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Thermochimica Acta 369 (2001) 87–93

thermochimica acta

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Thermal history of carbon-fiber polymer-matrix composite, evaluated by electrical resistance measurement

Zhen Mei, D.D.L. Chung*

Composite Materials Research Laboratory, State University of New York at Buffalo, Buffalo, NY 14260-4400, USA

Received 15 August 2000; received in revised form 28 September 2000; accepted 9 October 2000

Abstract

The thermal history of carbon-fiber nylon-6 matrix composite was evaluated by measuring the electrical resistance in the fiber direction during heating, as the resistance was affected by the degree of crystallinity and the thermal oxidative degradation. The resistance results were consistent with different scanning calorimetry (DSC) and thermomechanical analysis (TMA) results. The resistance measurement gave more information on the melting of the polymer-matrix than TMA. In particular, it distinguished more clearly between the melting of the reorganized crystalline phase and that of the original crystalline phase. The resistance measurement is more sensitive to the glass transition of the polymer-matrix than DSC.

Keywords: Composite; Thermoplastic; Nylon; Electrical resistance; Glass transition; Melting; Crystallinity

1. Introduction

Polymers, particularly thermoplastics, tend to change their microstructure, degree of polymerization, crystallinity and even chemical composition (as in the case of oxidation) upon heating [1–12]. These changes do not occur instantaneously, but take time to occur. Depending on the thermal history, in terms of both temperature and time, a polymer can structurally vary and, as a consequence, its behavior can also vary [1–12]. Therefore, by examining the structure and properties of a polymer, information on the thermal history can be obtained. Knowledge of the relationship between thermal history and polymer structure/properties is useful for manufacturing process development, quality control and polymer engineering.

There are numerous methods for examining the structure and properties of a polymer. They include thermal analysis, rheological testing, chromatography, mass spectrometry, optical spectroscopy and dielectric measurement. These methods, in most cases, involve substantial instrumentation and are limited to small specimens. In some cases, they are even destructive to the specimens.

A method which has received little prior attention is electrical resistance measurement, which involves the use of a direct current (dc) and requires a specimen which conducts electricity [13–16]. In contrast, dielectric measurement involves the use of an alternating current (ac) and requires a specimen which is a dielectric material.

Due to the dielectric nature of most polymers, electrical resistance measurement is not usually considered for the study of polymers. However, the embedding of electrically conducting fibers in the polymer provides a composite material which is

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* Corresponding author. Tel.: +1-716-645-2593; fax: +1-716-645-3875.
E-mail address: ddlchung@acsu.buffalo.edu (D.D.L. Chung).

PII: S0040-6031(00)00735-8

conducting. A particularly common type of conducting fibers is carbon-fibers, which are also attractive due to their high tensile modulus and strength, their low density, and their availability in the form of continuous fibers. Polymer-matrix composites with continuous fibers are widely used for lightweight structures, such as aircraft, rotating machinery and sporting goods [17–19]. In this work, we show that the measurement of the electrical resistance along the fiber direction of a polymer-matrix composite containing continuous carbon-fibers is effective for evaluating the thermal history. This is due to the effect of the polymer structure/properties on the fiber morphology (alignment, waviness, etc.). As the electrical resistivity of the composite is governed by the fibers, which are much more conducting than the matrix, the fiber morphology affects the resistivity of the composite. In this way, the electrical resistivity of the composite is sensitive to the thermal history.

The measurement of the electrical resistance involves simple and portable instrumentation (mainly a multimeter) and can be conducted for a large range of specimen sizes. Thus, the measurement can be performed in the field, say on actual structures. As 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 specimen).

In order to ascertain the interpretation of the electrical resistance results, this work also involved thermal analysis performed on the same composite material. The thermal analysis encompassed differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). Correlation was made among the resistance, DSC and TMA results.

The polymer used in this work is nylon-6, a thermoplastic that is widely used as films (e.g. packaging), fibers (e.g. carpet yarn) and matrix of fibrous composites (e.g. tennis rackets). Exposure of nylons to heat and/or oxygen may cause changes in the physical and chemical characteristics and thus, in the mechanical properties. Though these polymers often undergo a thermal treatment for the purpose of increasing the dimensional stability, reduction of residual stresses, and improvement of the mechanical properties [20,21], prolonged heat exposure may result in undesirable changes in the degree of polymerization and in the end groups, and may cause inter- and intra-molecular transamidation reactions, chain scissions and cross-linking. The rate and extent of these changes depend on the temperature, heating time, end groups, polymerization method and impurities [1].

