

# Glass Transition and Melting Behavior of Carbon Fiber Reinforced Thermoplastic Composite, Studied by Electrical Resistance Measurement

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DC electrical resistance measurement was applied to investigate the glass transition and melting behavior of carbon fiber reinforced nylon-6 composite. The electrical resistance exhibited temperature dependencies that were attributed to the matrix molecular movements associated with structural transitions. The electrical resistance was affected by the degree of crystallinity and the thermal oxidative degradation, which were governed by the thermal history. The resistance results are consistent with differential scanning calorimetry (DSC) results. The resistance is more sensitive to the glass transition than DSC.

## INTRODUCTION

The glass transition and melting behavior of a thermoplastic polymer depends on the degree of crystallinity, the crystalline perfection and other factors (1-6). Knowledge of this behavior is valuable for the processing and use of the polymer. This behavior is most commonly studied by differential scanning calorimetry (DSC) (1-6), although the DSC technique is limited to small samples and the associated equipment is expensive and not portable. As the degree of crystallinity and the crystalline perfection of a polymer depend on the prior processing of the polymer and the effect of a process on the microstructure depends on the size and geometry of the polymer specimen, it is desirable to test the actual piece (instead of a small sample) for the glass transition and melting behavior. This paper provides a new technique for this purpose.

DSC is a thermal analysis technique for recording the heat necessary to establish a zero temperature difference between a substance and a reference material, which are subjected to identical temperature programs in an environment heated or cooled at a controlled rate (7). The recorded heat flow gives a measure of the amount of energy absorbed or evolved in a particular physical or chemical transformation, such as the glass transition, melting or crystallization. The concept behind the technique of this paper is totally different from that of DSC. This technique involves measuring the DC electrical resistance when the polymer has been reinforced with electrically conducting fibers such as continuous carbon fibers. The resistance is in the fiber direction. The polymer molecular movements that occur at the glass transition and

melting disturb the carbon fibers, which are much more conducting than the polymer matrix, and affect the electrical resistance of the composite in the fiber direction, thereby allowing the resistance change to indicate the glass transition and melting behavior. The resistance measurement can be performed on large pieces of composite and the electronic equipment (a multimeter) involved is simple and portable. Thus, this technique is expected to be useful for the testing of composite parts in the process of fabrication as well as during use.

Exposure of polyamides to heat and oxygen may cause changes in the physical and chemical characteristics due to thermal oxidative degradation (8) and thus changes in the mechanical properties. Prolonged annealing at a high temperature results in undesirable changes in the degree of crystallization and in the end groups, and may cause inter- and intramolecular transamidation reactions, chain scission and crosslinking (9-14). This paper shows the capability of the electrical resistance technique by studying the effect of annealing in air at various temperatures below the melting temperature for various lengths of time on the glass transition and melting behavior of Nylon-6 thermoplastic polymer reinforced with unidirectional continuous carbon fibers (Nylon-6/CF). In addition, comparison is made between resistance and DSC results.

## EXPERIMENTAL METHODS

The thermoplastic polymer was nylon-6 (PA) in the form of unidirectional carbon-fiber (CF) prepregs supplied by Quadra Corp. (Portsmouth, Rhode Island; QNC 4162). The fibers were 34700 from Grafil, Inc.

(Sacramento, California). The fiber diameter was 6.9  $\mu\text{m}$ . The fiber weight fraction in the prepreg was 62%. The glass transition temperature ( $T_g$ ) was 40–60°C and the melting temperature ( $T_m$ ) was 220°C for the nylon-6 matrix. The prepreg thickness was 250  $\mu\text{m}$ .

A Keithley 2001 multimeter was used to measure the DC electrical resistance of the prepreg (single ply) in the fiber direction before and after annealing, which was conducted in air at 100, 180 and 200°C for 5 h and at 180°C for 5, 15 and 30 h, followed by furnace cooling to room temperature. In order to study the glass transition and melting behavior, the DC electrical resistance measurement was made during heating in air from 25°C to 350°C at a rate of 0.5°C/min. A prepreg strip that was 5 cm long and 1 cm wide was placed in a steel mold cavity lined with a PTFE film for electrical insulation. The DC electrical resistance of the prepreg strip in the fiber direction between the inner two of four electrical contacts was measured. The four electrical contacts were such that the outer two (4 cm apart) were for passing a current and the inner two (3 cm apart) were for measuring voltage, in accordance with the four-probe method of electrical resistance measurement. Each contact was in the form of a line drawn by silver paint all the way around the perimeter of the sample in a plane perpendicular to the fiber direction of composite. The four

contacts were positioned symmetrically relative to the mid-point of the length of the rectangular sample.

