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The effect of coupling agent on electrical and mechanical properties of carbon fiber/phenolic resin composites

M.H. Choi, B.H. Jeon, I.J. Chung*

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong, Yusong, Taejon 305-701, South Korea

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Abstract

Carbon fiber/phenolic resin composites were prepared by changing the content (5–10 wt%) of short carbon fibers. To investigate the effect of carbon fiber treatment on the electrical and mechanical properties of the composites, three specimens were prepared: the short carbon fiber treated to remove size (called USCF); the carbon fiber oxidized with nitric acid (called NAOCF); and the fiber oxidized with nitric acid and treated with coupling agent glutaric dialdehyde (called GTDACF). The GTDACF composite had higher electrical conductivity and better mechanical property than the other composites with the same content of carbon fibers. The surface treatment methods affected the dielectric behaviors of the composites with short carbon fibers while they did not affect those of the composites with fabric type carbon fibers. From these observations, the coupling agent improved adhesion between the carbon fiber and the phenolic resin by forming a chemical bond between fiber and resin. The coupling agent also affected the flow and dispersion of the short carbon fiber in the phenolic resin during compression molding, resulting in the higher electrical conductivity and better mechanical property of GTDACF composite. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Phenolic resin; Carbon fiber; Coupling agent

1. Introduction

Over the last four decades, carbon fibers have emerged as the main reinforcement filler for high performance composite materials. They have various useful properties: high strength and high modulus, fatigue resistance and vibration damping, corrosion resistance, good friction and wear qualities, low thermal expansion, thermal and electrical conductivity. So they are an attractive substitute for various metals, alloys and other materials [1]. They offer versatile applications in aerospace, robots, sporting leisure goods, solar cell, resistor, semiconductor elements, antistatics and electromagnetic shielding materials etc. [2,3].

The properties of a composite, such as strength and modulus, etc. are important factors to get the high quality of the composite. The properties of fiber and matrix make a critical contribution to the quality of a fiber-reinforced composite. In addition, the physical–chemical interaction at the fiber–matrix interface plays an important role in improving the mechanical properties of a fiber-reinforced composite.

Nowadays many researchers have tried to improve the

X-ray photoelectron spectroscopy (XPS) has been widely used to study carbon fiber surfaces after oxidative treatments. Ishitani has pointed out that the usage of XPS in the surface study of carbon fiber is advantageous, since carbon fibers are not disturbed by the strong absorption of

^{*} Corresponding author. Tel.: 182-42-869-3916; fax: 182-42-869-3910. *E-mail address:* chung@cais.kaist.ac.kr (I.J. Chung).

adhesion between carbon fiber and matrix resin by chemical reaction using a coupling agent. But there is almost no functional group on the carbon fiber surface that is able to react with matrix or coupling agent. Some functional groups can be generated by treating the carbon fiber surface. In general there are three fiber surface modification methods: chemical method, electrochemical method and plasma treatment method. The chemical treatments have been preferred since they afford improvement without degradation of the fiber properties. Electro-oxidative techniques have been developed and are conventionally used in the treatment of carbon fiber surfaces. These treatments remove weak boundary layers from the surface and produce the increased surface activity with formation of both acidic and basic moieties [4,5]. Low energy plasma processes have demonstrated the potential to control the acidity of the surface for the optimization of adhesion between the carbon fiber and the resin [6,7]. The plasma technique functionalizes the basal plane sites on the fiber surface and increases the level of surface activity.

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Fig. 1. Interfacial reaction involving a hemiacetal linkage between the carbon fiber treated in nitric acid solution using chemical oxidation method and the phenolic resin in the presence of glutaric dialdehyde (GTDA).

the electromagnetic wave but is selective to the surface structure [4]. It is extremely difficult to analyze the carbon fiber surface by FT-IR spectroscopy because of the absorption and the severe scattering of the infrared radiation. However, Sellitti et al. succeeded in obtaining the IR spectra of oxidized carbon fiber surfaces using the internal reflection technique [8]. XPS studies have confirmed that oxidative treatment of carbon fiber increases the surface functionality by creating additional carbonyl groups, carboxyl groups, carboxyl/ester groups and/or hydroxyl/ ether groups at the surface [9–14]. Different functional groups are obtained from different oxidation methods.

