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Calorimetric study of the effect of carbon fillers on the curing of epoxy

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Epoxy is widely used in industrial applications in relation to adhesives, coatings, electronics and aerospace structures. Due to its attractive mechanical and chemical properties, such as excellent bonding ability, high tensile and compressive strengths, good chemical resistance and high heat distortion temperature, epoxy is the dominant matrix material for lightweight polymer–matrix structural composites, such as carbon fiber composites. The superior mechanical and chemical properties of epoxy are due to the three-dimensional network structure that results from the curing process, in which a low molecular weight resin is transformed into a high molecular weight polymer. The interfacial strength between carbon fillers and epoxy resin varies with the surface structure of fillers [1–3]. As a result, the surface structure affects numerous properties, such as the interlaminar shear strength and the impact resistance.

Studies have been reported on the curing behavior of epoxy/carbon filler systems, particularly systems involving carbon nanotubes [4,7], carbon fiber [5,6] and carbon black [4]. It was shown by differential scanning calorimetry (DSC) that the heat of the epoxy curing reaction was higher in the presence of carbon nanotubes than in the presence of carbon black [4], and that the rate of the reaction was increased by surface treatment of carbon black [4–7]. However, DSC also showed that carbon fiber had very small effect on the curing kinetics [5]. Little attention was given to the comparison of the

effects of different carbon fillers and different carbon filler surface treatments on the curing of epoxy. Therefore, this work provides a comparative study of carbon fillers, including carbon fiber, carbon nanofiber and carbon black. In addition, this work addresses the effect of filler surface treatment on the curing process. Understanding the effect of fillers on the curing reactions is valuable for improving and/or optimizing the manufacturing process of epoxy–matrix composites.

Epoxy resin filled with various carbons (carbon fiber, carbon nanofiber and carbon black) was studied. The epoxy resin system consisted of a diglycidyl ether of bisphenol F (DGEBF) (epoxy resin, EPON 862, Shell Chemical Company, Troy, MI) and triethylene tetramine curing agent (EPI-CURE curing agent 3234, Shell Chemical Company, Troy, MI). The molecular structures of the resin and the curing agent are shown in Fig. 1. The resin and curing agent were used in the weight ratio of 100:15.4.

The carbon fiber was obtained by manual chopping of Thornel P-25 continuous pitch-based carbon fiber, which was obtained from BP Amoco Polymers, Alpharetta, GA. The carbon fiber had a density of 1.90 g/cm³, a specific surface area of 0.70 m²/g and a diameter of 11 μm. The length of the chopped carbon fiber was in the range from 2 to 4 mm. As-received and two types of surface-treated fibers were used. The surface treatments were ozone-treatment and activation. The ozone-treatment involved exposure of the carbon fiber to O₃ gas (0.6 vol.% in O₂) at 150 °C for 10 min. Prior to O₃ exposure, the fibers had been washed with acetone and dried at 90 °C for 24 h. The activation of the chopped carbon fiber in CO₂ involved (i) maintaining the carbon fiber

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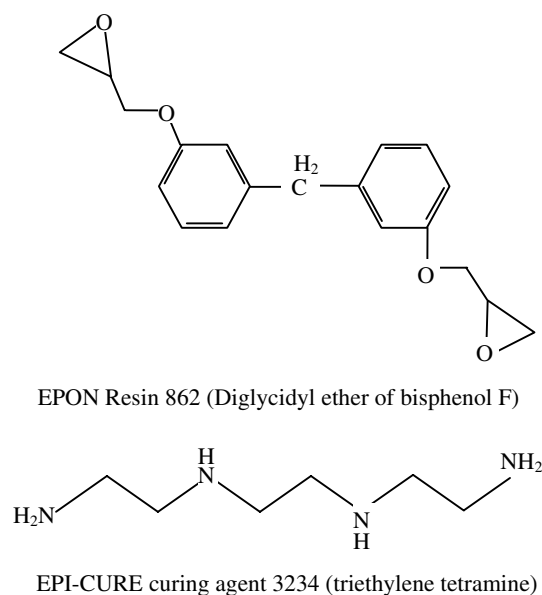


Fig. 1. Molecular structures of resin and curing agent.

under flowing N_2 in a tube furnace, which was heated from 25 to 1000 °C at a rate of 5 °C/min, and (ii) exposing the carbon fiber to a flowing mixture of 50% CO_2 in N_2 at 1000 °C for 60 min. Prior to activation, the as-received carbon fiber had been washed with acetone and dried at 90 °C for 24 h as well. The amount of carbon fiber used was 10% by volume of the epoxy resin.

The carbon black was Vulcan XC72R GP-3820 from Cabot Corp., Billerica, MA. It was a powder with an average particle size of 30 nm, a maximum ash content of 0.2% and a density of 1.7–1.9 g/cm³. The carbon black content was 10% by volume of the epoxy resin.

