would appear that one of the reasons for the different behavior of CMF from CB is the dissimilarity in their surface chemistry, morphology, and surface area.

(*c*) *Surface and Interfacial Chemistry.* As mentioned above, CB and CMF fillers seem to behave quite differently in the epoxy curing reaction, suggesting different surface chemistries for these two carbon systems and a possible utility for ESCA analysis. Conventional ESCA has substantial difficulties in the analysis of many carbon compounds, because carbon groups like C—H, C—C,

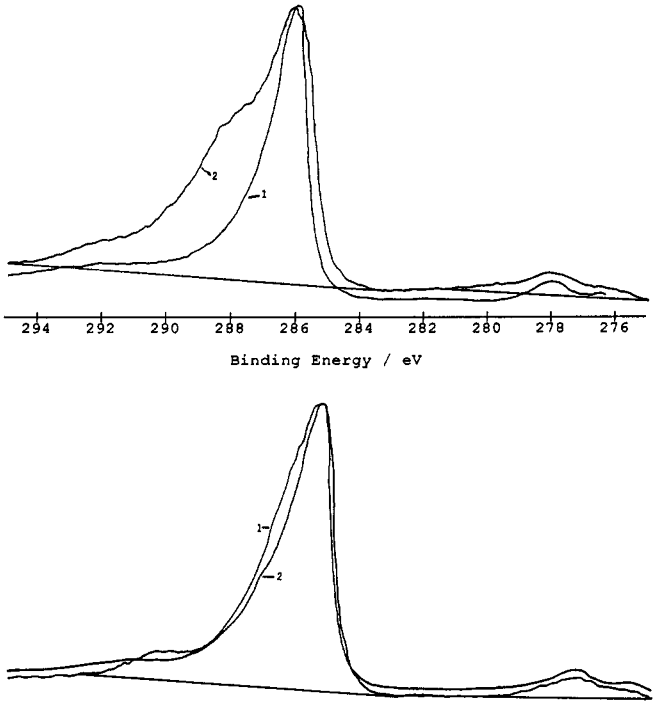

Figure 8. C_{1s} principal peaks: (A) carbon black (1) and ozone-treated carbon black (2) and (B) carbon microfiber (1) and ozone treated carbon microfiber (2). Note: charging shifts for (A) and (B) are 2.3 and 1.6 eV, respectively. Therefore positions for the component peaks are for C=O 287.2 + charging shift and for C-O 285.6 + charging shift (see Table V).

C=C, C≡C, etc., can not be differentiated by their principal (C_{1s}) peak chemical shifts.[9-11,19,20] As a result, our research group has recently developed an alternative analysis procedure based on the use of a C_{1s} loss method (labeled as ESCALOSS),[9] which has proved to be very useful (particularly in combination with valence band spectra) in explaining the surface and interfacial properties of a variety of carbonaceous systems,[21] including the present carbon fillers. All the ESCA data in this work were obtained with an Mg Kα X-ray source.

The C_{1s} loss peak of graphite has been found to be originated from the excitation of plasmons.[9-11] For relative pure graphite, a series of regularly spaced peaks, approximately 30 eV apart, arise from these plasmon excitations. Their intensities fall off progressively, in accordance with a normal Poisson distribution due to higher order interaction of plasmons. As indicated, the valence band features also can be used to supplement this ESCALOSS analysis. C_{1s} loss results suggest that the microfiber surfaces are more graphitic than the carbon black.

On the other hand, following the ozone treatment, the principal C_{1s} peak of CB exhibits a larger shoulder on its left side (Figure 8A) resulting from oxidized chemical states of carbon material, while for carbon microfibers, (Figure 8B), this effect is less prominent, apparently due to the more stable nature of its graphitic surface.[9,10] Note, there is some difference in C_{1s} peak positions caused by charging shifts. Similar shifts occur in Figures 9 and 10. The extent of this shoulder effect is thus related to the preferential formation of carbon–oxygen functionalities. This, we feel, is a reflection of the greater reactivity with ozone that generally exists on the surface of CB compared to CMF.

