Applied Surface Science 257 (2011) 8457–8461

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Effect of heat treatment on carbon fiber surface properties and fibers/epoxy interfacial adhesion

Zhishuang Dai[a,b], Baoyan Zhang[b,*], Fenghui Shi[b], Min Li[a], Zuoguang Zhang[a], Yizhuo Gu[a]

[a] Key Laboratory of Aerospace Materials and Performance (Ministry of Education), School of Materials Science and Engineering, Beihang University, Beijing, 100191, China
[b] Beijing Institute of Aeronautical Materials, Beijing 100095, China

ARTICLE INFO

Article history:
Received 10 April 2011
Received in revised form 27 April 2011
Accepted 28 April 2011
Available online 5 May 2011

Keywords:
Carbon fiber
Heat treatment
Surface energy
Wettability
Interfacial shear strength

ABSTRACT

Carbon fiber surface properties are likely to change during the molding process of carbon fiber reinforced matrix composite, and these changes could affect the infiltration and adhesion between carbon fiber and resin. T300B fiber was heat treated referring to the curing process of high-performance carbon fiber reinforced epoxy matrix composites. By means of X-ray photoelectron spectroscopy (XPS), activated carbon atoms can be detected, which are defined as the carbon atoms conjunction with oxygen and nitrogen. Surface chemistry analysis shows that the content of activated carbon atoms on treated carbon fiber surface, especially those connect with the hydroxyl decreases with the increasing heat treatment temperature. Inverse gas chromatography (IGC) analysis reveals that the dispersive surface energy γ_S^d increases and the polar surface energy γ_S^{sp} decreases as the heat treatment temperature increases to 200. Contact angle between carbon fiber and epoxy E51 resin, which is studied by dynamic contact angle test (DCAT) increases with the increasing heat treatment temperature, indicating the worse wettability comparing with the untreated fiber. Moreover, micro-droplet test shows that the interfacial shear strength (IFSS) of the treated carbon fiber/epoxy is lower than that of the untreated T300B fiber which is attributed to the decrement of the content of reactive functional groups including hydrogen group and epoxy group.

1. Introduction

The carbon fibers are widely used in aerospace, enginery, marine and sports appliance due to their outstanding properties such as high specific strength and stiffness, lower density, heat-resistance and favorable electrical conductivity [1–3]. In carbon fiber reinforced resin matrix composite; the carbon fiber provides strength and stiffness while the matrix transfers the load from one failed fiber to another via the interphase formed between the carbon fiber and matrix [4]. An effective interface is required in an excellent composite to obtained better stress transfer and crack-resistant [5], whereas favorable wettability is the precondition for excellent interfacial adhesion and mechanical properties of composite.

Carbon fiber surface properties could affect the interfacial adhesion and macro performance of composites. Carbon fiber surface physical properties include surface morphology, surface roughness, surface energy and the size of grooves, which are obtained by scanning electron microscope (SEM) [6–8], atomic force microscopy (AFM) and dynamic contact angle test (DCAT) [9,10]. Carbon fiber surface chemical properties are composed of elemental composition, variety and content of functional groups which are usually examined by X-ray photoelectron spectroscopy (XPS) [11] and Fourier transforms infrared spectroscopy (FTIR).

Heat treatment could affect the physico-chemical properties as well as the morphology of carbon fibers [12–14]. However, their studies focused on the influence of high temperature treatment method at 700 °C or above 1000 °C on the noumenal structure of carbon fibers. Guo et al. [15] reported the effect of epoxy coatings on the morphology and tensile strength of carbon fibers during manufacture of carbon fiber reinforced resin matrix composites, which could help to modify curing process of the carbon fiber reinforced resin matrix composites.