The carbon nanofiber was obtained from Applied Science Inc., Cedarville, OH. The nanofiber had a diameter of 0.1 μm , a length exceeding 100 μm and a density of 2 g/cm³. The carbon nanofiber content was 10% by volume of the epoxy resin.

The BET specific surface area of each type of filler (without epoxy) was determined by nitrogen adsorption (gas pressure measurement), using an ASAP 2010 analyzer (Micromeritics). Each specimen was outgassed at 150 °C for 2 h prior to the adsorption test.

Calorimetric study of the curing behavior of carbon filled epoxy resin was performed using the Perkin-Elmer DSC7 differential scanning calorimeter. Indium and zinc were used to calibrate the calorimeter. Specimens, with an approximate weight of 10 mg each, were prepared by mixing the epoxy system and filler manually until the mixture was visually homogeneous. All as-received and surface treated carbon fillers were assumed to be well dispersed in the epoxy/amine combination at that stage. Then the mixture was transferred to aluminum pans, which were subsequently covered by using aluminum lids. The specimens were maintained at room tem-

perature for 10 min. before temperature scanning began. Temperature scanning was performed in flowing air (50 ml/min) from 20 to 300 °C at a heating rate of 2 °C/min. The enthalpy change due to the reaction (ΔH) was obtained by integrating the area of the exothermic DSC peak after baseline subtraction. The temperature of the maximum exothermic heat flow (T_E) corresponded to the DSC peak temperature. Five specimens of each type were tested.

Table 1 shows the BET specific surface areas of the carbon fiber (as-received and surface treated types), carbon nanofiber (as-received) and carbon black (as-received). Ozone-treatment of chopped P-25 carbon fiber at our experimental conditions did not have any significant effect on the specific surface area, while CO_2 activation increased the specific surface area of P-25 carbon fiber from 7.6 to 90 m²/g. Carbon black has the highest specific surface area, due primarily to the smaller sizes of its particles.

Fig. 2a shows the representative DSC thermogram during curing of the epoxy resin system without filler, as obtained during first heating from 20 to 160 °C at a rate of 2 °C/min. Only one peak was observed. It was exothermic, with $T_E = 93.4$ °C.

After cooling, the specimen was immediately reheated, thus resulting in the DSC thermogram in Fig. 2b. No peak was observed, indicating that the epoxy resin had been completely cured after the first heating step. Thus the enthalpy change ΔH , as obtained from the peak area in the thermogram during first heating, is the heat of reaction due to complete cure of the epoxy resin.

Fig. 3 shows the DSC thermograms of epoxy with carbon nanofiber and activated carbon fiber during the first heating step. Table 2 lists the values of ΔH and T_E of the epoxy/amine resin with each of the carbon fillers. For any given specimen, only one DSC peak (exothermic) was observed. All of the fillers tested increase ΔH and also accelerate the curing reaction (i.e., decreases T_E).

As shown by comparing the data for epoxy with as-received carbon fiber and epoxy with activated carbon fiber (Table 2), activation accelerates the curing reaction by decreasing T_E from 85 to 80 °C, but does not have much effect on ΔH . Also, as shown in Table 1, activation increases the specific surface area from 7.6 to 90 m²/g.

Table 1
BET specific surface area of various carbon fillers

Filler	Specific surface area (m ² /g)
Carbon fiber (as-received)	7.6 ± 0.6
Carbon fiber (ozone-treated)	7.8 ± 0.6
Carbon fiber (activated)	90 ± 8
Carbon nanofiber (as-received)	12 ± 2
Carbon black (as-received)	254 ± 22

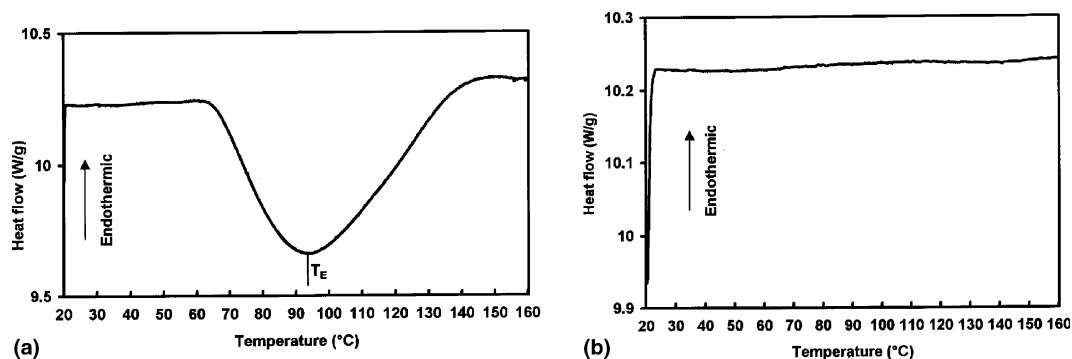


Fig. 2. DSC thermograms of epoxy system without filler (a) first heating, (b) second heating.