Various surface treatments of carbon fiber have been reported to improve the fiber–matrix adhesion, interfacial shear strength, and toughness [15–18]. However they are mostly restricted to epoxy-based composites. Sherwood et al. reported XPS studies of carbon fiber surfaces including interfacial interactions between phenolic resin and carbon fiber oxidized electrochemically in nitric acid, phosphoric acid, and ammonium carbonate solutions, accompanying ab initio calculations to interpret spectral features in the core and valance band spectra [19,20]. They showed the generation of various functional groups such as $-C=O$, $-C-OH$, – COOH, –NH2, depending on various kinds of solution, but the generation of hydroxyl groups for most solutions. Using XPS they studied the chemical reactions between phenolic resin and glutaric dialdehyde (i.e. coupling agent) as well as between hydroxyl group on the carbon fiber surface and the coupling agent. As shown in Fig. 1, the formation of acetal and hemiacetal linkages between phenolic resin and carbon fiber by the glutaric dialdehyde can improve the adhesion between phenolic resin and carbon fiber.

In this study, carbon fibers were oxidized chemically in nitric acid. The oxidized carbon fiber was also treated with a coupling agent of glutaric dialdehyde. Carbon fiber/phenolic resin composites were prepared with these surface treated carbon fibers. The electrical and mechanical properties of carbon fiber/phenolic resin composites were investigated.

2. Theoretical background

Dielectric storage ε' is a measure of the degree of charge polarization, or the energy involved for the separation between charges. On the other hand, dielectric loss ε ^{*n*} is a direct measure of the energy dissipated irreversibly in the relaxation of polarization. The dielectric loss ε'' is divided into two terms.

$$
\varepsilon'' = \varepsilon''_{AC} + \varepsilon''_{DC} \tag{1}
$$

where $\varepsilon_{\rm DC}''$ represents the contribution from DC conduction, i.e. the long-range electronic transport, and is well fitted by the following empirical relationship reported by Ngai et al. [21]

$$
\varepsilon_{\text{DC}}'' = A\omega^{-n} \qquad (0 < n < 1) \tag{2}
$$

where ω is the frequency of the applied AC electric field, A is a frequency-independent constant and *n* is a coarse morphological parameter relating to the transport pathway of the electronic charge. Ngai et al. reported that Eq. (2) is a universal response and can be applied to ionic interaction, dipolar interaction and electronic hopping system etc. The morphological parameter *n* varies from 0 to 1 depending on various transport situations. $n = 1$ corresponds to the ideal case that charge-conducting paths span the sample dimension in a direct fashion, and charge drift is dominant. $n = 1/2$ indicates a totally tortuous and random pathway as in Brownian motion. Of course, a hybrid situations between drift and random diffusion-dominant cases can be envisioned and may yield the effective values of *n* neither 1 nor 1/2.

3. Experimental

3.1. Matrix resin

Resol type of phenolic resin used in this study was obtained from Kolon Chemical Co., Ltd. and its commercial name is KRD-HM2, which is a mixture of 60 wt% phenolic resin and 40 wt% methanol. Its density was 1.0630 g/cm³ and gel time was 52 s at 150° C.

3.2. Carbon fiber surface treatments

The carbon fiber used was TZ-307 epoxy sized highstrength PAN-based carbon fiber (pre-heat temperature, 350 $^{\circ}$ C; carbonization temperature, 1500 $^{\circ}$ C) produced from Taekwang Ind. Co., Ltd. It was a short fiber with the following characteristics: diameter, $6.8 \mu m$; length, 2 mm ; and electrical conductivity, 6.67×10^2 S/cm at 25°C. To investigate the effect of carbon fiber surface treatments on the properties of carbon fiber composites, epoxy sizing was removed from the carbon fiber with acetone in sonicator. The unsized carbon fiber was named as USCF. The USCF was oxidized for 1 h in 60% nitric acid (Junsei Chemical co., Ltd) at 25° C, washed with distilled water and dried in a vacuum oven. This oxidized carbon fiber was named as NAOCF. A coupling agent, glutaric dialdehyde (GTDA) purchased from Aldrich, was used in an attempt to produce interfacial chemical bonds. The NAOCF was immersed in an aqueous coupling agent solution (25 wt% of coupling agent) for 1 h at 25° C. Just before the NAOCF was immersed into the coupling agent solution, this solution was acidified by adding a drop of concentrated sulfuric acid purchased from Aldrich. The NAOCF treated with coupling agent was washed with distilled water and dried in a vacuum oven. This carbon fiber was named as GTDACF.

