Latent Curing Agent Modified Epoxy Sizing Agent for High Modulus Carbon Fiber

Xuejun Zhang*, Sumei Kang and Zhanqing Liu

Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

Abstract: A new kind of latent curing agent (LCA) for epoxy resin was synthesized to improve the properties of epoxy sizing agent for high modulus carbon fiber by the reaction of ethylenediamine with butylacrylate in equal molar ratios, and the chemical structure and thermal property of the LCA were studied with FTIR and TGA, respectively. Moreover, LCA modified epoxy resin used as sizing agent for high modulus carbon fiber was studied. The results show that the wettability of sized high modulus carbon fiber tends to increase due to the increase of LCA content in sizing agent on the surface of the carbon fiber; while absorbability of sized high modulus carbon fiber tends to decrease; and drape of the sized high modulus carbon fiber which indicates the shaping effect of the fiber changes with the content of LCA, and interlaminar shear strength (ILSS) of the sized high modulus carbon fiber/epoxy composites is improved to 78MPa, which increased by 8.6% compared with the composites reinforced by high modulus carbon fiber with unmodified sizing agent, indicating that using LCA modified epoxy resin as sizing agent for high modulus carbon fiber is a feasible method to improve the interfacial performance of high modulus carbon fiber/epoxy composites.

Keywords: Latent curing agent, epoxy resin, high modulus carbon fibers, sizing agent.

1. INTRODUCTION

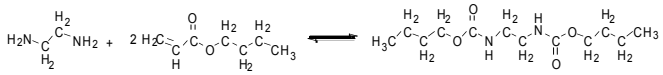
High modulus carbon fibers are widely used as reinforcement for advanced composite materials. As for composites, the resulting mechanical properties not only depend on the reinforcement and matrix materials but also have relationship with the interfaces between fibers and matrix, which are stated to be important in improving composites performance [1-4]. In order to achieve good adhesion between the reinforcement and matrix materials, carbon fibers are usually modified by surface treatment to enhance the physical and chemical properties of their surface such as wetting properties, bond forming possibility [5-9]. There are many methods, and polymer coating is one of the most basic methods of surface treatment for carbon fiber [5, 10-12]. In this paper, a new kind of latent curing agent (LCA) for epoxy resin was synthesized, and epoxy resin modified with LCA was used as sizing agent for high modulus carbon fiber. During the sizing process, the LCA will release ethylenediamine and butyl acrylate, and ethylenediamine can react with functional groups of epoxy resin under the suitable temperature; meanwhile, linear butyl acrylate can cross-link into a network structure and cross with epoxy resin and improve the mechanical properties of epoxy. Therefore, there is a tough coating on high modulus carbon fiber which can toughen the composite material after curing, enhancing the capability of the carbon fiber and strength of interface between carbon fiber and matrix.

*Address correspondence to this author at the Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China; Tel: +86-10-64418679; Fax: +86-10-64418679; E-mail: zhangxj@mail.buct.edu.cn

2. EXPERIMENTAL

2.1. Synthesis of Latent Curing Agent

A 250-mL four-neck dry round-bottom flask equipped with a mechanical stirrer, thermometer, and a reflux condenser and a dropping funnel was used as a reactor. The reaction was carried out in a water bath with constant temperature. Absolute ethanol (30ml) and stoichiometric amounts of ethylenediamine (13ml) were charged into the reactor. While stirring, the mixture was heated to 60°C, followed by dropping butyl-acrylate (55ml) to the homogenized mixtures. When all of the butylacrylate was added into the reactor, the mixture was maintained at the temperature of 60°C for 3 hours until the smell of butyl acrylate disappeared. Total chemical reaction time was about 7 hours [13]. The polymerization was detected by IR spectroscopy until no more $-NH_2$ bands left. Synthetic route was successfully designed as follow:



2.2. Polymer Coating of Carbon Fiber

High modulus carbon fibers with elastic modulus larger than 420 GPa were placed under tension and passed through LCA modified sizing agent (concentration of 2% wt), then dried immediately in a hot oven to get sized carbon fibers.

2.3. Characterizations

A Fourier transform infrared (FTIR) measurement was carried out on a Nicolet 8700 FTIR spectrometer to characterize the chemical structure of the synthesized LCA.