This paper shows the capability of the electrical resistance technique by studying the effect of heating in air at various temperatures (below and above the melting temperature of the polymer) for various lengths of time on the glass transition and melting behavior of nylon-6 reinforced with unidirectional continuous carbon-fibers.

2. Experimental methods

The thermoplastic polymer was nylon-6 (PA) in the form of unidirectional carbon-fiber (CF) prepregs supplied by Quadrax Corp. (Portsmouth, Rhode Island; QNC 4162). The fibers were 34–700 from Grafil, Inc. (Sacramento, California). The fiber diameter was 6.9 μm. 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 μm.

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 150, 180, 200 and 250°C for 30 h and at 200°C for 1, 10, 20 and 30 h, followed by furnace cooling to room temperature.

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.

For DSC, a Perkin-Elmer Corp. (Norwalk, CT) 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.

For TMA, a Perkin-Elmer Corp. (Norwalk, CT) TMA-7 thermomechanical analyzer was used. The specimen size was 5 mm × 5 mm × 0.25 mm. The probe (3 mm diameter) resting of the top large surface of the specimen was at a load of 10 mN, which corresponded to a compressive stress of 1415 Pa. TMA scans were made in air at a heating rate of 10°C/min.

3. Results and discussion

3.1. DSC analysis

Fig. 1(a) shows the DSC thermogram of the as-received Nylon-6/CF composite. The glass transition was not observed by DSC. The T_{m} (melting temperature, as indicated by the peak temperature) was 218.5°C. Fig. 1(b)–(e) show the effect of annealing for 30 h at different temperatures (150, 180, 200 and 250°C, respectively) on the melting peak. The DSC results are summarized in Table 1. Fig. 1(b) shows the DSC thermogram of the sample annealed at 150°C. It reveals two endothermic melting peaks with peak temperatures of 171.6 and 216.0°C. The lower temperature peak may be because of the structural reorganization during annealing, in which the amorphous portion partly developed crystallinity. As the annealing temperature increased to 180°C (Fig. 1(c)), the high-temperature peak shifted to a lower temperature and the low-temperature peak shifted to a higher temperature. The height of the low-temperature peak increased while that of high-temperature peak decreased. As the annealing temperature increased to 200°C (Fig. 1(d)), the low-temperature peak shifted to a still higher temperature while its height increased further. The high-temperature peak became a shoulder. After annealing at 250°C for 30 h (Fig. 1(e)), no DSC peak was observed. These effects are probably due to the reorganization and thermal oxidative degradation of the nylon-6 matrix, as explained below. Typically the low-temperature melting peak is attributed to the melting of the portion that had reorganized during annealing. The lower melting temperature (T_{m1}, Table 1) increased as the annealing temperature increased. As the annealing temperature increased from 150 to 200°C, the portion that had reorganized during annealing increased thus, the height of the low-temperature peak increased. However, as the annealing temperature increased, the extent of degradation increased due to thermal oxidation, which occurred during annealing at a high-temperature thus, resulting in lower crystalline perfection. Therefore, the high-temperature peak shifted to a lower temperature and its height decreased. When the annealing temperature was too high (250°C), the extent of degradation was so great that the melting of the crystalline phase was not observed (Fig. 1(e)).

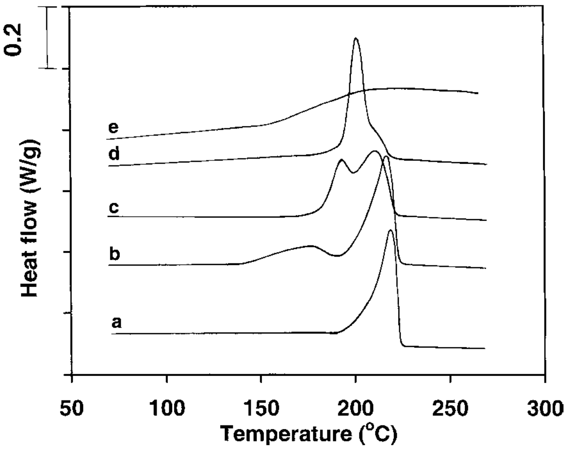

Fig. 1. DSC thermograms showing the melting endothermic peaks before and after annealing at the temperatures shown for 30 h. (a) As-received; (b) 150°C; (c) 180°C; (d) 200°C; (e) 250°C.