A Perkin-Elmer DSC-7 differential scanning calorimeter was used. About 10 mg of each sample before and after annealing were weighed and placed in standard aluminum DSC pans. DSC scans were made in air at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### DSC Analysis

Figure 1a shows the DSC thermogram of the as-received composite. The glass transition was not observed by DSC.  $T_m$  (melting temperature, as indicated by the peak temperature) was 218.5°C. Figure 1b, 1c, 1d, 1e and 1f show the effect of annealing time and temperature on the melting peak. The DSC results are summarized in Table 1. Since  $T_m$  and  $\Delta H$  of as-received and 100°C (5 h) annealed samples were almost the same (Fig. 1a and Fig. 1b), it was attributed to the little change of the crystal perfection or the degree of crystallinity during annealing at 100°C for 5 h. Figure 1c shows the DSC thermogram of the sample annealed at 180°C for 5 h. It reveals two endothermic melting peaks with peak temperatures 216 and 195°C. The lower temperature peak may be because of the structural reorganization during annealing, in which the

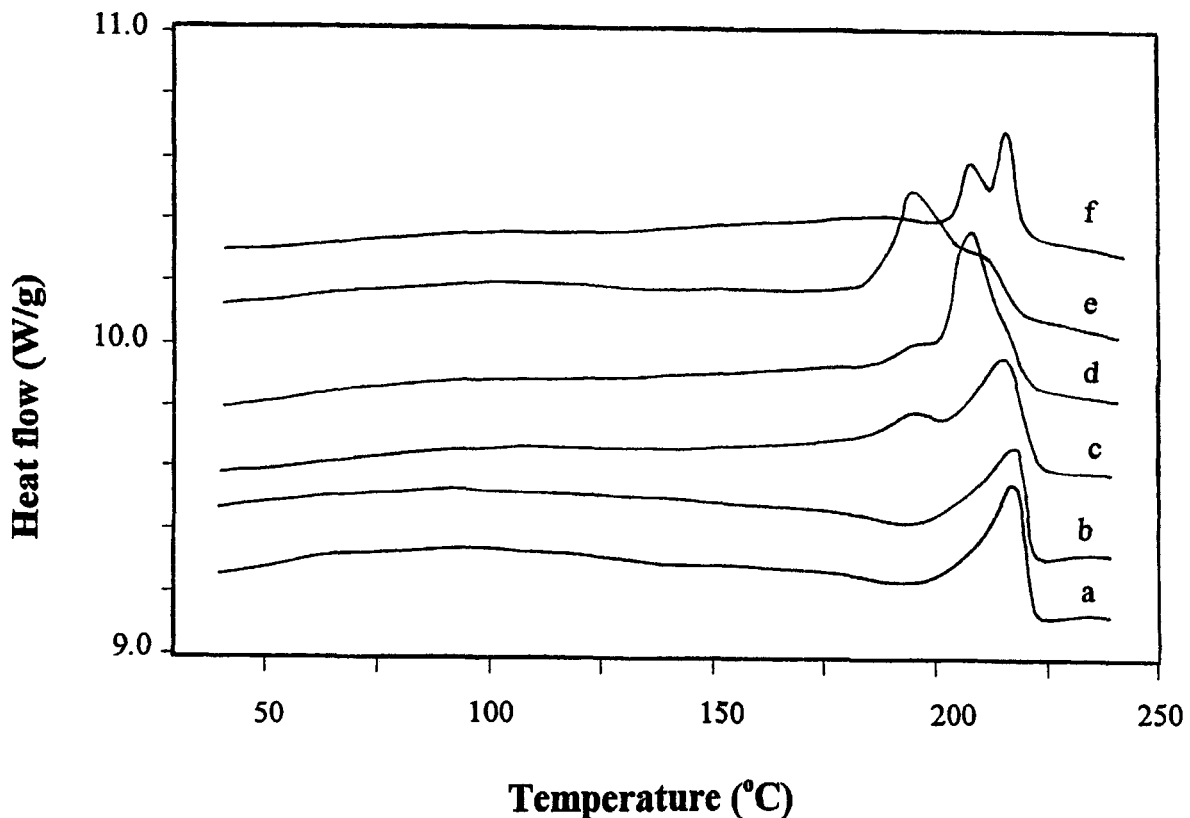


Fig. 1. DSC thermograms showing the melting endothermic peaks before and after annealing at the temperatures and for the times shown. a. As-received. b. 100°C, 5 h. c. 180°C, 5 h. d. 180°C, 15 h. e. 180°C, 30 h. f. 200°C, 5 h.

Table 1. Calorimetry Data for Nylon-6/CF Composite Before and After Annealing.

Annealing		Condition			
Temperature (°C)	Time (h)	$T_{m1}^a$ (°C)	$T_{onset}^b$ (°C)	$T_m^c$ (°C)	$\Delta H^d$ (J/g)
e	e		200.9	218.5	26.7
100	5		205.5	218.2	26.6
180	5	194.8	201.3	215.5	34.8
180	15	196.3	201.4	208.9	39.1
180	30	196.3	200.0	209.0	38.6
200	5	208.3	212.9	216.4	16.5

<sup>a</sup>Peak temperature of the low-temperature melting peak.

<sup>b</sup>Onset temperature of the high-temperature melting peak.

<sup>c</sup>Peak temperature of the high-temperature melting peak.

<sup>d</sup>Heat of fusion.

<sup>e</sup>As-received.