TGA that characterizes the thermal properties of LCA was carried out using a Q100DSCSYSTEM instrument at a

1874-088X/11 2011 Bentham Open

heating rate of 10°C/min from room temperature to 300°C under the N_2 atmosphere.

Mass fraction of sizing agent on the surface of high modulus carbon fiber was studied: Carbon fiber samples with weight of 1g were put in soxhlet extractor, washed for 5 hours. Make the weight of the carbon fiber that with sizing agent "m_1"and the fiber that without sizing agent "m_2", then calculate the mass fraction of the sizing agent, m%.

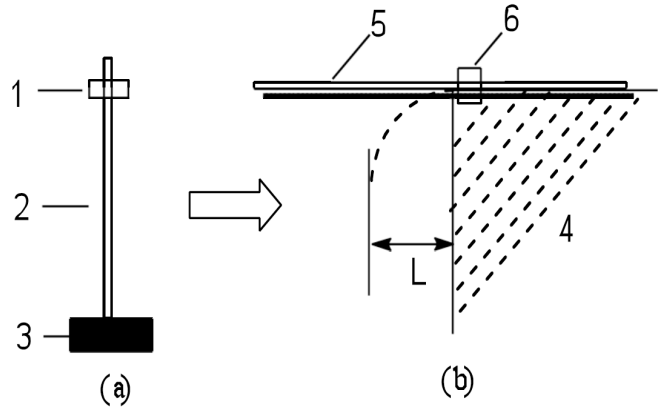
$$m\% = \frac{m_1 - m_2}{m_1} \times 100\%$$

The wet ability of sized carbon fiber was tested by capillary effect. Carbon fiber samples with length of 20cm were fixed at one end, and the other end was dip into the methyleneblue solution (0.5% wt) with the length of 1 cm. After 30 min, the length of the color infiltration was measured [14]. The larger the length is, the better the wettability is.

The absorbability of sized carbon fiber was invested as follows: Carbon fiber samples that weigh 10g were put in oven with temperature 40°C, then weighed after 1hour, and heated to 110°C, then weighed after 2 hours and 5 hours. Let the weight of the carbon fiber before drying "w" and the fiber that dried "w_d", and then calculate the absorbability, w%.

$$w\% = \frac{w\text{-}w_d}{w_d} \times 100\%$$

The drape of sized carbon fiber (D) was studied by the method shown in Fig. (**1**) [15]: Carbon fiber(2) with length 40cm was collected, then one end was fixed(1) and the other end hung an object (3) with weight of 100g for half an hour. Then the object was taken away and the sample was put on a plane table (4) and fixed (6). The sized carbon fiber (5) with length of 25cm would bend when the support was taken away, after two minutes; the value of "L" was measured as D.



1-strap; **2**-carbon fiber; **3**-weight; **4**- plane table; **5**-carbon fiber; **6**-strap

Fig. (1). The process to measure the drape of sized high modulus carbon fiber.

The sized high modulus carbon fibers and epoxy resin 648 were used to prepare composites samples to measure the interlaminar shear strength (ILSS) of carbon fiber/epoxy resin composites, which was conducted with INSTRON5567 universal testing machine according to the standards of GB 3357-82. A total of 10 data points were collected and then averaged. The fracture surfaces of the samples were examined by scanning electron microscopy (SEM).

3. RESULTS AND DISCUSION

3.1. Chemistry Structure of LCA

Fig. (**2**) was the FTIR spectrum of ethylenediamine. Because $-NH_2$ has two H with symmetric and asymmetric stretching vibration, so there are two peaks between 3500 cm^{-1} and 3100 cm^{-1}. Fig. (**3**) showed the FTIR spectrum of LCA. Compared Fig. (**2**) with Fig. (**3**), it is found that there is only one absorption peak at 3312 cm^{-1} resulted from the stretching vibration of N–H groups. The absorbance at 2959 cm^{-1} is due to the stretching vibration of saturated C–H groups, and the absorbance at 1733 cm^{-1} is caused by the stretching vibration of C=O groups of the saturated esters. And there is no C=C absorption peak which belongs to butyl-acryl ate. All these characteristic peaks reveal that synthesis of LCA is carried out as expect, resulting in sample with the desired chemical structure.