Table 1
Calorimetry data for Nylon-6/CF composite before and after annealing at different temperatures for 30 h

Annealing temperature (°C)	T_{m1} [a] (°C)	T_{onset} [b] (°C)	T_{m} [c] (°C)	ΔH [d] (J/g)
[e]		200.9	218.5	26.7
150	171.6	202.2	216.0	28.8
180	192.7	–	209.2	–
200	200.4	–	209.9	–
250	–	–	–	–

[a] Peak temperature of the low-temperature melting peak.

[b] Onset temperature of the high-temperature melting peak.

[c] Peak temperature of the high-temperature melting peak.

[d] Heat of fusion.

[e] As-received.

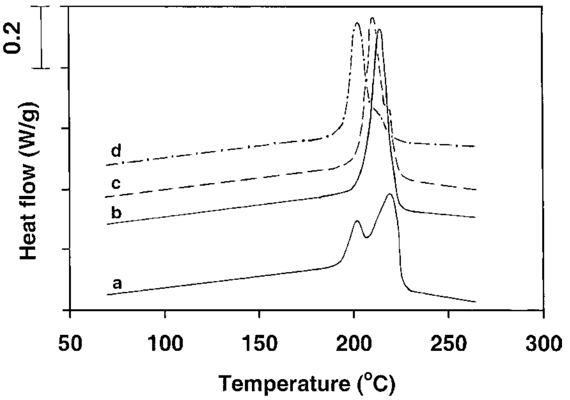

Fig. 2. DSC thermograms showing the melting endothermic peaks after annealing at 200°C for the times shown. (a) 1 h (——); (b) 10 h (——); (c) 20 h (– –); (d) 30 h (– · –).

The thermograms of Nylon-6/CF composites annealed at 200°C for different times (1, 10, 20 and 30 h, respectively) are shown in Fig. 2. The DSC results are summarized in Table 2. Fig. 2(a) shows the DSC thermogram of the sample annealed at 200°C for 1 h. It reveals two melting peaks (T_{m1} and T_m, Table 2) with peak temperatures 199.2 and 214.7°C. As the annealing time increased to 10 h (Fig. 2(b)), T_{m1} shifted to a higher temperature while T_m shifted to a lower temperature and they overlapped to become a single peak. As the annealing time increased to 20 h (Fig. 2(c)), the single peak separated into a peak and a shoulder at T_{m1} and T_m, respectively; T_{m1} was at a lower temperature relative to the single peak while T_m remained at about the temperature of the single peak. As the annealing time increased to 30 h (Fig. 2(d)), both T_{m1} and T_m shifted to lower temperatures. The effects of a long annealing time on T_{m1} and T_m (Fig. 2) are consistent with those of a high annealing temperature (Fig. 1). The effects are probably due to the reorganization and thermal oxidative linkage.

Table 2
Calorimetry data for Nylon-6/CF composite after annealing at 200°C for different times

Annealing time (h)	T_{m1}[a] (°C)	T_{onset}[b] (°C)	T_m[c] (°C)	ΔH[d] (J/g)
1	199.2	201.0	214.7	35.3
10	211.7	203.7	211.7	34.2
20	207.5	–	213.7	33.6
30	200.4	–	209.9	24.0

[a] Peak temperature of the low-temperature melting peak.
[b] Onset temperature of the high-temperature melting peak.
[c] Peak temperature of the high-temperature melting peak.
[d] Heat of fusion.

