Evolution of the Wettability Between Carbon Fiber and Epoxy as a Function of Temperature and Resin Curing

Min Li,[1] Chao Yuan,[1] Shao Kai Wang,[1] Yi Zhuo Gu,[1] Kevin Potter,[2] Zuo Guang Zhang[1]

[1]Key Laboratory of Aerospace Materials and Performance (Ministry of Education), School of Materials Science and Engineering, Beihang University, Beijing 100191, China
[2]Advanced Composites Centre for Innovation and Science, University of Bristol, University Walk, Bristol BS8 1TR, United Kingdom
Correspondence to: M. Li (E-mail: leemy@buaa.edu.cn)

ABSTRACT: This article focuses on experimental studies on the wetting behavior between different carbon fibers (CFs) and epoxy as function of temperature, hardener addition, and progressive curing of the resin. The results indicate that surface sizing plays a key role in wettability of the CF with epoxy. There is a critical temperature for good-wetting of DGEBA-DDS mixture/CF. Complete wetting can be obtained for resin/CF after a period of curing time. Moreover, chemical reactions can not only improve the wettability but also strengthen interactions between the curing resin and CF. These results could provide an essential implication for understanding the formation process of interphase region of CF/epoxy composites. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 4095–4101, 2013

INTRODUCTION

Good wetting between fiber and resin plays a key role in the formation of composite interphase which often limits the overall performance of the bulk composites.[1,2] Wettability is often quantitatively expressed in terms of contact angle (CA), given by the Young's equation:

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta \qquad (1)$$

where θ is the CA, γ_S, γ_{SL}, γ_L represent the surface energy (SE) of the fiber, the fiber/resin interface, and the resin, respectively. According to the thermodynamic principle, SE of the fiber must be greater than that of a matrix for proper wetting to take place. However, previous studies revealed that SEs of carbon fibers (CFs) and liquid epoxy were the same order of magnitude, e.g., 39.4 mJ/m² of Herceles AS-4 CF and 39.44 mJ/m² of DER 330 epoxy,[2] and the surface tension (SFT) of HexPly 8552 epoxy was reported of 42.5 mN/m.[3] Additionally, during the curing process of epoxy, chemical reactions can induce changes of the intermolecular interactions, which will influence the interfacial adhesion between CF and epoxy. For instance, our studies showed that SE of cured DGEBA-DDS resin system was about 46 mJ/m². To improve wettability and compatibility between CF and resin, great achievements have been obtained by fiber surface treatments, especially by increasing content of oxygen type functional groups on CF, the composite interfacial strengths were significantly improved, as well as the CF surface energetics.[4–7]

In addition, cross-link reaction of thermoset resins can impact their wetting behavior, which has been extensively studied.[8–11] Chen and Pascault analyzed SFT of the epoxy mixture with comonomers and additives.[8] Page et al. demonstrated the resin surface energetics has close relationship with the cure degree.[9,10] Synytska et al. studied the SFT of amine-cured epoxy under different environments to develop adhesive formulations.[11] However, influence of resin curing on its wetting behavior with CF has not yet been reported. This is essentially significant to understand the formation and the fine structure of interphase region in CF/thermoset composites.[12]

This article aims to explain the wetting behavior between CFs and epoxy as function of temperature, hardener addition, and progressive curing of the resin. The resin SFTs, the CF SEs, and the dispersive and polar components are also tested. Effect of CF sizing on the wetting is studied by desized CF comparing with the original sized CF. Moreover, wettability between curing resin and CFs is analyzed with evolution analysis of the resin viscosity, cure degree, and content changes of typical functional groups in the epoxy system.

EXPERIMENTAL

Materials

A typical epoxy diglycidyl ether of bisphenol A (DGEBA) was used with the epoxy value of 0.48–0.54 mol/100 g, provided by Wuxi Diaisheng Co. A high-temperature cure agent, diamino diphenyl sulfone (DDS) was used to investigate the hardener

Table I. The Surface Properties of CFs Measured by IGC, as Well as the Diameter Tested by the Modified Wilhelmy Method

Fiber type	Total SE (mJ/m^2)	Dispersion component (mJ/m^2)	Polar component (mJ/m^2)	Polarity $X_S^p = \gamma_S^p/\gamma_S$	Measured diameter (µm)
T300	40.30	31.17	9.13	0.23	7.1 ± 0.1
Desized T300	45.15	39.71	5.44	0.12	6.9 ± 0.2
T700	49.29	32.71	16.58	0.34	7.1 ± 0.3

addition and curing effect on the SFT and wettability of epoxy system. The weight ratio of the DGEBA:DDS was 100 : 31.5.