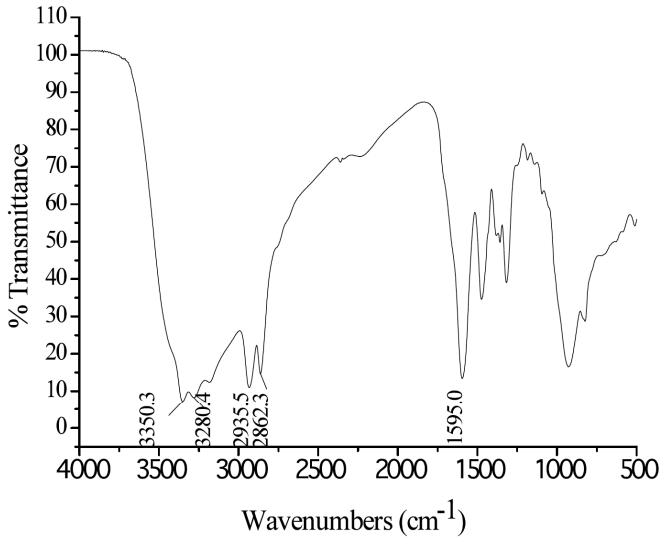


Fig. (2). FTIR spectrum of ethylenediamine.

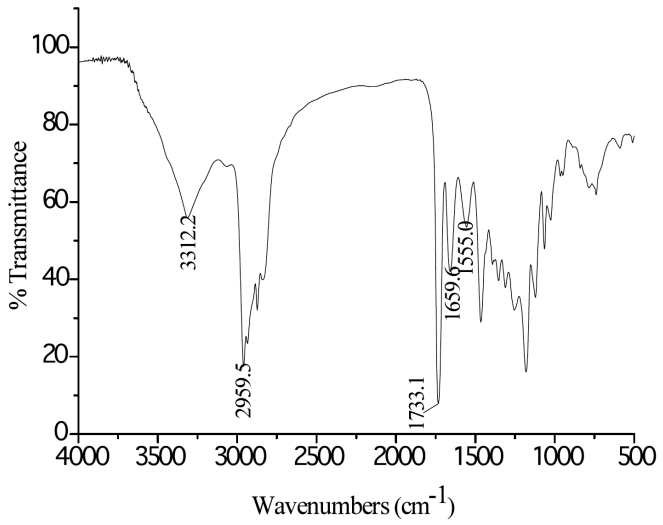


Fig. (3). FTIR spectrum of LCA.

3.2. Thermal Properties of LCA

TGA curve of LCA was shown in Fig. (**4**). From the curve we can see the onset temperature of thermal degradation is about 174°C, belonging to the fracture of bond between ethylenediamine and butyl acrylate. So we can determine the sizing temperature which can fluctuate between 174°C and 178°C. Under the sizing temperature, LCA will decompose, releasing ethylenediamine and butylacrylate that can cure and toughen the epoxy resin, respectively.

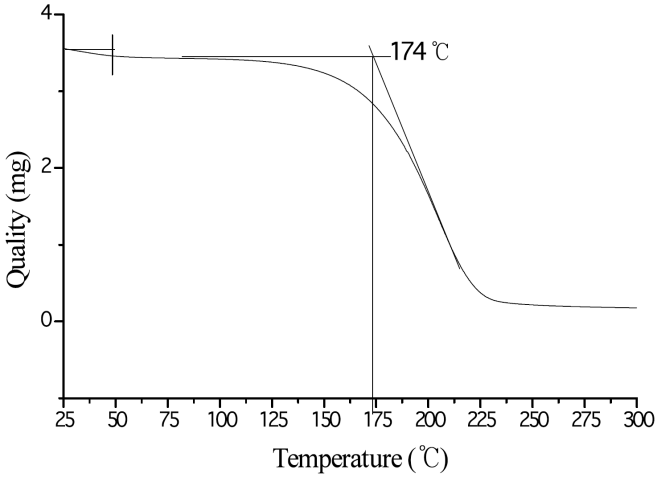


Fig. (4). TGA curve of the LCA.