In the present work, heat treatment on the T300B fiber was carried out referring to the curing process of high performance carbon fiber reinforced epoxy matrix composites in order to simulate and investigate carbon fiber changes during manufacturing carbon fiber reinforced resin matrix composite. The surface chemical properties and surface energy of carbon fiber were studied by X-ray photoelectron spectroscopy and inverse gas chromatography (IGC), respectively. The changes of wettability and interfacial adhesion between carbon fiber and epoxy resin matrix with the increasing heat treatment temperature were analyzed, which could provide theoretic foundation for the investigation of interaction and polar-

---

* Corresponding author. Tel.: +86 10 62496609; fax: +86 10 62496609.
E-mail address: zhangbaoyan0916@yahoo.com (B. Zhang).

0169-4332/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2011.04.129

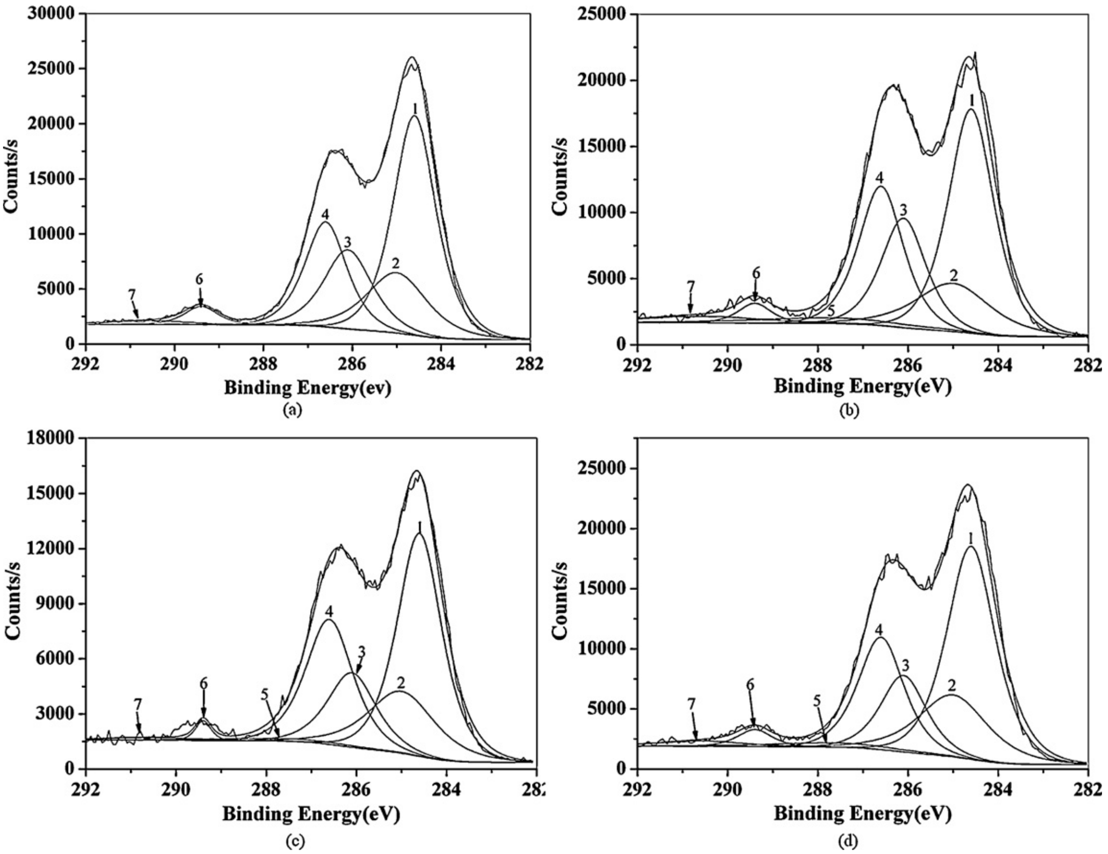

Fig. 1. Curves fitted C1s of T300B after heat treated at different temperatures: (a) untreated, (b) 150 °C, (c) 180 °C, (d) 200 °C.

ity matching between carbon fiber and matrix and therefore the improvement of the interfacial properties of composite.