Two commercially available high-strength CFs, i.e., T300B-3000-40B (denoted as T300) and T700SC-12000-50C (denoted as T700) with nominal diameters of 7 µm (Toray, Japan) were used. Desizing of the commercial CF was carried out by acetone extraction at 75°C for 6 h and then dried at 60°C in a vacuum oven for 8 h, and stored in a dryer before use. The IR spectra, as presented in Ref. 13, indicated that the extracted sizing agents of T300 and T700 are mainly epoxy type (915 cm^{-1}).

SFT and CA Measurements
The resin SFT was tested by Wilhelmy method with a standard platinum plate using DCAT21 (DataPhysics). Based on the balance force (F) recorded at zero-buoyancy, γ_L can be obtained by complete wetting ($\theta = 0$) assumption between liquid resin and the platinum plate:

$$F = \gamma_L p \cos \theta \tag{2}$$

where p denotes the wetted perimeter (i.e., 40.20 mm in this study). During the measurement, the resin was slowly moved upward at a rate of 1.00 mm/s with the target elevated temperatures controlled within ±0.2°C. For the DGEBA-DDS mixture, the heating was carefully controlled and the SFT tests were conducted immediately to ensure no chemical reaction take place. For the curing DGEBA-DDS system, to obtain more data on SFT, relatively low temperatures (i.e., 110, 120, and 135°C) were used rather than the standard composite fabrication temperature of 180°C.

CAs between CFs and resin were measured by the modified Wilhelmy method based on eq. (2). In practice, five individual fibers were placed parallel to each other onto a PTFE holder so as to eliminate effect of heterogeneity of the fiber surface. To minimize the fiber bending when submerged into resin, each

fiber was cut to a protruding length of 5 mm, and the contact rate was carried out at 0.01 mm/s. Diameters of the CFs were calculated from the wetted perimeter with the test liquid silicone oil ($\gamma_L = 20.31$ mN/m), which is able to wet the fiber completely with low evaporation rate. Table I gives the diameter results of T300, desized T300, and T700. Before CA test, the fibers were all heated at 70°C for 2 h in a vacuum oven for surface desorption. At least, five measurements were successfully achieved for each.

The work of adhesion, W_A, is evaluated by Young-Dupré equation as follows, in which the liquid SFT and CA are easily available:

$$W_A = \gamma_{LV}(1 + \cos \theta) + \pi_e \tag{3}$$

where π_e is the equilibrium spreading pressure of a liquid's vapor upon a solid surface which is negligible for low SE CFs.[14]

CF Surface Analysis by IGC
Inverse gas chromatography (IGC) was used for assessing the CF surface properties including the SEs, the dispersive (γ_S^d) and polar (γ_S^p) components. Measurements were carried out at 30°C with a helium carrier gas flow of 10 ccm/min. The probe concentration was 0.04 p/p^0. About, 0.8 g CF was packed in silanized glass columns (30 cm length and 4 mm inner diameter). Before measurement, the CF was pretreated by pure helium flow for 30 min to eliminate the surface absorbs impurities. The probes used in the dispersive component determination were n-alkane, including decane, nonane, octane, and heptane, whereas the polar interactions were measured by dichloromethane and toluene probes. All the probe liquids were HPLC grade (J&K) with their propertied listed in Table II.

Since the theory of IGC has been well developed and reviewed elsewhere,[15] the detailed derivation and calculation of the free energy of sorption ΔG and energy of adhesion W_A, are omitted

Table II. Properties of the Probe Liquids Used in the IGC Experiments

Probe	Cross-sectional area, $\alpha \times 10^{-19}$ (m^2)	$\gamma_{L,P}^d$ (mJ/m^2)	$\gamma_{L,P}^+$ (mJ/m^2)	$\gamma_{L,P}^-$ (mJ/m^2)	Specific character
Decane	7.5	23.4	–	–	Neutral
Nonane	6.9	22.7	–	–	Neutral
Octane	6.3	21.3	–	–	Neutral
Heptane	5.7	20.3	–	–	Neutral
Dichloromethane	2.5	24.5	124.6	0.00	Acidic
Toluene	4.6	28.5	0.00	16.2	Basic

here. The interaction of n-alkane with the substrate material is dominated by the van der Waals dispersive forces of interaction. It has been shown that under conditions of infinite dilution of the injected probe vapor, the dispersive component of the substrate, γ_S^d, is related to the net retention volumes, V_R^o, by the following equation[16]:

$$-\Delta G = RT \ln V_R^o = 2N_A(\gamma_S^d)^{1/2} \times \alpha(\gamma_{L,P}^d)^{1/2} + \text{const.} \quad (4)$$

where R is the gas constant, T the column temperature, N_A the Avogadro constant, and α the cross sectional area of the adsorbate probe.