3.3. Mass Fraction of Sizing Agent

Mass fraction of sizing agent around carbon fiber was studied, and the results were shown in Table **1**. It is clear the mass fraction of sizing agent increased with the increase of LCA content. As we all know, in order to ensure the strength of composite materials, the mass fraction of sizing agent is not too high, the better the combined effect is. If the mass fraction is too low, it can result in damages on cluster of fiber and wearability. So as to reduce the broken filament and be convenient in operation, the suitable rang is 0.5% ~ 1.2%. From Table **1**, we can see the mass fraction of sizing agent is appreciative when LCA content is lower than 20%.

Table 1. Mass Fraction of Sizing Agent

Latent Curing Agent Content % (wt)	Mass Fraction of Sizing Agent %
5	0.8
10	1.0
15	1.0
20	1.1
50	1.4

3.4. Wettability Analysis of Sized Carbon Fiber

The wettability data of sized carbon fiber were presented in Fig. (**5**). It can be clearly observed that the length of the color infiltration increased with the increasing content of LCA, and then reached a maximum value. With continually increasing the content of LCA, the length decreased. This result shows LCA modified epoxy sizing agent can increase the roughness of the fiber surface, resulting in increase of infiltration length. This also reveals the infiltration length is larger, and the wettability is better, also contact angle is smaller. When LCA content is larger than 20%, sized fiber surface will become compact due to excessive cross-linkage in cured epoxy resin, so the wettability decreased.

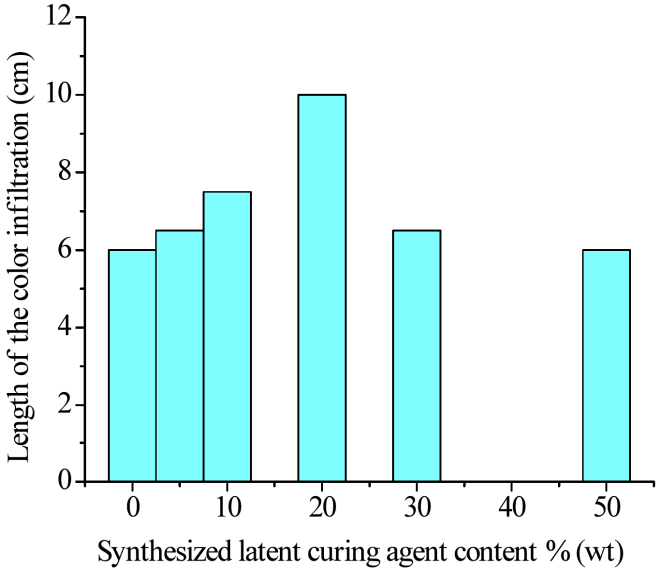


Fig. (5). Infiltrating color length of sized high modulus carbon fiber.

3.5. Absorbability Analysis of Sized Carbon Fiber

Table **2** showed the absorbability of sized carbon fiber. For high-performance carbon fiber and graphite fiber, the absorbability is usually between 0.03% and 0.05%, no more than 0.1%. If the absorbability exceeds 0.1%, the quality of carbon fiber or graphite fiber/polymer composites can be affected which can reduce the life-span of composites. According to Table **2**, the absorbability decreased with the increasing content of LCA, and then reached a minimum value. So the agreeable content of LCA is 20% that can not only protect the fiber, but also reduce the absorbability to 0.02%.

Table 2. The Absorbability of Sized High Modulus Carbon Fiber

Latent Curing Agent Content % (wt)	The Absorbability (%)
5	0.10
10	0.07
15	0.03
20	0.02
30	0.04
50	0.05

3.6. The Drape of Sized Carbon Fiber

The drape of sized carbon fiber can be used to indicate the shaping effect of fiber, and the result was shown in Table **3**. The greater the drape is, the more rigid carbon fiber is, while the smaller the drape is, the more flexible the fiber is. If D<5 cm, the sized carbon fiber is flexible, so it will easily bend and twist during the process of using after passing the roller. Under this condition, the fiber is difficult in partial splitting, resulting in uneven splitting. If D>12 cm, carbon fiber is rigid and difficult in splitting. Therefore, the feasible D is between 5 and 12 cm. From Table **3** we can see sized carbon fibers had different D with different content of LCA, but they were all in the range of 5 to 12 cm.