2. Experiments

2.1. Materials

Commercially available T300B-3000-40B (T300B for short) carbon fibers with a diameter of about 6–7 μm, purchased from Japan Toray, was used in the present work. Diglycidyl ether of bisphenol A epoxy resin, E51 and the hardener 4, 4′-diaminodiphenyl sulphone were provided by Wuxi Resin Factory (China) and Suzhou Yinsheng Chemical Co., Ltd. (China) respectively. The probes used in IGC experiment were decane, nonane, octane, heptane, toluene, dichloromethane, ethanol, 1,4-dioxane, and acetone, which were all high performance liquid chromatographic grade and provided by J&K Chemical Ltd.

2.2. Heat treatment

The carbon fiber was heat treated in a vacuum drying chamber at 150 °C, 180 °C and 200 °C for certain times. The control processing cycles were as follows: heating from 25 °C to 150 °C at 2 °C/min; holding at 150 °C for 2 h; heating from 150 °C to 180 °C at 2 °C/min; holding at 180 °C for 2 h; heating from 180 °C to 200 °C at 2 °C/min holding at 200 °C for 4 h. The called each step contained previous all steps. Taking the second step of heat treatment at 180 °C as an example, the removed specimen has undergone process of 150 °C for 2 h and 180 °C for 2 h.

2.3. Characterization

The chemical compositions of untreated and treated T300B were analyzed using a Thermo Fisher Scientific ESCALAB 250 X-ray photoelectron spectroscopy. The spectra were collected using a monochromatic Al Kα X-ray source (1486.6 eV) in an evacuated chamber at approximately 5.0E10−9 mbar. A spot of 400 μm in diameter, 150 eV of pass energy for survey scan and 30 eV for high resolution scans (293.7–273.7 eV) were used in all the measurements. The C1s spectra were fitted according to Gaussian–Lorentzian function by taking 284.6 eV as the reference peak.

The surface energy (including dispersive γ_S^d and polar γ_S^{sp} component) measurements were performed on the carbon fibers by means of inverse gas chromatography at 30 °C with a helium carrier gas flow of 10 sccm/min. The probe concentration was 0.04 p/p_0. Carbon fiber samples about 0.800 g were packed into presilanized glass columns (30 cm long, 4 mm inner diameter) when the surface properties of carbon fibers were studied. Prior to measurement, the sample was pretreated at the measurement temperature for 30 min in situ so as to eliminate impurities absorbed on the sample surface. The theory of IGC has been well developed and reviewed in previous work [11,16–18].

The dynamic contact angle analysis test (DCAT21, Dataphysics, German) was used to determine wettability between the carbon fibers and epoxy E51 resin. Four single fibers were first cut to connect to a circular clamp in equidistance, and the assembly was hung on the arm of the electronic balance. The DCAT experiments were performed at a stage motor speed of 0.05 mm/s (surf. detection), 0.01 mm/s (measurement adv.), 0.20 mm/s (measurement rec.) with surface detection threshold of 0.15 mg, immersion depth of 3 mm respectively.

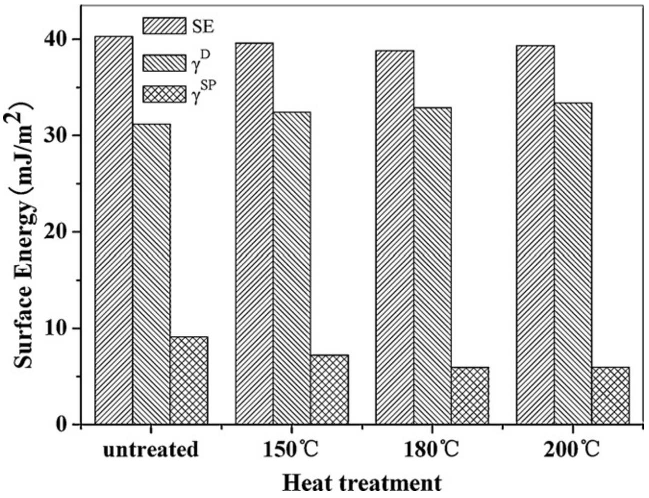

Fig. 2. Change of surface energy measured at 30 °C with the increasing heat treatment temperature.