3.3. Infrared spectroscopy (FT-IR)

The chemical bonding between the NAOCF and the coupling agent was verified in the report of Sherwood et al. [20] in which the carbon fiber was oxidized electrochemically. In this study chemical rather than electrochemical oxidization of the carbon fiber surface was performed. The surface functionality resulting form the oxidation and the coupling agent treatment process was determined by FT-IR spectroscopy. Infrared spectra on KBr pellets were averaged over 20 scans taken at 4 cm^{-1} resolution using a FT-IR spectrometer (Bomem 102 model).

3.4. Preparation of carbon fiber/phenolic resin composites

Surface treated carbon fibers $(5-10 \text{ wt})$ and phenolic resin were mixed and stirred in a beaker at 30°C. Then the composite plate was prepared with 2 mm thickness. It was dried in a convection oven at 40° C to remove methanol.

The carbon fiber/phenolic resin composite was prepared by stacking 4 plies of plate and pressing with a hot press isothermally at 150° C for 30 min. The composite had dimensions of $12 \text{ mm} \times 12 \text{ mm}$ with 1 mm thickness. In order to measure its electrical and mechanical properties, it was cut in dimensions of 5 mm \times 2.5 mm.

3.5. Measurement of electrical properties

Electrical conductivity, impedance and dielectric constant of the composite were measured over a frequency range from 100 Hz to 10 MHz at 25 and 70° C using a Solatron SI1255 frequency response analyzer (FRA). The power of FRA was 1000 V/m and the surface area of electrode was 1.13 cm^2 . Table 1 lists a description of the samples and the sample codes.

Fig. 2. FT-IR spectra of various surface treated carbon fibers: (a) USCF; (b) NAOCF; and (c) GTDACF.

3.6. Measurement of mechanical properties and investigation of morphology

A three-point flexural test was performed to measure the mechanical properties of the composites using an Instron test machine (model 4201). The test was carried out according to the procedure described by the ASTM specification (ASTM D 790M). At least, five specimens were tested for each set of samples and the mean values were reported.

The fracture surfaces of the samples were examined by means of scanning electron microscope (SEM). Secondary electron images of the fracture surface (sputter-coated with gold) were analyzed.

4. Results and discussion

4.1. FT-IR spectroscopy

It is well known that the interface between carbon fiber and matrix resin of a composite plays an important role in affecting the mechanical property of the composite. The surface treatment of carbon fiber with a nitric acid solution called chemical oxidation is one method to improve the interfacial strength. This method is similar to the electrochemical oxidation reported by Sherwood et al. Fig. 1 shows the chemical reaction proposed by Sherwood et al. They also reported that a few functional groups were formed including –OH group on the surface of the carbon fiber. In this study, FT-IR is used to detect the functional group. The FT-IR spectra of USCF, NAOCF and GTDACF are illustrated in Fig. 2. As shown in Fig. $2(a)$, there is no peculiar peak except around 3400 cm^{-1} associated with –OH peak on the surface of the USCF. It reveals that the epoxy sizing is almost removed. The peak is not so intense

indicating a little –OH functional groups in the USCF. In the NAOCF case, the –OH peak increases. It is also well known that when the USCF is treated chemically in the nitric acid solution, only –OH functional groups are formed on the surface of the carbon fiber. In Fig. $2(c)$, the $-OH$ peak decreases a little but the –CO peak increases clearly around 1200 cm^{-1} . This reveals that the coupling agent reacts with the –OH groups on the surface of the NAOCF to form hemiacetal linkages. Thus, the FT-IR spectra indicate that the coupling agent reaction in this study is similar to Sherwood's results when the case is confined to the –OH functional groups formed on the surface of the carbon fiber.