Table 3. The Drape of Sized High Modulus Carbon Fiber

Latent Curing Agent Content % (wt)	The Draped, D (cm)
10	11.7
15	8.4
20	6.8
30	8.5
50	10.5

3.7. Interlaminar Shear Strength

Fig. (**6**) showed the change of interlaminar shear strength (ILSS) of composites from epoxy resin and sized high modulus carbon fiber with different LCA content. The change trend is similar to the wettability of sized carbon fiber. There is the maximum value (78MPa) of ILSS for carbon fibers/epoxy composites when the weight ratio of LCA to epoxy sizing is 20%. This may be attributed to the enhanced toughness and surface roughness of the carbon fibers. However, when the curing agent content is more than 20% wt, the ILSS values decreased slightly, which may be due to the excessive cross-linking in the epoxy resin and less toughness. Fig. (**7**) showed the SEM images of the surface of sized carbon fiber and fractured surface of the composites. We can see that there is a film on the surface of carbon fiber. Each carbon fiber is embedded in epoxy resin, and very little fiber pull-out is observed. It means the adhesion between the carbon fiber and the resin is very strong. Thus, it reveals that LCA modified epoxy resin is a good sizing agent for high modulus carbon fiber to improve fiber-matrix interactions, contributing to higher ILSS.

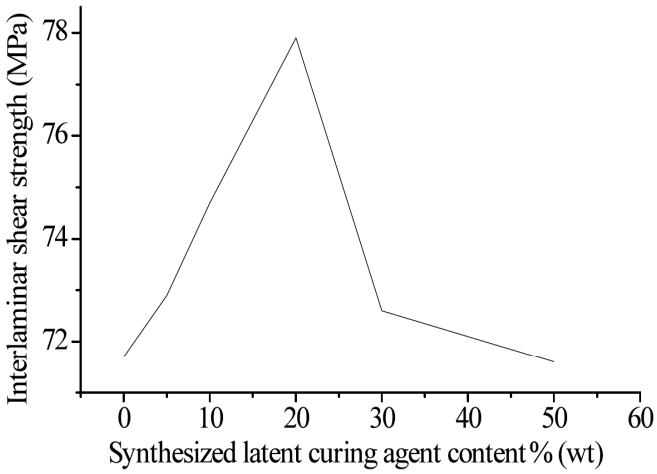


Fig. (6). Interlaminar shear strength of composites.

4. CONCLUSIONS

Latent curing agent for epoxy resin has been synthesized from ethylenediamine and butylacrylate, which cures and toughens epoxy resin at temperature of 174℃ when used in sizing agent for carbon fiber. The surface activity of sized carbon fiber is enhanced by LCA modified epoxy sizing agent. When LCA content is 20 wt%, absorbability of sized carbon fiber is reduced to 0.02% and the suitable drape of carbon fiber is 6.8 cm. The surface wettability of sized carbon fiber is increased, and toughness of the interface of the carbon fibers/epoxy composites also is enhanced, leading ILSS of high modulus carbon fiber/ epoxy resin up to 78 MPa.