The interfacial shear strength of carbon fibers/epoxy composites was investigated by micro-droplet test. The matrix resin was wetted onto the single carbon fiber to form a micro-droplet surrounding the diameter of carbon fiber due to the function of surface tension. The micro-droplet resin was cured for 2 h at 130 °C, 1 h at 150 °C, 2 h at 180 °C. After forming a micro-droplet, the single fiber was fixed on a paper framed. The embedded length of each micro-droplet was measured through optical microscopic observation. The knives came in contact with the solid resin droplet and the force required to debond the droplet from the fiber was recorded. The interfacial shear strength (IFSS) was calculated from Eq (1)

$$\tau_{\mathrm{IFSS}} = \frac{F_{\max}}{\pi d \cdot 2r} \tag{1}$$

where τ_{IFSS} is interfacial shear strength, $F_{\max}$ is the maximum load, d is the fiber diameter and $2r$ is the embedded length. The experiment should be repeated at least 20 times for each kind of samples.

3. Results and discussion

3.1. Surface chemical properties of carbon fiber

In order to investigate the changes of functional groups with the increasing heat treatment temperature, the C1s curves are fitted, which are shown in Fig. 1, indicating that the spectra shape of de treated samples have little differences with the untreated one. The C1s peak of each sample was analyzed using XPSPEAK. Values of the binding energy and the percent contribution of each curve fit to the total C1s are listed in Table 1. As can be seen from Table 1, the content of peak 3 (including C–OH, C–O–C and C–NH_2) whose binding energy is about 286.1 eV and peak 6 (COOH) whose binding energy is 289.4 eV decrease while the content of peak 4 (including *C–O–C=O and epoxy group) with the increasing heat treatment temperature, indicating that the C–OH and C–NH_2 take part in the reaction and the *C–O–C=O are generated by the esterification of C–OH and COOH. Moreover, content of activated carbon atoms, which are defined as the carbon atoms conjunction with oxygen and nitrogen decreases with the increasing heat treatment temperature.

3.2. Surface energy of carbon fiber

The surface energy of the untreated and heat treated carbon fiber was measured at 30 °C by inverse gas chromatography. As shown in Fig. 2, the dispersive surface energy increases and polar surface energy decreases with the increasing heat treatment temperature and the ratio of dispersive surface energy to total surface energy is three times more than that of polar surface energy. As can be seen from XPS analysis, the content of C–O and activated carbon atoms reduced with the increasing heat treatment temperature, which leads to the decrement of polar surface energy. It is reported that the main ingredients of sizing for T300B fiber are bisphenol A epoxy resin and amino compounds [19]. Therefore the curing of sizing as the heat treatment process induce the declination of polar surface energy [20] which might be a governing factor in the adhesion between the fiber and epoxy matrix.

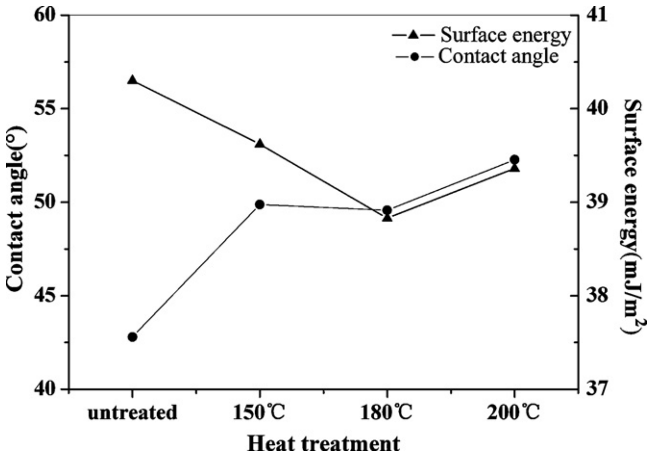

Fig. 3. Change of contact angle between carbon fiber and epoxy E51, which is measured at 30 °C and the surface energy of carbon fiber with the increasing heat treatment temperature.