4.2. Electrical conductivity of the carbon fiber/phenolic resin composite

Fig. 3 shows the Cole–Cole plots of various composites as a function of surface treatment, carbon fiber mass fraction and measurement temperature. Z_R and Z_I are the real and imaginary parts of the complex impedance Z^* , respectively. The radius of semicircle Z_R indicates the electrical resistance of the composite. The Cole–Cole plot shows a semicircle for each case, which indicates a single relaxation mode and a resistive and capacitive network structure of the composite. The electrical conduction in the carbon fiber/phenolic resin composite would occur mainly through the carbon fiber because the carbon fiber is a conductor and the phenolic resin is an insulator. Thus, ionic or dipolar interaction in the composite, if ever, is not significant, resulting in the single relaxation mode. The radius of the semicircle decreases as the amount of carbon fiber increases and temperature decreases. Also it is interesting to note that the radius of the semicircle decreases in the sequence of NAOCF, USCF and GTDACF composites with the same carbon fiber mass fraction and at the same temperature.

The electrical conductivity of a composite can be calculated from the radius of the semicircle using the following equation.

$$
\sigma(S/cm) = \frac{\text{sample thickness (cm)}}{\text{electrode area (cm}^2) \times \text{resistance (}\Omega)}\tag{3}
$$

where σ is the electrical conductivity. The resistance in Ω is obtained from the radius of the semicircle. Fig. 4 shows the electrical conductivity as a function of carbon fiber content and temperature for various composites. The electrical conductivity increases with the carbon fiber content, but decreases with temperature for each composite. The electrical conductivity is about $10^{-3} - 10^{-1}$ S/cm, which is a fairly high value. Thus, it is well understood that the randomly oriented short carbon fibers in the all composites are well connected themselves. The decrease of electrical conductivity with the temperature is considered to be caused by the thermal expansion which reduces the contacts between the fibers and the rotation of graphite crystallite axes [22–24]. In Fig. 4, the GTDACF composite has higher electrical conductivity than the other composites at the same

6

Fig. 4. Electrical conductivity of the carbon fiber/phenolic resin composites as a function of carbon fiber content and temperature. N stands for NAOCF; U for USCF; and G for GTDACF composites.

 $\overline{7}$

8

Carbon fiber wt %

9

 10

carbon fiber content. This is an unexpected result. It can be thought that the dispersion of the short carbon fiber or the various surface treatments may cause this anomalous behavior. This behavior is explained later in the analysis of the dielectric constant data.

4.3. Phase angle change versus frequency

5

Fig. 5(a) shows the dependence of phase angle upon frequency at room temperature for the NAOCF composite as a function of carbon fiber content. The phase angle is defined as arctangent (Z_I/Z_R) . The phase angle of N5-25 changes from 0 to -90° as the frequency increases. Nevertheless, N8-25 and N10-25 have the maximum phase angles of -80 and -70° , respectively. The phase angles of the perfect resistor and capacitor are 0° at a low frequency and -90° at a high frequency, respectively. Thus, only N5-25 can function as a perfect resistor and a capacitor. The others can only function as perfect resistors. In Fig. 4, it can be seen that the electrical conductivity of the composite increases with the carbon fiber content. Consequently, the higher the electrical conductivity, the lower the absolute value of the maximum phase angle the composite shows. USCF and GTDACF composites show a similar behavior to the NAOCF composite even though the data are not given here.

In Fig. 5(b), the maximum phase angles are -70 , -60 and -45° for NAOCF, USCF and GTDACF composites, respectively. Thus, the GTDACF composite shows more resistive behavior than the other composites, indicating

Fig. 3. Complex impedance diagrams of the carbon fiber/phenolic resin composites as a function of carbon fiber content and temperature: (a) USCF composites; (b) NAOCF composites; and (c) GTDACF composites.

Fig. 5. Phase angle versus frequency plots for various surface treated carbon fiber/phenolic resin composites: (a) as a function of carbon fiber content at the room temperature for the NAOCF composite and (b) as a function of surface treatment and temperature for NAOCF, USCF and GTDACF composites containing 10 wt% carbon fiber.

higher electrical conductivity (see Fig. 4). Fig. 5(b) shows that the phase angle does not significantly change with increasing temperature. From Figs. 4 and 5(b), we conclude that the electrical conductivity is more sensitive to temperature than phase angle in the carbon fiber/phenolic resin composite.