Table V. Speculations about Detected Carbon–Oxygen (Bulk) Compounds

Clark Results: C(1s) Polymer = 284.2

	C(1s)	O(1s)
C—OH	285.4	532.95
C—O—C	285.6	532.65
C—C(=O)—C	287.2	532.05
C—C(=O(1))—O(2)	(1) 288.5; (2) 286.1	(2) 533.7; (1) 532.2
O—C(=O(1))—O(2)	(1) 290.0; (2) 286.2	(2) 534.2; (1) 532.2

Our Results

	C(1s)	speculation
(1)	290.0	O—C(=O)—O
(2)	288.2	C—C(=O)—O
(3)	287.2	C—C(=O)—C

Note

	C(1s)
polypropylene	284.4
adventitious carbon	284.0

From the binding energies of the C_{1s} and O_{1s} principal peaks, one can determine that there were more C—O single bonds formed in the treatment than C=O double bonds by referring to Clark's results listed in Table V[11] (peak positions may vary with charging shifts). In the valence band region, a peak also emerges at 28 eV (primarily due to O_{2s} [Note, in a recent publication,[9] we have determined that for C-O-C systems, the peak at ~28 eV has substantial mixing of carbon valence states.]) thus providing further evidence for the occurrence of oxidation.

There are also some interesting features in the development in the C_{1s} loss spectra for these oxidized systems. For example, as elaborated upon in a previous paper,[9] oxidation of graphite surfaces generally shifts the C_{1s} loss peaks to smaller splittings from their principal peak, whereas oxidation of polymeric carbon surfaces shifts their C_{1s} loss peak further away from the principal peak. This may suggest the disruption of the double bond conjugated electron system in the first case and an increased conjugation in the latter case. The loss splittings of the two extremes thus approach each other after significant oxidation. In the present case, we note that the C_{1s} ESCALOSS of ozone treated CMF exhibit decreases in their C_{1s} loss splittings. This probably suggests some alteration of the large conjugating system of this material, induced through the creation of carbon–oxygen functionalities onto the graphite surface.

This ozone-treated CMF-epoxy composite has a lower maximum curing temperature than the sample without treatment (Figure 5 (2) 84.3 °C versus Figure 6(4) 106.7 °C) suggesting that a relatively stable, delocalized graphite surface was replaced by a more active one after formation of some oxide functionalities, which may be helpful in initiating the curing reaction. These effects were reversed for the CB composites (Figure 7 (1) versus (4)). The speculation here is that the original reactive CB surface, when attacked by O_3, may have lost some special types of functionalities which are relevant for the curing reactions, particularly when accompanied by the formation of certain new types of oxidized species. These speculations also seem to be supported by the O_{1s} spectra of CB. An obvious narrowing of O_{1s} principal peak can be observed after the

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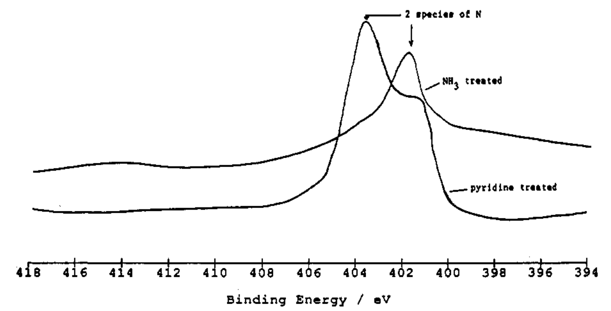

Figure 9. N_{1s} principal peak for pyridine treated carbon black shown here (as well as carbon microfiber) and for ammonium-treated carbon black (same as background).

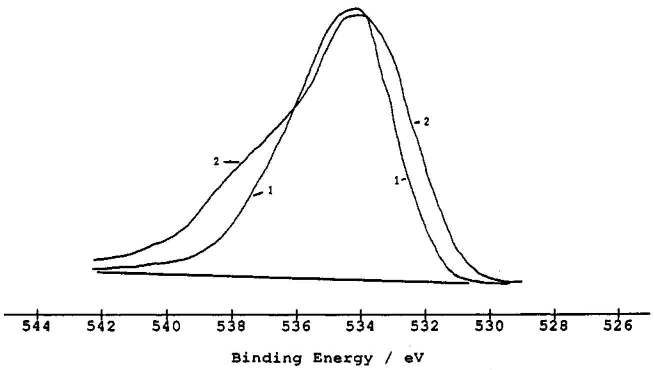

Figure 10. O_{1s} principal peak for O_3-treated carbon black (1) compared with same peak before the O_3 treatment (2). Note: same charging shifts as for Figure 8A.

ozone treatment of CB (relative to similarly treated CMF surfaces) indicating possible destruction of some of the diverse oxide species for the CB system, while the total oxygen content was increasing (Figure 10).