According to Fowkes,[17] W_A can be split into two terms $W_A = W_A^d + W_A^p$, with W_A^d denoting the van der Waals forces and W_A^p the specific, mainly polar interactions. He proposed that when only dispersive interactions are occurring, for example when performing measurements with n-alkane probes, the work of adhesion W_A may be expressed in terms of the dispersive SE components of the solid substrate (γ_S^d) and the liquid phase ($\gamma_{L,P}^d$),

$$W_A = 2(\gamma_S^d \cdot \gamma_{L,P}^d)^{1/2} \quad (5)$$

Hence, a plot of $RT \ln V_R^o$ vs. $\alpha(\gamma_{L,P}^d)^{1/2}$ should give a straight line with slop $(\gamma_S^d)^{1/2}$ according to Schultz's method.[18] The interactions of polar probes with the substrate involve both dispersive and acid–base interactions. The specific free energy ΔG^{SP}, corresponding to acid–base surface interactions, can be evaluated by the distance between each point of the polar probe and the straight alkane line of the plot $RT \ln V_R^o$ vs. $\alpha(\gamma_{L,P}^d)^{1/2}$. Van Oss subdivided the polar (i.e., the specific) SE into two nonadditive parameters γ_S^+ and γ_S^-, representing the electron acceptor and donor properties, respectively.[15]

$$\gamma_S^p = 2\sqrt{\gamma_S^+ \cdot \gamma_S^-} \quad (6)$$

Then, the acceptor and donor parameters of the CF SE are related to ΔG^{SP} as the following equation, which can be calculated when the $\gamma_{L,P}^+$ and $\gamma_{L,P}^-$ values are known.

$$\Delta G^{SP} = 2N_A \cdot \alpha \cdot \{(\gamma_{L,P}^+ \cdot \gamma_S^-)^{1/2} + (\gamma_{L,P}^- \cdot \gamma_S^+)^{1/2}\} \quad (7)$$

Furthermore, polar component γ_S^d of the CF SE can then be estimated by eq. (6).

Resin Curing Analysis

The conversion degree of DGEBA-DDS system was analyzed using isothermal measurements by differential scanning calorimeter (DSC) based on advanced model free kinetics of Vyazovkin integral method.[19] A METTLER TOLEDO was used to conduct the test with the heating rate of 200°C/min before approaching the target constant temperature and the Nitrogen flow rate of 40 mL/min. Besides, the dissolving behavior of DDS in DGEBA was also detected by DSC with the heating rate of 2, 5, 7, and 10°C/min, respectively.

A Gemini rheometer made by Bohlin Instruments was used to determine the complex viscosity of DGEBA-DDS system in
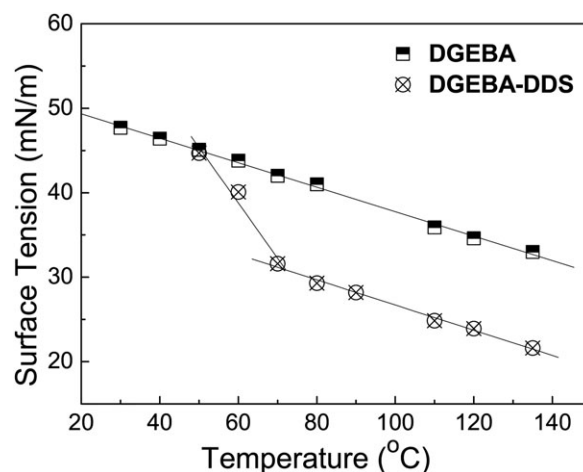

Figure 1. The SFT of DGEBA and the DGEBA-DDS mixture under elevated temperatures.

curing process at 110°C. The rheometer was used in parallel-plate configuration with a disc radius of 25 mm and gap size 0.6 mm. Data were generated with the disc oscillating at 1.0 Hz and 10 Pa stress. The temperature was kept within ±0.1°C of the set point.