The surface energy of cured epoxy resin was investigated by IGC at 30 °C. The result shows that the total surface energy is 45.78 mJ/m², which is approximately equivalent to values for the carbon fibers, with the dispersive component 37.71 mJ/m² and the polar component 8.07 mJ/m².

3.3. Wettability of epoxy resin on carbon fiber

Contact angle between carbon fiber and epoxy E51 decreases with the increasing heat treatment temperature, indicating the deteriorative wettability, which is given in Figs. 3 and 4. Contact angle between carbon fiber and epoxy E51 increases with the decrement of carbon fiber surface energy (Fig. 3) when the heat treatment

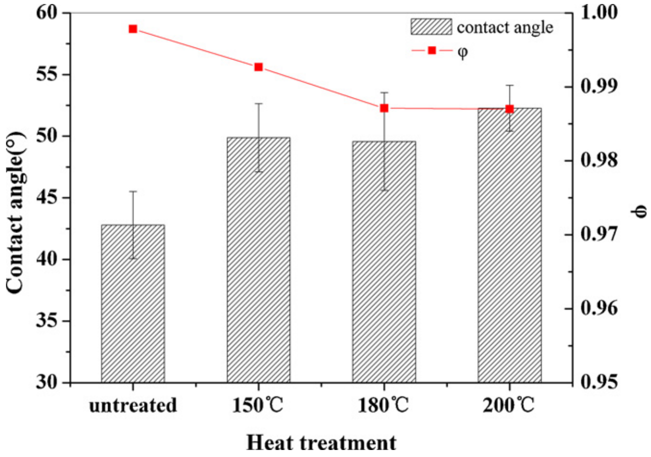

Fig. 4. Change of contact angle between carbon fiber and epoxy E51, which is measured at 30 °C and ϕ with the increasing heat treatment temperature.

Table 1
C (1s) peaks of carbon fiber and relative peak area.

Samples	C (1s) peaks in different states B.E., eV (area, %)							Activated Carbon atoms (%)
	Peak 1 284.6 eV	Peak 2 285.0 eV	Peak 3 286.1 eV	Peak 4 286.6 eV	Peak 5 287.7 eV	Peak 6 289.4 eV	Peak 7 290.6 eV	
Untreated	31.94	15.68	21.78	18.70	5.02	2.45	4.43	52.38
150 °C	37.56	13.30	18.01	22.79	3.06	2.38	2.90	49.14
180 °C	40.53	16.98	14.62	24.04	1.51	1.25	1.09	42.50
200 °C	41.72	17.29	14.02	20.71	2.11	2.35	1.81	41.00
Peak assignment	Reference	–C–C –C–H	–C–OH–C–O–C–C–NH_2	*C–O–=O Epoxy groups	–C=O C=N	–COOH–COOR	$–COO^{-}\pi–\pi^{*}$	

temperature is lower than 180 °C. However, this relationship does not happen when the heat treatment temperature increases from 180 °C to 200 °C, which is attributed to that the wettability depends not only the carbon fiber properties, but also on the character of resin. Interface defects model points out that the optimum condition for wettability is the polarity match of the two phases [21]. Good–Girifalco proposed an interaction parameter, ϕ in order to investigate the interaction between two phases, as follows:

$$\phi = \frac{W_{ad}}{(W_{co1} \times W_{co2})^{1/2}} = (x_1^d x_2^d)^{1/2} + (x_1^{sp} x_2^{sp})^{1/2} \tag{2}$$