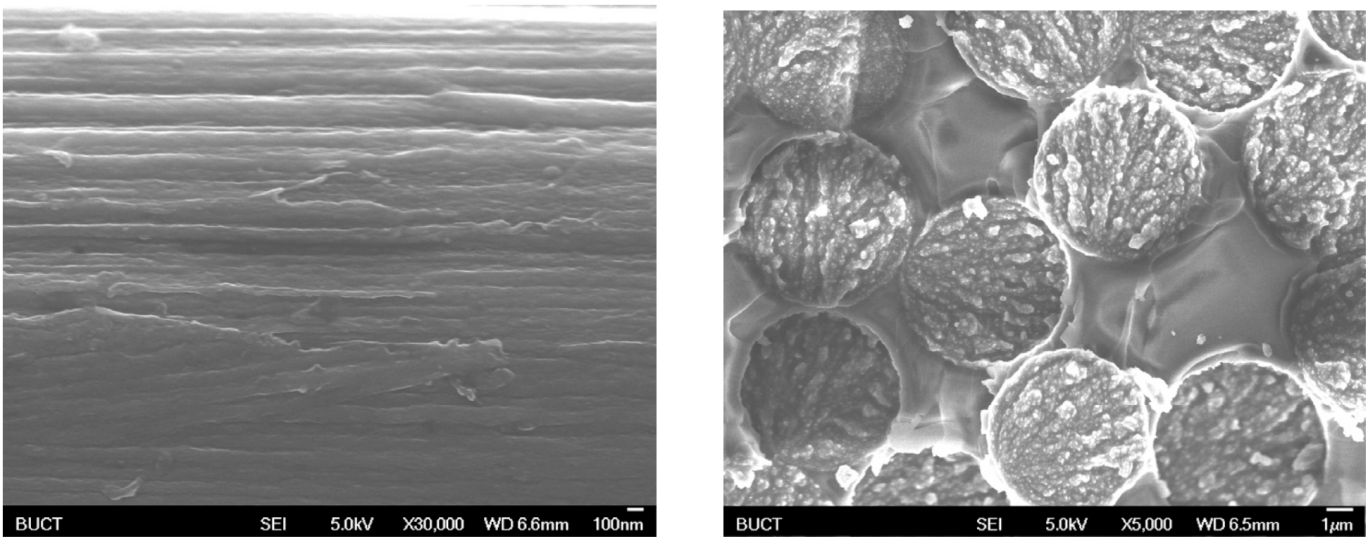


Fig. (7). SEM images of sized high modulus carbon fiber and epoxy resin composites.

REFERENCES

[1] Dilsiz N. Wightman JP. Effect of acid-base properties of unsized and sized carbon fibers on fiber/epoxy matrix adhesion. Colloids Surf A 2000; 164: 325-36.

[2] Yang Y, Lu CX, Su XL, Wang XK. Effects of emulsion sizing with nano-SiO_2 on interfacial properties of carbon fiber/epoxy composites. J Mater Sci 2007; 42: 6347-52.

[3] Mäder E, Gao SL, Plonka R. Static and dynamic properties of single and multi-fiber/epoxy composites modified by sizings. Compos Sci Technol 2007; 67: 1105-15.

[4] Ramanathan T, Bismarck A, Schulz E, Subramanian K. Investigation of the influence of surface-activated carbon fibres on debonding energy and frictional stress in polymer-matrix composites by the micro-indentation technique. Compos Sci Technol 2001; 61: 2511-8.

[5] Li J, Fan Q, Chen ZH, Huang KB, Cheng YL. Effect of eletropolymer sizing of carbon fiber on mechanical properties of phenolic resin composites. Trans Nonferrous Metal Soc China 2006; 16: 457-61.

[6] Choi MH, Jeon BH, Chung IJ. The effect of coupling agent on electrical and mechanical properties of carbon fiber/phenolic resin composites. Polymer 2000; 41: 3243-52.

[7] Xu ZW, Chen L, Huang YD, *et al*. Wettability of carbon fibers modified by acrylic acid and interface properties of carbon fiber/epoxy. Eur Polym J 2008; 44: 494-503.

[8] Zhang XZ, Huang YD, Wang TY, Liu L. Influence of fiber surface oxidation-reduction followed by silsesquioxane coating treatment on inerfacial mechanical properties of carbon fiber/polyarylacetylene composites. Composites Part A 2007; 38: 936-44.

[9] Fukunaga A, Ueda S. Anodic surface oxidation for pitch-based carbon fibers and the interfacial bond strengths in epoxy matrices. Compos Sci Technol 2000; 60: 249-54.

[10] Thomason JL, Adzima LJ. Sizing up the interphase: an insider's guide to the science of sizing. Composites Part A 2001; 32: 313-21.

[11] Zhang ZZ, Song HJ, Men XH, Luo ZZ. Effect of carbon fibers surface treatment on tribological performance of polyurethane(PU) composite coating. Wear 2008; 264: 599-605.

[12] Xu ZW, Wu XQ, Sun Y, *et al*. Surface modification of carbon fiber by redox-induced graft polymerization of acrylic acid. J Appl Polym Sci 2008; 44: 494-503.

[13] Zhong WB, Huang QG, Zou AL, Wang XY. The synthesis and characterization of a new latent curing agent of epoxy resin. Adhesion China 2002; 21: 22-3. (In Chinese)

[14] You ZQ, Hu ZM, Chen L, *et al*. Study of the surface modification of Technora fiber. Hi-Tech Fiber Appl 2009; 34: 30-3. (In Chinese)

[15] He F. Carbon Fiber and Graphite Fiber. Chemical Industry Press: Beijing; 2010. (In Chinese)

Received: August 28, 2010 Revised: November 26, 2010 Accepted: December 23, 2010