amorphous portion partly developed crystallinity (2, 15, 16). As the annealing time increased to 15 h (Fig. 1d), the high-temperature peak shifted to a lower temperature, but  $\Delta H$  increased. As the annealing time increased to 30 h (Fig. 1e), the height of the low-temperature peak increased while that of the high-temperature peak decreased. These effects are probably due to the reorganization and thermal oxidative degradation of the nylon-6 matrix, as explained below. When the annealing time increased from 5 h (Fig. 1c) to 15 h (Fig. 1d), the degree of the crystallinity increased, so  $\Delta H$  increased. However, at the same time, the extent of degradation increased because of thermal oxidation, which occurred during annealing at a high temperature (180°C), thus resulting in lower crystal perfection. Therefore, the high-temperature peak shifted to a lower temperature. When the annealing time was long enough (30 h, Fig. 1e), the crystalline portion from the reorganization process became dominant, as indicated by the increase of the height of the low-temperature peak. When the sample had been annealed at 200°C for 5 h (Fig. 1f), both  $T_m$  and  $\Delta H$  decreased relative to the as-received sample. One possible explanation is that when the annealing temperature was very high, the extent of thermal degradation was extensive, resulting in less crystalline perfection as well as a lower degree of crystallinity.

### DC Electrical Resistance Analysis

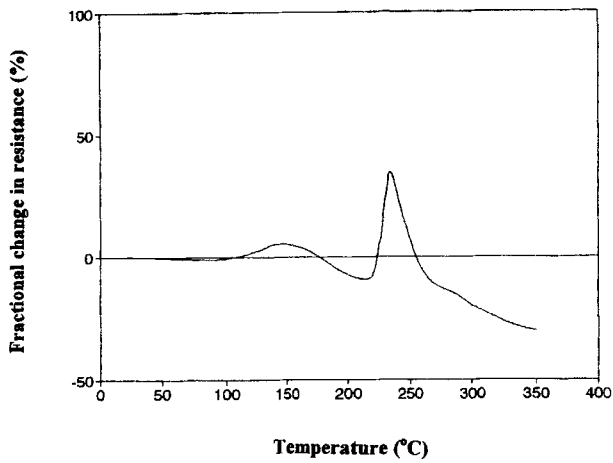
Figure 2a shows the fractional change in resistance for the as-received composite during heating, in which the temperature was raised from 25 to 350°C at a rate of 0.5°C/min. Two peaks were observed. The onset temperature of the first peak was 80°C and that of the second peak was 220°C. The first peak is attributed to matrix molecular movement above  $T_g$ ; the second peak is attributed to matrix molecular movement above  $T_m$ . Because the molecular movement above  $T_g$  is less drastic than that above  $T_m$ , the first peak is much lower than the second one. As indicated before, the DSC thermogram of the as-received composite does not show a clear glass transition (Fig. 1a). Therefore, the resistance is more sensitive to the glass transition