$$x^{sp} = \frac{\gamma^{sp}}{\gamma}, \quad x^d + x^{sp} = 1, \quad x^d = \frac{\gamma^d}{\gamma} \tag{3}$$

where W_{ad} is the work of adhesion, W_{co} is the work of cohesion, γ, γ^d and γ^{sp} are total surface energy, dispersive surface energy and polar surface energy respectively. ϕ is a thermodynamic parameter, which could be used to characterize the relation of W_{ad} and W_{co} for the two phases. The value of ϕ reaches maximum ($\phi_{max} = 1$) when the polarities of the two phases are the same. The interaction parameter between carbon fiber and epoxy E51 is estimated according to the surface energy and its components [22]. Results show that the value of ϕ is 0.9978 between untreated T300B fiber and epoxy E51 and decreases with the increasing heat treatment temperature, which is illustrated in Fig. 4. The change trend of contact angle between carbon fiber and epoxy E51 is contrary to that of the interaction parameter, indicating that the similar polarity could result in the small contact angle and favorable wettability.

3.4. Interfacial shear strength of carbon fiber/epoxy composite

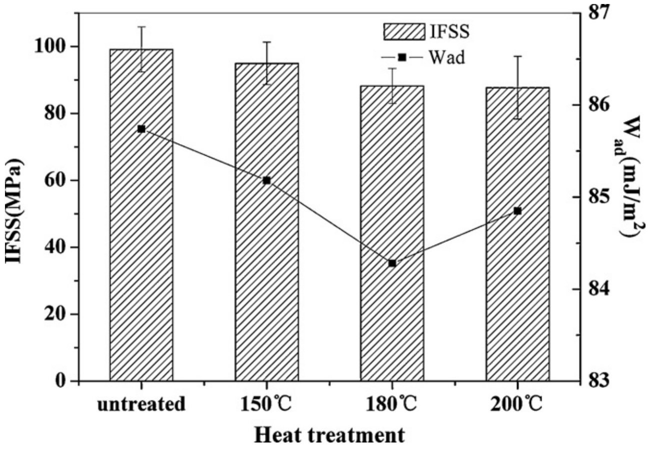

Fig. 5. Change of IFSS and W_{ad} with the increasing heat treatment temperature.

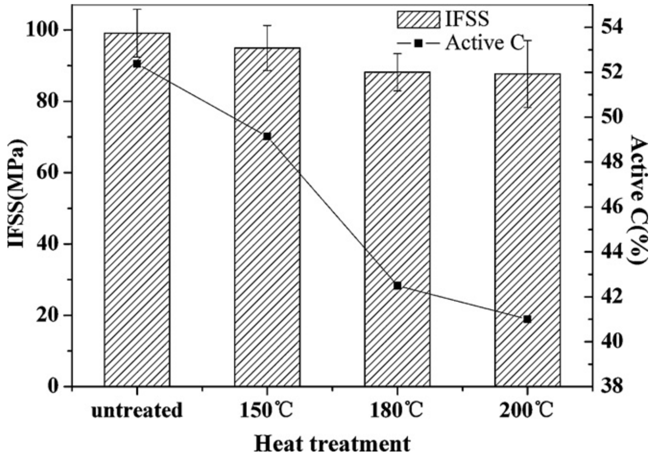

Fig. 6. Change of IFSS and activated carbon atoms content on carbon fiber surface with the increasing heat treatment temperature.