3.2. TMA analysis

TMA curves of Nylon-6/CF composites before and after annealing at different temperatures (150, 180, 200 and 250°C, respectively) for 30 h are shown in Fig. 3. Fig. 3(a) shows the TMA curve of the as-received Nylon-6/CF composite. The dimension started to decrease at 215°C, due to the softening of the nylon-6 matrix. As the annealing temperature increased, the decrease in dimension was smaller (Fig. 3(b), (c), and (d)). When the annealing temperature increased to 250°C, no decrease in dimension was observed (Fig. 3(e)). This is consistent with the DSC result (Fig. 1(e)). When the annealing temperature increased, the extent of degradation due to thermal oxidation increased thus, resulting in less decrease in dimension during melting.

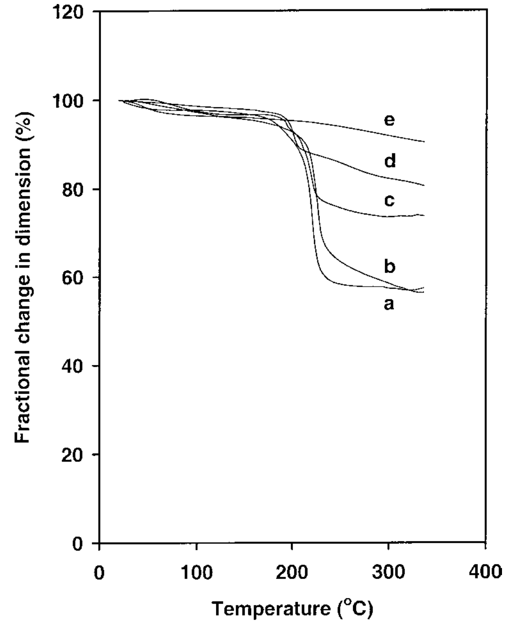

Fig. 3. TMA curves of Nylon-6/CF composite before and after annealing at the temperatures shown for 30 h. (a) As-received; (b) 150°C; (c) 180°C; (d) 200°C; (e) 250°C.

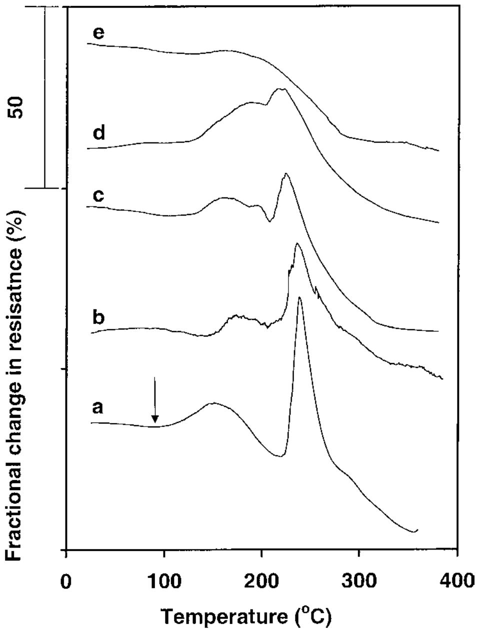

Fig. 4. Effect of annealing temperature for 30 h on the variation of the electrical resistance with temperature. Arrow indicates T_g. (a) As-received; (b) 150°C; (c) 180°C; (d) 200°C; (e) 250°C.