than DSC. The onset temperature (220°C) of the second peak (Fig. 2a) is higher than the onset temperature ( $T_{onset} = 200.9^\circ\text{C}$ ) of the DSC melting peak (Fig. 1a) and is close to the melting temperature ( $T_m = 218.5^\circ\text{C}$ ) indicated by DSC (Fig. 1a). The matrix molecular movement at  $T_{onset}$  is less intense than that at  $T_m$ , thereby giving no effect on the resistance curve at  $T_{onset}$ . Another reason may be a time lag between the matrix molecular movement and the resistance change.

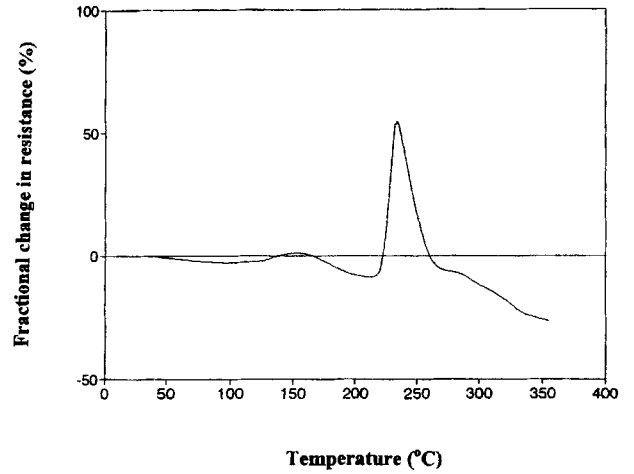
Figure 2b, 2c and 2d show the effect of the annealing temperature. Comparison of Fig. 2a and 2b shows that annealing at 100°C for 5 h (Fig. 2b) had little effect on the glass transition and melting behavior of the nylon-6 matrix; this is consistent with the DSC results (Fig. 1a and 1b). When the annealing temperature increased to 180°C (Fig. 2c), the peak due to molecular movement above  $T_g$  disappeared. This is attributed to the increase of the degree of crystallinity due to annealing. Because the crystalline portion has constraint on the molecule mobility, the higher the degree of crystallinity, the less is the possibility of molecular movement above  $T_g$ .

Not only the degree of crystallinity but also the extent of thermal degradation affects the molecule mobility above  $T_g$ . Figure 2d shows the fractional change in resistance of the sample annealed at 200°C for 5 h. No peak due to molecular movement above  $T_g$  was observed. The degree of crystallinity was less than that of the as-received sample, as shown by  $\Delta H$  in Table 1. However the higher extent of thermal degradation resulted in less molecular movement above  $T_g$ .

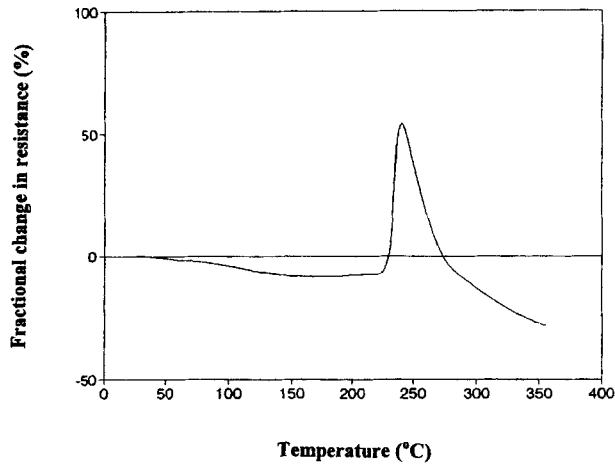
Figure 2c and 2e show the effect of annealing time from 5 to 15 h at 180°C. The height of the peak due to molecular movement above  $T_m$  decreased as the annealing time increased. A longer annealing time resulted in a higher extent of thermal degradation of the matrix, which retarded the molecular movement above  $T_m$ . That this effect is due to a change of the thermal degradation is also supported by the effect of annealing temperature, as shown in Fig. 2c and 2d. A higher annealing temperature likely enhanced the extent of thermal degradation, thus resulting in a decrease of the