According to the above analysis, the surface chemical composition and surface energy of the carbon fibers are changed with the increasing heat treatment temperature, which might have effect on the carbon fiber/epoxy interfacial adhesion. The interfacial shear strength of carbon fiber/epoxy was measured by micro-droplet test. As can be seen from Figs. 5 and 6, the IFSS of treated-T300B/epoxy decreases when the heat treatment temperature increases to 180 °C, while no evident differences are found between T300B/epoxy composites after treated at 180 °C and 200 °C. When irreversible chemical interaction are neglected and only physical interaction are present, the interfacial adhesion increases with the work of adhesion, W_{ad}, which can be estimated by applying the Young–Dupré equation [23] and Fowke's theory [4,24] according to the geometric mean method, as follows:

$$W_{ad} = 2(\gamma_f^d \gamma_r^d)^{1/2} + 2(\gamma_f^{sp} \gamma_r^{sp})^{1/2} \tag{4}$$

As shown in Fig. 5, the W_{ad} of T300B/epoxy decreases with the increasing heat treatment temperature, which is accordant with the IFSS tendency when the heat treatment temperature is lower than 180 °C. However, the work of adhesion does not reveal close correlation with IFSS trend when the heat treatment temperature increases from 180 °C to 200 °C, which illustrates that interactions between carbon fiber matrix are not only physical but also chemical bonding in interface region.

The change of interfacial shear strength and activated carbon atoms content with the increasing heat treatment temperature is shown in Fig. 6. The decrement of activated carbon atoms content which is mainly caused by the reduced content of hydroxyl group would result in the decrease IFSS, which is attributes to that the content of reactive functional group in interface region decreases and the possibility of forming powerful chemical bonding between carbon fiber and matrix decreases, accordant with the theory proposed by Wu Souheng [21], as follows:

$$f = KC^n \tag{5}$$

where f is bond strength, C is the concentration of reactive groups in interface region, K and n are constant and $n \approx 0.6$. Meanwhile, the decrement in the surface polarity or active sites for van der

Waals linking and hydrogen bonding could worsen the interfacial adhesion between the fiber and surrounding polymer matrix [25].

4. Conclusions

By comparing untreated T300B, the content of hydroxyl group and activated carbon atoms on carbon fiber surface decreases and the polar surface energy becomes lower with the increasing heat treatment temperature. The dispersive surface energy of carbon fiber and contact angle between carbon fiber and epoxy E51 increases, while the interfacial shear strength of T300B/epoxy reduces with the heat treatment process. The wettability of resin on carbon fiber depends not only by the surface energy values of carbon fiber and resin, but also on the polarity match of surface energy. And close correlation can be found between IFSS and the concentration of reactive groups in interface region. The results can be theoretical guidance for the manufacture of carbon fiber and carbon fiber reinforced resin matrix composite. In order to improve the performance of carbon fiber reinforced resin matrix composite, the surface energy should be raised, the polar surface energy of carbon fiber and resin should be modified to be closed and the concentration of reactive functional groups in interface region should be improved.

References

[1] F. Rezaei, R. Yunus, N.A. Ibrahim, Effect of fiber length on thermo-mechanical properties of short carbon fiber reinforced polypropylene composites, Mater. Des. 30 (2009) 260–263.

[2] M.K. Seo, S.J. Park, Surface characteristics of carbon fibers modified by direct oxyfluorination, J. Colloid Interface Sci. 330 (2009) 237–242.

[3] Z.W. Xu, L. Chen, Y.D. Huang, J.L. Li, X.Q. Wu, X.M. Li, et al., Wettability of carbon fibers modified by acrylic acid and interface properties of carbon fiber/epoxy, Eur. Polym. J. 44 (2008) 494–503.

[4] N. Dilsiz, J.P. Wightman, Surface analysis of unsized and sized carbon fibers, Carbon 37 (1999) 1105–1114.

[5] X.J. Wang, G.Z. Liang, W. Zhang, et al., Surface analysis of high properties carbon fibers and study on mechanical properties, J. Aeronautical Mater. 26 (2006) 119–122.

[6] H.C. Huang, D.Q. Ye, B.C. Huang, Nitrogen plasma modification of viscose-based activated carbon fibers, Surf. Coat. Technol. 45 (2007) 9533–9540.