4.4. Dielectric constant of the carbon fiber/phenolic resin composite

The complex impedance Z^* can be converted to the complex dielectric constant ε^* using the following

Fig. 6. Dielectric constant versus frequency plots at room temperature for the NAOCF composites as a function of carbon fiber content: (a) dielectric storage and (b) dielectric loss.

equation

$$
\varepsilon^* = \frac{l}{i\omega\varepsilon_0 A_C Z^*} = \varepsilon' - \varepsilon''
$$
\n(4)

where *l* is the thickness of the specimen, ε_0 is the dielectric constant of free space and A_C is the surface area of the electrode. Fig. 6(a) and (b) show the variation of dielectric constant versus frequency at the room temperature for the NAOCF composites. The dielectric storage spectra show the monotonic decrease with increasing frequency in Fig. 6(a). This is due to the fact that the mobile electronic transport such as an electronic hopping becomes less able to follow the applied electric field reversal, which is the typical behavior of

Fig. 7. The variation of dielectric constant versus frequency as a function of surface treatment and temperature for various surface treated carbon fiber/ phenolic resin composites containing 10 wt% carbon fiber: (a) dielectric storage and (b) dielectric loss.

all dielectrics regardless of the relaxation mechanism. Also the linear decrease in ε'' up to about 10⁶ Hz is shown in Fig. 6(b). This linear behavior contains the $\varepsilon_{\text{DC}}^{\prime\prime}$ part, which is related to the long-range electronic transport and is dominant in the low frequency range. In Fig. 6(b), the ε'' starts to deviate from the linearity at 2×10^6 Hz. ε' spectra are almost constant in the range of $10^3 - 10^4$ Hz but show a little decrease above 10^4 Hz in Fig. 6(a). This small change of ε' with frequency may be due to electronic interfacial polarization (the Maxwell–Wagner process) of the carbon fibers [24]. With the results of ε' and ε'' , some mixed effects of long- and short-range relaxation are considered to

appear above 10^4 Hz. Eq. (2) with $n \approx 1$ fits the data in the range $10^3 - 10^4$ Hz indicating the electronic transport in direct manner. In this region the change of ε' is small and ε'' shows the linearity. It is not yet clear why the change in ε' is smaller than that of ε'' . The behavior is also shown in the ionic system [25]. The phenolic resin is an insulator, but the carbon fiber has the high electrical conductivity. The electronic transport in direct manner means that the short carbon fibers are well connected themselves in the composite. USCF and GTDACF composites show a similar dielectric behavior to NAOCF composite.

The dielectric constants show similar shapes of curves and the decrease with temperature for the different composites with 10 wt% of carbon fiber. It is noted that as the temperature increases, both the electrical conductivity and the dielectric constant of the composite decrease. Because the coarse morphological parameter has the value $n = 1$ for different temperatures, the temperature change does not affect the electronic transport pathway but the rate of the electronic transport. This behavior is partly due to good thermal stability of phenolic resin and partly due to the fact that the overall electronic transport is limited to only the carbon fiber with high electrical conductivity.

Mauritz et al. have recently introduced an ionic cluster to ionic systems and showed various dielectric behaviors [26,27]. They also reported that the DC conduction part of ε ^{*i*} spectrum at a lower frequency involved the long-range intercluster ionic hopping, while the intracluster-confined ions contributed to the interfacial polarization at the interface between hydrophilic and hydrophobic parts at a higher frequency [26]. From these mechanisms, the relaxation times derived from the relaxation peak positions at a high frequency in ε'' spectrum are thought to represent the natural time scales during which intracluster electronic charge relaxations occur.

In this study, the electronic charge hops through the carbon fibers. Hence, we can assume an electronic charge relaxation within some boundary and some clusters of carbon fibers (i.e. intercluster and intracluster). But it is very difficult to define the boundary because an electronic charge has a much shorter relaxation time scale than an ionic charge.

In Fig. 7(b), a small relaxation peak is shown above 2×10^6 Hz for every specimen. The relaxation peak shifts to a lower frequency in the order of NAOCF, USCF and GTDACF composites. We rationalize that the GTDACF composite has the lowest electronic mobility and the longest relaxation time.