To study the functional group changes in curing DGEBA-DDS system, *in situ* FTIR was carried out by using Nicolet 6700 Spectrometer. The resin sample was heated, and the FTIR spectra were collected by signal averaging 32 scans at a resolution of 4 cm^{-1} in the wavenumber range from 4000 to 400 cm^{-1}. The concentrations of typical functional groups were quantitatively analyzed in accordance to the infrared absorbance, in which vibration of benzene ring at 1610 cm^{-1} was chosen as the internal standard reference peak. During the DGEBA-DDS curing process, the content change of epoxide at 915 cm^{-1} and that of primary amine at 3240 cm^{-1} were estimated.

RESULTS AND DISCUSSION

Temperature-Dependent SFT of Epoxy

First, SFTs of DGEBA and the DGEBA-DDS mixture were measured at elevated temperatures, as shown in Figure 1. The DGEBA SFTs present a monotonic regression linear relation with the increasing temperature as expected.[20] However, SFTs of the DGEBA-DDS mixture exhibit a two-stage temperature-dependent decreasing tendency with the demarcation occurring at 70°C. By contrast, the SFTs of the DGEBA-DDS mixture decrease more considerably than those of pure DGEBA. From Figure 2, the DSC tests suggest that DDS can dissolve into DGEBA at about 83°C. As mentioned above, the heating rate of the DGEBA-DDS mixture was fairly fast during the SFT measurement, which is necessary to prevent possible chemical reactions from initiating. It can be inferred that DDS could begin to melt in DGEBA at 70°C, thereafter induced steady decrease of the SFT of the mixture similarly to that of the pure DGEBA. Anastasiadis et al. reported similar observation with two-stage interfacial-tension curve as a function of temperature in immiscible polymer blends.[21] Hence, dissolving state of DDS
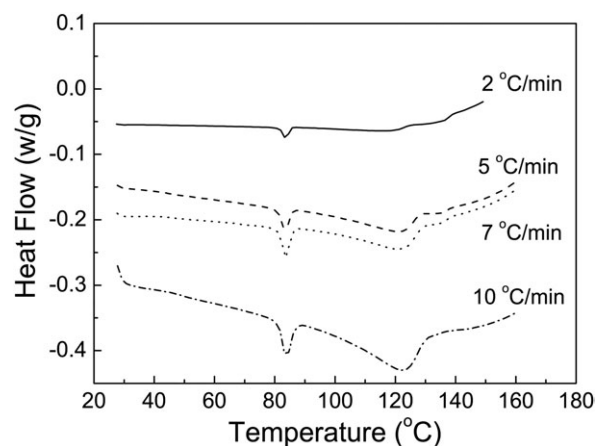
Figure 2. Heat flow profiles of the DGEBA-DDS mixture under ramping rates of 2, 5, 7, 10°C/min, respectively, measured by DSC.

in DGEBA will influence the wetting behavior of the liquid resin with CF.

Temperature-Dependent Wetting of CF/DGEBA

From Figure 3(a) we can see that CAs between DGEBA and CFs of T300, desized T300, and T700 all slightly decrease with increasing temperature. From theoretical viewpoint, the CAs may either decrease or increase with temperature depending on the relative magnitude of the surface entropies of the two phases, i.e., $d\gamma_L/dT$ versus $d\gamma_S/dT$. Our additional tests showed that CAs of small molecule liquids (e.g., diiodomethane, formamide, and water) kept almost constant at different temperatures with a reference-solid plate, indicating negligible temperature effect. However, CAs of pure epoxy with the reference-solid plate slightly decreased with increasing temperatures.

Comparing T300 with T700, the two CFs reveal almost equivalent CAs with DGEBA in Figure 3(a). From Table I, it can be seen that T700 has higher SE and much larger polarity than T300, whereas desized T300 has higher SE but much smaller polarity than T300. Moreover, desized T300 shows relatively larger CAs with DGEBA than those of T300. Therefore, in comparison with the fiber SE and polarity, the fiber surface sizing is more effective to the wettability of CFs with DGEBA.