[7] J. Mentz, M. Müller, H.P. Buchkremer, et al., Carbon-fibre-reinforced carbon composite filled with SiC particles forming a porous matrix, Mater. Sci. Eng. A 425 (2006) 64–69.

[8] I.D. Harry, B. Saha, I.W. Cumming, Surface properties of electrochemically oxidised viscose rayon based carbon fibers, Carbon 28 (2007) 766–774.

[9] C.N.C. Lam, R. Wu, D. Li, et al., Study of advancing and receding contact angle: liquid sorption as a cause of contact angle hysteresis, Adv. Colloid Interface Sci. 96 (2002) 169–191.

[10] M.H.V.C. Adão, B.J.V. Saramago, A.C. Femandes, Estimation of the surface properties of styrene–acrylonitrile random copolymers from contact angle measurements, J. Colloid Interface Sci. 217 (1999) 94–106.

[11] B. Lindsay, M.-L. Abel, J.F. Watts, A study of electrochemically treated PAN based carbon fibers by IGC and XPS, Carbon 45 (2007) 2433–2444.

[12] J.-S. Lee, T.-J. Kang, Changes in physico-chemical and morphological properties of carbon fiber by surface treatment, Carbon 35 (1997) 209–216.

[13] S. Wang, Z.H. Chen, W.J. Ma, et al., Influence of heat treatment on physical–chemical properties of PAN-based carbon fiber, Ceram. Int. 32 (2006) 291–295.

[14] J.B. Donnet, T.K. Wang, Z.M. Shen, Atomic scale STM study of pitch-based carbon fibers: influence of mesophase content and the heat treatment temperature, Carbon 34 (1996) 1413–1418.

[15] H. Guo, Y.D. Huang, L. Liu, et al., Effect of epoxy coatings on carbon fibers during manufacture of carbon fiber reinforced resin matrix composites, Mater. Des. 31 (2010) 1186–1190.

[16] R.H. Mills, W.T.Y. Tze, D.J. Gardner, A. van Heiningen, Inverse gas chromatography for the determination of the dispersive surface free energy and acid–base interactions of a sheet molding compound. I. Matrix material and glass, J. Appl. Polym. Sci. 109 (2008) 3519–3524.

[17] A. van Asten, N. van Veenendaal, S. Koster, Surface characterization of industrial fibers with inverse gas chromatography, J. Chromatogr. A 888 (2000) 175–196.

[18] P. Jandura, B. Riedlb, B.V. Kokta, Inverse gas chromatography study on partially esterified paper fiber, J. Chromatogr. A 969 (2002) 301–311.

[19] B.Y. Zhang, F.H. Shi, Z.G. Zhou, et al., Surface characteristics of carbon fibers and interfacial properties of carbon fibers reinforced BMI matrix composites, J. Wuhan Univ. Technol. 21 (2009) 69–72.

[20] Q.S. Ma, M. Li, Z.J. Sun, et al., Surface energy and polar component evolution of epoxy resin system after gelation, Acta Mater. Compos. Sin. 5 (2009) 74–79.

[21] Wu. Souheng, Polymer Interface and Adhesion, Marcel Dekker, Inc., New York, 1982.

[22] F.H. Shi, Z.S. Dai, B.Y. Zhang, Characterization of surface tension solubility parameter of epoxy resin by using inverse chromatography, Chin. J. Chromatogr. 28 (2010) 480–483.

[23] H.J. Barraza, M.J. Hwa, K. Blakley, Wetting behavior of elastomer-modified glass fibers, Langmuir 17 (2001) 5288–5296.

[24] M. Gindl, G. Sinn, W. Gindl, et al., A comparison of different methods to calculate the surface free energy of wood using contact angle measurements, Colloids Surf. A: Physicochem. Eng. Aspects 18 (2001) 279–287.

[25] M.C.R. Paiva, C.A. Bernardo, M. Nardin, Mechanical, surface and interfacial characterization of pitch and PAN-based carbon fibers, Carbon 38 (2000) 1323–1327.