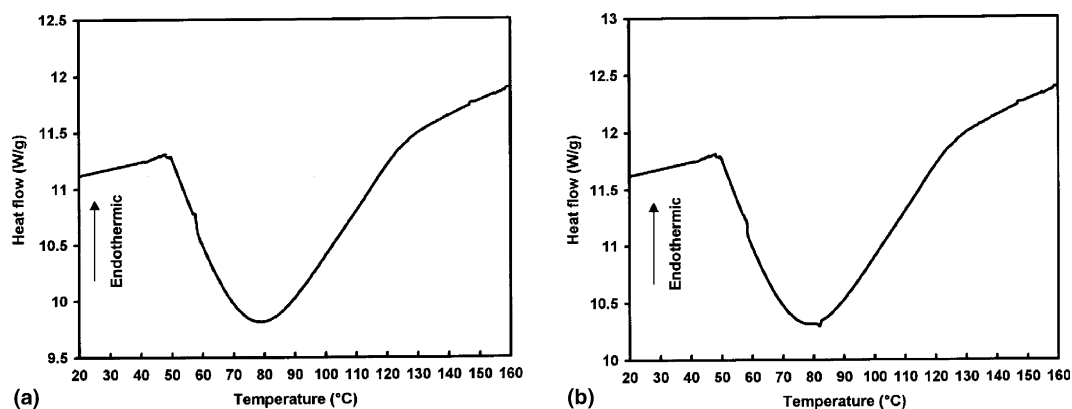


Fig. 3. DSC thermograms of epoxy with (a) carbon nanofiber, (b) activated carbon fiber.

Table 2

Heat of reaction (ΔH) and maximum exothermic heat flow temperature (T_E)

Material	H (J/g) ^a	T_E (°C) ^a
Epoxy without filler	121.6 ± 6.4	93.4 ± 0.7
Epoxy with as-received carbon fiber	137.4 ± 6.2	85.2 ± 0.5
Epoxy with ozone-treated carbon fiber	197.8 ± 7.9	84.5 ± 0.5
Epoxy with activated carbon fiber	140.2 ± 8.1	79.8 ± 0.4
Epoxy with carbon nanofiber	138.6 ± 8.8	82.1 ± 0.6
Epoxy with carbon black	144.6 ± 9.1	71.8 ± 0.3

^a The \pm deviations represent single standard deviations.

Thus it appears that an increase in the specific surface area accelerates the curing reaction, but has a negligible effect the heat of the reaction.

In contrast, ozone-treatment increases ΔH from 137 to 198 J/g, but has a negligible effect on T_E . Ozone-treatment is known to generate oxygen-containing functional groups on the surface of carbon fiber [8,9]. The functional groups may participate in the curing reaction, thereby increasing the heat of the reaction. The negligible effect of ozone-treatment on T_E is consistent with the absence of an effect of this treatment on the specific surface area (Table 1).

Carbon nanofiber and carbon black affect ΔH similarly as as-received or activated carbon fiber, but carbon black decreases T_E more than any of the fillers studied. This large effect of carbon black on T_E is consistent

with the high specific surface area of carbon black (Table 1).

The results of this work are consistent with those of prior work [4,5,7] in relation to the small effect of carbon fiber on the curing kinetics and the increase of the reaction rate (decrease in T_E) by surface treatment. That the heat of the curing reaction is higher for carbon nanotubes in epoxy than for carbon black in epoxy [4] is probably due to the high specific surface area of carbon nanotubes. Carbon nanofiber is different from carbon nanotubes in its lower specific surface area, so it is reasonable to expect that the heat of reaction is quite similar for carbon nanofiber and carbon black (as shown in this work).

In summary, the presence of a carbon filler in an epoxy resin with a linear amine curing agent increases the heat

of the curing reaction, especially if the filler is ozone-treated carbon fiber (with oxygen-containing functional groups on its surface). Ozone-treated carbon fiber increases the heat of curing more than carbon nanofiber or carbon black. The presence of a carbon filler also accelerates the curing reaction by decreasing the maximum exothermic heat flow temperature, especially if the filler is carbon black (with a relatively high specific surface area). Carbon black accelerates the curing process more than carbon nanofiber or carbon fiber. Increasing the specific surface area of a filler accelerates the curing of epoxy, but it has a negligible effect on the heat of the curing reaction. Ozone-treatment increases the heat of curing of epoxy filled with carbon fiber more than activation, but it accelerates the curing less than activation.

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