In Figure 3(b), values of the Young W_A for all the CFs present no significant changes over the studied temperatures range from 30 to 70°C. Likewise the W_A values of T700 are approximately the same as those of T300, whereas those of desized T300 are slightly smaller than T300 suggesting weaker interactions at the interface for the desized CF. Our studies showed that the sizing agents of T300 and T700 both are epoxy type.[13] Moreover, with increasing heat-treatment temperatures for the fiber, the sizing extract content of T300 decreased and the content epoxy group of the sizing decreased as well.[22] These suggested that the sizing agents were chemically reactive at high temperatures. Therefore, it can be concluded that, due to chemical similarity between the sizing and epoxy resin, the existence of sizing agent has profound effect on the wetting behavior of the CF with the epoxy resin.
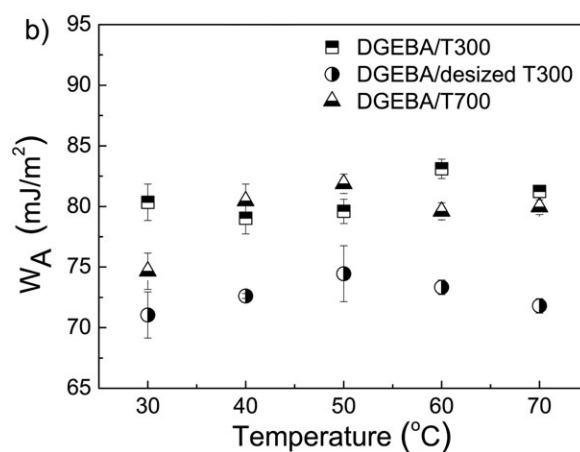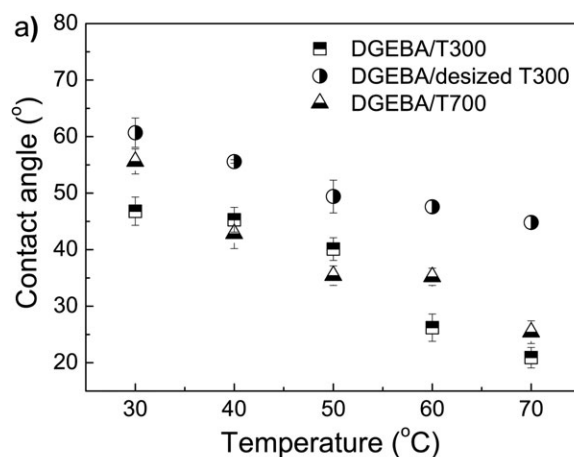

Figure 3. Wettability between DGEBA and the CFs: (a) contact angle and (b) the Young WA as a function of temperature.

Effect of Hardener Addition on the Wettability

Figure 4 gives wetting properties for the DGEBA-DDS mixture/T700 as a function of temperature. Both CA and W_A profiles show a two-stage tendency with the demarcation temperature occurring at 70°C, similar to the SFT plot of the DGEBA-DDS
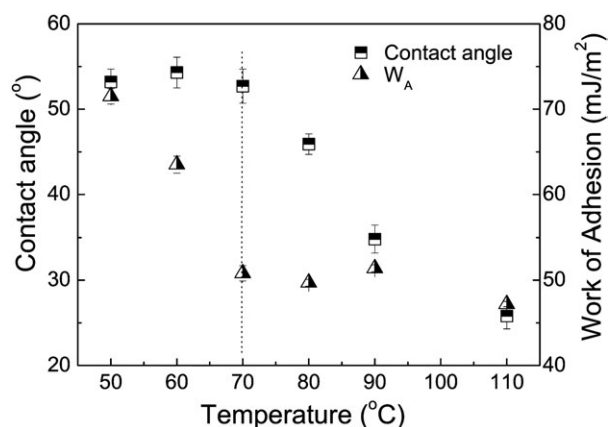

Figure 4. The contact angle and Young WA of DGEBA-DDS/T700 at elevated temperatures.

mixture. In Figure 4, the CAs remain almost constant from 50 to 70°C, whereas the W_A values decrease considerably. Correspondingly, from Figure 1 we can see significant decrease of the mixture SFT at the same temperature range. Thus, it implies that the special wetting performance of the DGEBA-DDS mixture/T700 should be associated with the dissolving behavior of DDS in DGEBA.