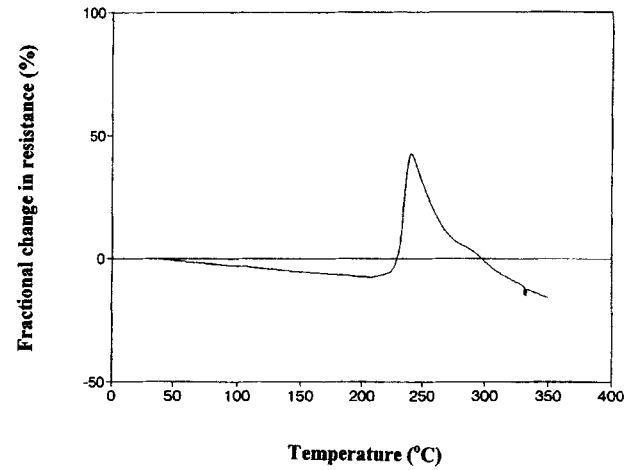
(a)



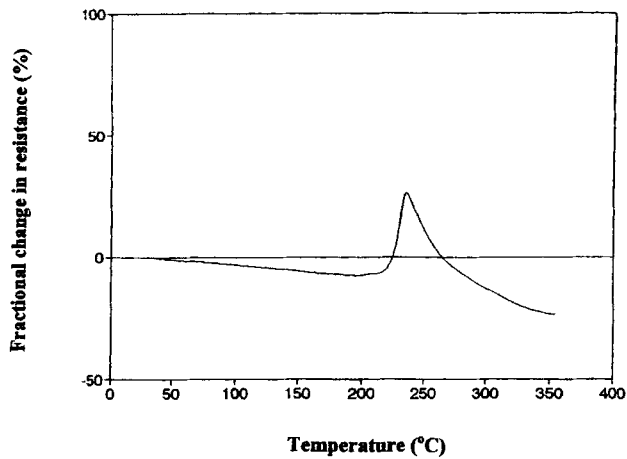
(b)



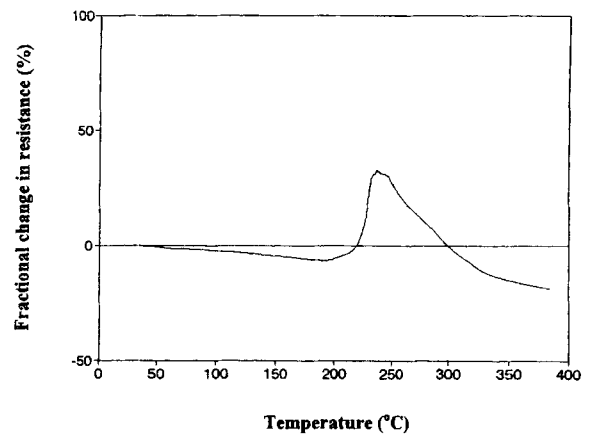
(c)



(d)



(e)



(f)

Fig. 2. Effect of annealing condition on the variation of the electrical resistance with temperature. a. As-received. b. 100°C, 5 h. c. 180°C, 5 h. d. 200°C, 5 h. e. 180°C, 15 h. f. 180°C, 30 h.

height of the peak associated with molecular movement above  $T_m$ . Since the tail is more pronounced for samples with a higher extent of thermal degradation, as shown in Fig. 2d and 2f, it may be attributed to the lower molecular mobility due to extensive thermal degradation.

### CONCLUSION

The DC electrical resistance of thermoplastic/carbon-fiber (nylon-6/CF) composite along fiber direction is decided by carbon fiber ordering, which was affected by the matrix molecular movement above  $T_g$  and that above  $T_m$ . The molecular movement was affected by the degree of crystallinity and the extent of thermal degradation of the matrix, as controlled by the annealing conditions. Therefore, the DC electrical resistance measurement is useful for studying the thermal history and thermal properties of thermoplastic/carbon-fiber composite.

Comparison of resistance and DSC data shows consistency between these results and that resistance measurement is more sensitive to the glass transition of the polymer matrix than DSC. Although the work presented in this paper is based on a nylon-6/carbon fiber composite, the observed correlation between the thermal properties and the DC electrical resistance can be expected for most semicrystalline polymers reinforced with carbon fibers.

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