After surface treatment of carbon fillers with ammonia, there is little change in the carbon and nitrogen ESCA spectra (Figure 9), indicating that very little ammonia was adsorbed on the surfaces of both carbon species. To test the extent of this property, pyridine was used as an alternative amine reactant. As an aromatic compound, pyridine should be adsorbed more readily on most graphitic carbon surfaces. On the basis of the N_{1s} ESCA spectrum illustrated in Figure 9, we find a significant increase in nitrogen content compared to the background on the carbonaceous surfaces, suggesting substantial nitrogen adsorption on these surfaces. The chemistry indicated by the C_{1s} and N_{1s} binding energies for these species suggests the appearance of a new N_{1s} peak after the pyridine treatment of both carbon fillers. This corresponds to an oxidized chemical state.

It should also be noted that after pyridine treatment, the maximum curing temperature from DSC of the CMF-epoxy composite was decreased (Figure 5 (3) 101.2 °C versus Figure 6 (4) 106.7 °C) suggesting that a number of the strong adsorption sites on that surface may have been occupied by the chemical and/or physical linkages formed by the adsorbed pyridine. As a result, the curing reaction was enhanced because the adsorption of the curing agent on the carbon surface was decreased. Similar pyridine treatment had little effect on the CB surfaces with respect to the DETA curing reaction (see Table IV). One may speculate, therefore, that there are many more adsorption sites on the CB surface than on the CMF surface, and many of those are unaffected by the pyridine adsorption. Also, DETA is much less likely to be strongly held by either carbon surfaces.

Conclusion

A novel form of carbon filler, designated as carbon microfibers (CMF), is described from their catalytic preparation to their subsequent morphological characterization. Optimization of the alloy catalyst employed and the resulting sizes and shape of the microfibers are discussed. The name "carbon microfiber" was chosen because of the relation of the very small diameter and large aspect ratio. The graphitic sheath of these fibers makes them excellent candidates to compare with graphitic carbon powders, such as carbon black (CB), in terms of their relative ability to form polymer matrix composites. This study, therefore, also reports the preparation and comparative analyses of composites involving CMF and CB fillers in epoxy resin matrices.

Generally, the reported DSC and ESCA studies have revealed that the CMF, with its predominant graphitic surface, is less active than the CB filler system for epoxy curing reactions involving amines. The chemically reactive surface character of the CB is suggested to be a major feature in this difference. The incorporation of large amounts of carbon material (40 wt %) into the epoxy surprisingly promoted the curing reaction, suggesting that the reaction may be activated by a carbon-epoxy interface interaction caused by the presence of certain chemical functionalities. Carbon surfaces also may adsorb certain curing agents and catalysts when their interaction becomes very strong and this adsorption appears to partially inhibit the curing reaction, particularly when the amount of curing agent or catalyst is small. The DMBA catalyst studied here is an example of this effect.

Several common surface chemical treatments of the carbon fillers were imposed and found to change the reaction mechanisms with epoxy resin. For example, pyridine treatments may cover some of the adsorption sites, thus favoring enhanced curing reactions for the epoxy resin. Ozone treatments evidently activate the graphitic surfaces of the CMF to enhance the epoxy curing reactions. On the other hand, the epoxy curing reaction was not enhanced by surface treatments of CB, perhaps because it already is extensively activated for the reaction. A C_{1s} loss technique [ESCALOSS] and carbon–oxygen valence band spectra were employed to determine several features, such as the presence and retention of graphitic character on the carbon surfaces. Many of these features are not discernible by conventional ESCA.

In summary, after a brief description of the novel CMF, our results show that CB and CMF as fillers exhibit differences in their composite curing reactions with epoxy. These differences are compromised when surface chemical treatments were applied to both carbon fillers. Therefore, we would predict that alterations in curing mechanisms may also lead to differences in the mechanical and electrical properties of the composites thus formed. Studies of these features are in progress, and their results will be explored in a subsequent paper.