From a quantitative point of view, the DGEBA-DDS mixture/T700 reveals larger CAs than those of DGEBA/T700 at the same temperatures, indicating lower wettability of the DGEBA-DDS mixture versus the pure epoxy with the CF. Furthermore, the W_A values for the DGEBA-DDS mixture are smaller suggesting weaker interactions at the interface with T700 than those for DGEBA. Taking consideration of Figures 1–4, we can find that 70°C is a minimum threshold temperature for achieving good wetting for the DGEBA-DDS mixture with the CF, below 70°C DDS cannot completely dissolve into DGEBA, which would certainly influence the wetting behavior of the DGEBA-DDS mixture. By contrast, temperature effect is simple and moderate on the wetting behavior of the pure epoxy with the CF. Besides, surface enrichment of amine hardener was proved in epoxy-benzylalcohol solutions.[11] This is why researchers oppose to characterize resin SFT by its mixture with diluents.

Effect of Resin Curing on the Wettability

Figure 5 gives the SFT evolution of the curing DGEBA-DDS at constant temperatures 110, 120, and 135°C respectively, which shows monotonic increase with the reaction time. Higher the temperature, earlier and faster the SFT increases. This should be associated with the temperature-dependent reaction dynamics of the epoxy system, which will be discussed in the follow.

The CA and W_A profiles of the DGEBA-DDS system/T700 are plotted as function of time at 110°C in Figure 6(a), in which the CA values decrease slightly with time, whereas the Young W_A presents a simultaneous increase tendency. It should be noticed that zero CA can be achieved after 80 min, indicating complete wetting property between the curing resin system and T700, which implies that the CF sizing may dissolve into the epoxy resin after a period of time at 110°C.
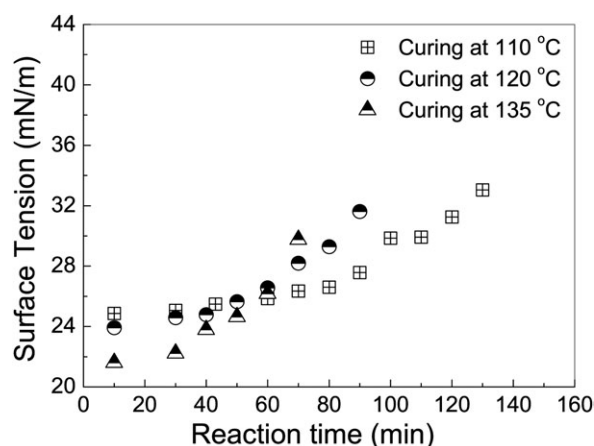

Figure 5. Plots of SFT for the curing DGEBA-DDS system versus the reaction time at different constant temperatures.
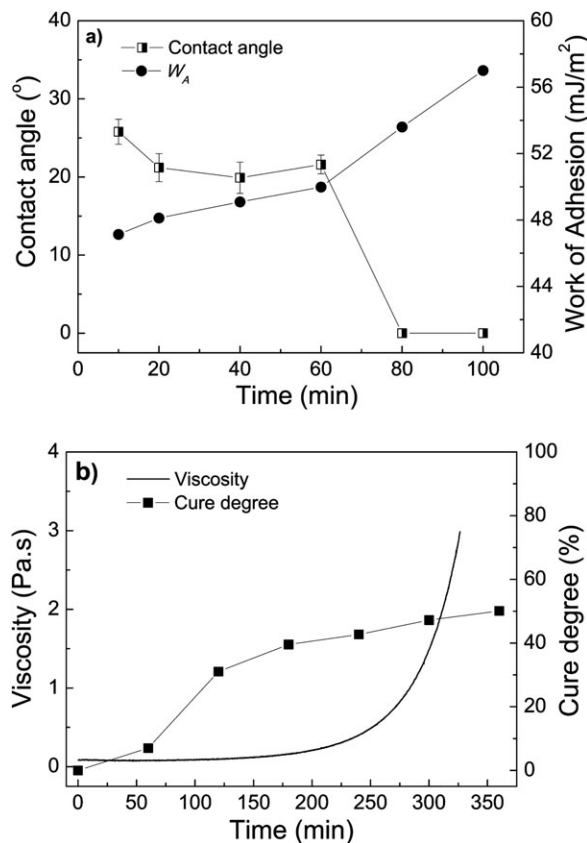

Figure 6. (a) Plots of CA and Young WA for the DGEBA-DDS system/T700 and (b) the conversion and viscosity curves of DGEBA-DDS system, as a function of time at 110°C.