Recall again the anomalous behavior that the GTDACF composite has higher electrical conductivity than the other composites with the same carbon fiber content. Generally the electrical conductance is represented as the product of the charge carrier density and the charge mobility. The GTDACF composite has the smallest charge mobility because of the longest relaxation time, but the highest

Fig. 8. Dielectric loss spectra versus frequency plots at room temperature as a function of diamine content in the fabric type of carbon fiber composite.

electrical conductivity. Thus, we can conclude that the GTDACF composite has higher charge carrier density than other composites. This different behavior may be explained by a difference of electronic transport affected by carbon fiber dispersion and coupling agent. There is a possibility that the unreacted or physically adsorbed coupling agent on the carbon fiber in the GTDACF composite as an impurity can increase the charge carrier density. However, such charge carriers have a difficulty in the movement in the composite because the carbon fiber/phenolic resin composite has a very rigid morphology. Thus we can exclude the impurity effect.

To identify the difference in the charge carrier density among NAOCF, USCF and GTDACF composites, the fabric type carbon fiber/phenolic resin composites were prepared following the same surface treatments used in this study. And to confirm again no effect of impurity on the charge carrier density, diamine was added in the fabric type carbon fiber composite. Fig. 8 shows the dielectric behavior of the composite treated with the coupling agent of GTDA as a function of diamine content. It is recognized that diamine content does not affect the relaxation time and the charge carrier density of the carbon fiber composite. Fig. 9 shows the dependence of the dielectric loss on the surface treatment. The spectra almost coincide and the relaxation time does not change no matter how the fabric type carbon fibers are treated. The surface treatment of fabric type carbon fiber does not affect the charge carrier density as well as the relaxation time. Thus, it is concluded that the different dielectric behaviors between short carbon fiber composites are caused by the dispersion of the carbon fiber rather than the surface treatment methods.

The GTDACF composite has the highest electrical conductivity but the lowest mobility as shown in the

Fig. 9. The dielectric loss spectra change of the composite with various surface treated fabric type carbon fibers.

dielectric behavior. Thus, the GTDACF composite must have the highest charge carrier density if the GTDACF composite have the highest electrical conductivity because the electrical conductivity is the product of charge carrier density and charge mobility. This anomalous behavior cannot be accurately explained here, but the clue may be suggested. The GTDACF treated with the coupling agent has a strong adhesion between carbon fiber and phenolic resin. So the GTDACF flows with the phenolic resin and is dispersed very well during the hot pressing.

4.5. Mechanical property of the carbon fiber/phenolic resin composite

The flexural strength of the composite regardless of the method of surface treatment increases with carbon fiber content in Fig. 10. At a fixed carbon fiber content, the GTDACF composite has higher flexural strength than the other composites, indicating that the coupling reaction improves the interfacial strength between the carbon fiber and the phenolic resin. The GTDACF composite is found to have 2–2.5 times the flexural strength of NAOCF composite. The USCF composite has higher strength than the NAOCF composite. Manocha reported the similar phenomenon that carbon fiber composite treated with nitric acid solution had a lower strength than the untreated carbon fiber composite [28]. The flexural strength of the composite follows the same order as $GTDACF > USCF > NAOCF$ composites in electrical conductivity.

4.6. Surface morphology of the carbon fiber/phenolic resin composite

Fig. 11 shows the SEM images of the fractured surface of the composites. The carbon fibers are randomly dispersed in

Fig. 10. The mechanical properties of various surface treated carbon fiber/ phenolic resin composites as a function of carbon fiber content.

the matrix resin. There are some holes in the composite formed by pulling carbon fibers out of the matrix resin during the mechanical test as shown in Fig. 11(a). It means that the adhesion between the carbon fiber and the phenolic resin is very poor. But it is easy not to find a hole in the GTDACF/phenolic resin composite but to find some attached matrix resins on the surfaces of the carbon fibers in Fig. 11(b). Thus, it reveals that the interfacial adhesion between carbon fiber and phenolic resin is improved by treating carbon fibers with the coupling agent.