The viscosity and conversion degree profiles of the DGEBA-DDS system as function of time at 110°C were tested. In Figure 6(b), the resin viscosity shows no significant change until after 150 min at 110°C, which indicates that the SFT evolution of the resin (in Figure 5) has no correlation with the viscosity. However, the cure degree of the DGEBA-DDS system gradually increases from the initial moment and approaches 50% at 360 min. Therefore, Figure 6(b) suggests that DGEBA can chemically react with DDS at 110°C, which will certainly influence the wetting and interfacial interactions between the epoxy resin and T700. Moreover, the W_A values in Figure 6(a) suggest stronger molecular interactions at the interface with T700 due to the curing progress of the DGEBA-DDS system. Comparing with the CA value of the DGEBA-DDS mixture, i.e., at the beginning time when the chemical reactions are negligible in Figure 6(a), much better wettability can be achieved by the resin curing with T700 (the surface sizing of which was proved epoxy type[13]).

Furthermore, *in situ* FTIR spectra of the curing DGEBA-DDS at 110°C are shown in Figure 7(a). From the image, we can see twin peaks of primary amine group range from 3240 to 3380 cm^{-1}, for which the intensities decrease obviously. The absorbance of the epoxy group occurs at 915 cm^{-1} and that of hydroxyl group at 3480–3490 cm^{-1}. Based on the standard reference absorbance of the benzene ring at 1610 cm^{-1}, the concentration changes of typical functional groups are shown in Figure 7(b). As illustrated,
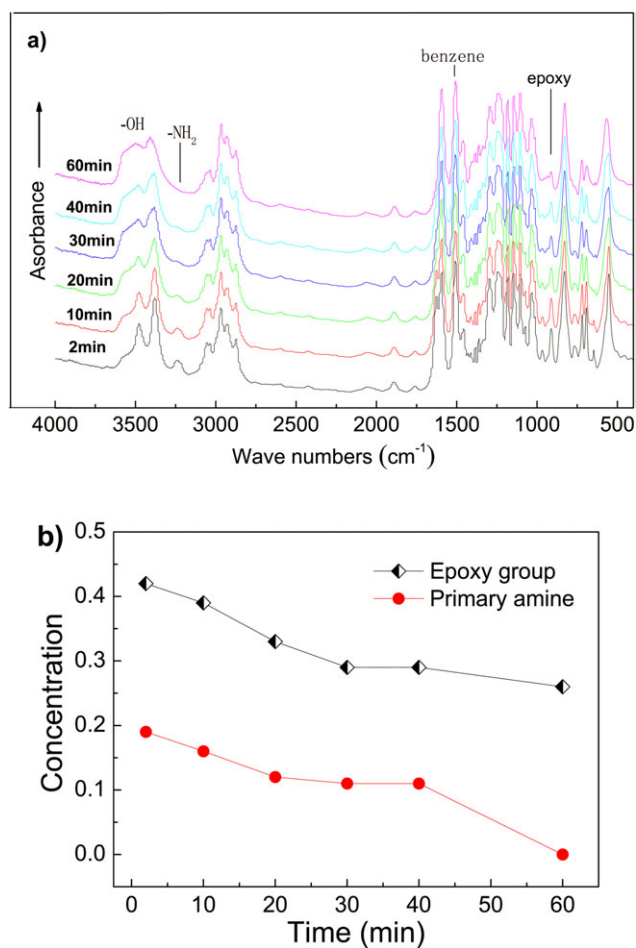
Figure 7. (a) The *in situ* FTIR spectra and (b) the concentration changes of typical functional groups of DGEBA-DDS system as a function of the reaction time at 110°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DGEBA-DDS mixture with negligible chemical reactions, good wetting can only be achieved at temperatures higher than 70°C. CFs of T300 and T700 exhibit almost equivalent wettability with DGEBA according to the CA and the Young W_A, nevertheless T700 possesses much larger polarity and higher surface energies. The desized T300 reveals lower wetting and smaller W_A with epoxy in contrast with T300. We can, therefore, conclude that the surface sizing plays a vital role in the wetting behavior between the CF and epoxy resin. The curing DGEBA-DDS shows quite different wetting behavior from that of the DGEBA-DDS mixture. Complete-wetting can be obtained between the curing DGEBA-DDS and T700 after a period of time, nevertheless the resin SFT increases simultaneously. Moreover, the Young W_A for the DGEBA-DDS system/T700 increases with the curing progress. FTIR analysis indicates that the stronger molecular interactions at the interface should be attributed to chemical reactions of the DGEBA-DDS system, which could lead to acid–base interactions, hydrogen bond, and even possible covalent bond at the epoxy resin/CF interface.

REFERENCES

1. Jancar, J. *J. Mater. Sci.* **2008**, *43*, 6747.
2. Kim, J. K.; Mai, Y. w.; Gutowski, T. G. In Engineered Interfaces in Fiber Reinforced Composites; Kim, J. K., Mai, Y. W., Eds.; Elsevier: Oxford, **1998**; Chapter 1, 2, pp 1–12.
3. Qian, H.; Bismark, A.; Greenhalgh, E. S. *Chem. Mater.* **2008**, *20*, 1862.
4. Thostenson, E. T.; Li, W. Z.; Wang, D. Z.; Ren, Z. F.; Chou, T. W. *J. Appl. Phys.* **2002**, *91*, 6034.
5. Zhao, F.; Huang, Y. D. *Mater. Lett.* **2010**, *64*, 2742.
6. Ramanathan, T.; Bismarck, A.; Schulz, E.; Subramanian, K. *Compos. Sci. Technol.* **2001**, *61*, 599.
7. Barraza, H. J.; Hwa, M. J.; Blakley, K.; O'Rear, E. A.; Grady, B. P. *Langmuir* **2001**, *17*, 5288.
8. Chen, D.; Pascault, J. P. *Macromol. Chem.* **1991**, *192*, 867.
9. Page, S. A.; Mezzenga, R.; Boogh, L.; Berg, J. C.; Manson, J. A. E. *J. Colloid Interface Sci.* **2000**, *222*, 55.
10. Page, S. A.; Berg, J. C.; Manson, J. A. E. *J. Adhes. Sci. Technol.* **2001**, *1*, 153.
11. Synytska, A.; Michel, S.; Pleul, D.; Bellmann, C.; Schinner, R.; Eichhorn, K. J.; Grundke, K.; Neumann, A. W.; Stamm, M. *J. Adhes.* **2004**, *80*, 667.
12. Gu, Y. Z.; Li, M.; Wang, J.; Zhang, Z. G. *Carbon* **2010**, *4*, 3229.
13. Dai, Z. S.; Shi, F. H.; Zhang, B. Y.; Li, M.; Zhang, Z. G. *Appl. Surf. Sci.* **2011**, *257*, 6980.
14. Van Oss, C. J.; Giese, R. F.; Wu, W. *J. Dispersion Sci. Technol.* **1998**, *19*, 1221.

the epoxide and the primary amine contents gradually decrease with time. Note that the epoxide content remains 0.26, whereas the primary amine groups deplete after 60 min at 110°C. This demonstrates that the epoxy group reacts with amines, generating hydroxyl and ether groups in accordance to the principal reaction mechanisms of the system. Hence, the polar functional groups can generate strong acid–base interactions and hydrogen bonds between adjacent molecules, which will increase the SFT of the curing resin (Figure 5). Moreover, chemical reactions may even take place between the resin molecules and the sizing agent,[22] which will lead to complete-wetting and strengthen interactions at the interface of the curing DGEBA-DDS/T700, as illustrated in Figure 6(a). Although this study is only valid for the resin before gel point, the results can provide an essential implication to understand formation of the interphase region of CF/epoxy composites.

CONCLUSIONS

Our study reveals that wettability of the DGEBA/CF depends strongly on the resin SFT. The CA and SFT both decrease considerably with increasing temperatures. However, for the

15. Van Oss, C. J.; Good, R.; Chaudhury, M. *Langmuir* **1988**, *4*, 884.

16. Rebil, J.; Rebio, F.; Fierro, J. L.; Guteirro, M. C.; Oteo, J. L. *J. Mater. Res.* **2002**, *17*, 413.

17. Fowkes, F. M.; Mostafa, M. A. *Ind. Eng. Chem. Prod. Res. Dev.* **1978**, *17*, 3.

18. Allington, R. D.; Hamerton, I.; Howlin, J. N. *High Perform. Polym.* **2005**, *17*, 561.

19. Gan, L.; Sun, Z. J.; Gu, Y. Z.; Li, M.; Zhang, Z. G. *Acta Polym. Sinica* **2010**, *10*, 1016.

20. Dee, G. T.; Sauer, B. B. *Adv. Phys.* **1998**, *47*, 161.

21. Anastasiadis, S. H.; Gancarz, I.; Koberstein, J. T. *Macromolecules* **1988**, *21*, 2980.

22. Dai, Z. S.; Zhang, B. Y.; Shi, F. H.; Li, M.; Zhang, Z. G.; Gu Y. Z. *J. Appl. Polym. Sci.* **2012**, *124*, 2127.