5. Conclusions

The effect of coupling agent on electrical and mechanical properties of carbon fiber/phenolic resin composites was studied. The electrical conductivity of the carbon fiber/ phenolic resin composite was about 10^{-3} – 10^{-1} S/cm. The composite had the morphological parameter *n* of unity, which means that the carbon fibers connected themselves well in the matrix resin.

The relaxation peak maxima at a high frequency in the ε'' spectra shifted to a lower frequency in the order of NAOCF, USCF and GTDACF composites with the same carbon fiber content. Therefore, it was recognized that the GTDACF composite had the longest relaxation time of electronic charge. From the test of the fabric type carbon fiber composite, it was found that the electrical conductivity did not depend on the surface treatment methods. But the composite with short carbon fibers showed increasing electrical conductivity in the order NAOCF < USCF < GTDACF composites. It could be concluded from these observations that the

Fig. 11. The scanning electron micrographs of the fractured surfaces of the carbon fiber/phenolic resin composites containing 8 wt% carbon fiber: (a) NAOCF composite and (b) GTDACF composite.

electrical conductivity of the composite prepared from short carbon fibers depended upon the dispersion of the carbon fibers in the matrix.

It also showed that the flexural strength increased in the order $NAOCF < USCF < GTDACF$ composites. It was confirmed that the interfacial strength of the composite was improved by using the coupling agent.

The use of a coupling agent could improve the electrical and mechanical properties of the composite by the flow and dispersion of carbon fibers in the phenolic resin and chemical bond between carbon fiber and phenolic resin during compression molding.

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References

- [1] Mark HF, Gaylord NG. Encyclopedia of polymer science and technology, 2. New York: Wiley, 1969.
- [2] Bigg DM. Polym Engng Sci 1979;19:1188.
- [3] Jana PB, Mallick AK, De SK. Polym Compos 1991;22:1.
- [4] Ishitani A. Carbon 1981;19(4):269.
- [5] Fitzer E, Weiss R. Carbon 1987;25(4):455.
- [6] Wesson SP, Allred RE. J Adhes Sci Technol 1980;4(4):277.
- [7] Donnet JB, Brendle M, Dhami TL, Bahl OP. Carbon 1986;24(6):757.
- [8] Sellitti C, Koenig JL, Ishida H. Carbon 1990;28:221.
- [9] Harvey J, Kozlowski C, Sherwood PMA. J Mater Sci 1987;22:1585.
- [10] Nakayama Y, Soeda F, Ishitani A. Carbon 1990;28:42.
- [11] Takahagi T, Ishitani A. Carbon 1984;22:43.
- [12] Kozlowski C, Sherwood PMA. J Chem Soc Faraday Trans 1984;80:2099.
- [13] Kozlowski C, Sherwood PMA. J Chem Soc Faraday Trans 1984;81:2745.
- [14] Kozlowski C, Sherwood PMA. Carbon 1984;24:357.
- [15] Subramanian RV, Crasto AS. Polym Compos 1986;7:201.
- [16] Dujardin S, Lazzaroni R, Rigo L, Riga J, Verbist JJ. J Mater Sci 1986;21:4342.
- [17] Dagli G, Sung NH. Polym Compos 1989;10:109.
- [18] Wimolkiatisak AS, Bell JP. Polym Compos 1989;10:162.
- [19] Wang T, Sherwood PMA. Chem Mater 1994;6:788.
- [20] Wang T, Sherwood PMA. Chem Mater 1995;7:1020.
- [21] Ngai KL, Jonscher RK, White CT. Nature 1979;277:185.
- [22] Ahmad MS, Zihilif AM. Polym Compos 1992;13:53.
- [23] Ramadin Y, Jawad SA, Musameh SM, Ahmad M, Zihilif AM. Polym Int 1994;34:145.
- [24] Jawad SA, Ahmad M, Ramadin Y, Zihlif A. Polym Int 1993;32:23.
- [25] Kim HT, Park JK, Lee KH. J Membr Sci 1996;115:207.
- [26] Mauritz KA. Macromolecules 1989;22:4483.
- [27] Deng ZD, Mauritz KA. Macromolecules 1992;25:2369.
- [28] Manocha LM. J Mater Sci 1982;17:3039.