3.3. DC electrical resistance analysis

Fig. 4(a) 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 90°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. When the temperature was above T_g or T_m, the resistance increased due to matrix molecular movement. At the same time, thermal stress, which was due to the thermal expansion mismatch between fiber and matrix, began to be relieved, resulting in the decrease of the resistance. The latter effect dominated as the temperature increased. These two effects combined together caused a peak in the resistance versus temperature plot. As a result, two resistance peaks with onset temperatures at T_g and T_m were observed. Because the molecular movement above T_g was less drastic than that above T_m, the first peak is much lower than the second one [16]. Fig. 4(b)–(d) shows the effect of the annealing temperature. After annealing at 150°C for 30 h (Fig. 4(b)), the peak due to molecular movement above T_g disappeared. A new peak with an onset temperature of 150°C was observed. This is consistent with the DSC results (Fig. 1(b)). This new peak is probably partly attributed to the melting of the crystalline phase that had reorganized during annealing and partly attributed to the melting of the crystalline phase which had lower perfection than that associated with the main melting peak at the higher temperature. Because the crystalline portion has constraint on the molecular mobility, the molecular movement above T_g is inhibited by the crystalline phase formed during annealing. When the annealing temperature increased to 180°C (Fig. 4(c)), an intermediate-temperature peak with an onset temperature of 180°C appeared while the height of the high-temperature peak decreased. The melting temperature of the crystalline phase that had reorganized during annealing increased with the annealing temperature. Hence, the portion of the low-temperature peak of Fig. 4(b) which is due to the melting of the reorganized crystalline phase shifted to a higher temperature and separated from the portion of the low-temperature peak associated with the melting of the crystalline phase which had lower perfection, thereby resulting in the intermediate-temperature peak with an onset temperature of 180°C. As the annealing temperature increased to 200°C (Fig. 4(d)), the height of the intermediate-temperature peak increased and this peak overlapped with the peak associated with the melting of the crystalline phase which had lower perfection (i.e. the low-temperature peak). The intermediate-temperature peak also overlapped with the high-temperature peak while the height of the high-temperature peak decreased further. As the annealing temperature increased to 250°C (Fig. 4(e)), no peak was observed. This is consistent with the DSC and TMA results (Fig. 1(e) and Fig. 3(e)). However, the resistance decreased as the temperature increased, due to thermal stress relief.

Fig. 5 shows the effect of the annealing time at 200°C. Fig. 5(a), obtained after annealed at 200°C for 1 h, shows two peaks. As in Fig. 4(b) the low-temperature peak is partly attributed to the melting of the crystalline phase that had reorganized during annealing and partly attributed to the melting of the crystalline phase which had lower perfection; the

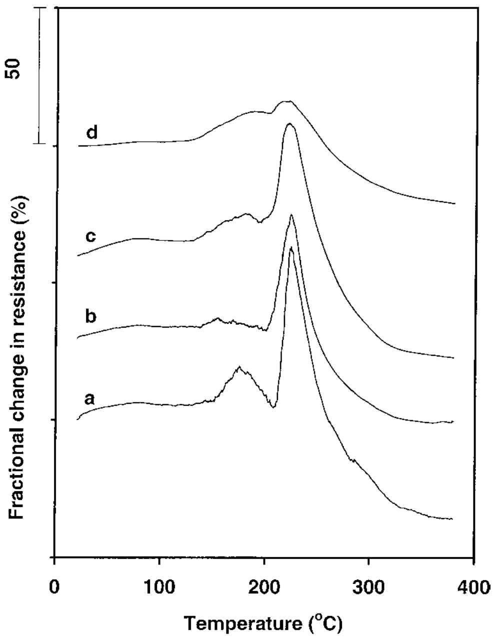

Fig. 5. Effect of annealing time at 200°C on the variation of the electrical resistance with temperature. (a) 1 h; (b) 10 h; (c) 20 h; (d) 30 h.

high-temperature peak is attributed to matrix molecular movement above T_m. As the annealing time increased from 1 to 10 h (Fig. 5(b)), the height of the low-temperature peak decreased while the high-temperature peak (as indicated by the onset temperature) slightly shifted to a lower temperature. This is consistent with the DSC result (Fig. 2(b)). As the annealing time increased from 1 to 10 h, the portion of the low-temperature peak of Fig. 5(a) which is due to the melting of the reorganized crystalline phase shifted to a higher temperature and merged with the high-temperature peak. However, at the same time, the extent of degradation increased due to thermal oxidation, thereby causing the high-temperature peak to shift to a lower temperature. As the annealing time increased to 20 h (Fig. 5(c)), the high-temperature peak (as indicated by the peak temperature) shifted to a lower temperature and its height decreased. As the annealing time increased to 30 h (Fig. 5(d)), the high-temperature peak shifted to still lower temperature and its height decreased further. Comparison of Fig. 2(d) and Fig. 5(d) shows that the high-temperature peak is higher than the low-temperature peak in the resistance curve while it is lower than the low-temperature peak in the DSC thermogram. The matrix molecular movement is more intense at a higher temperature than at a lower temperature, thereby giving a higher peak on the resistance curve at a higher temperature.

4. Conclusion

The DC electrical resistance of thermoplastic/carbon-fiber (Nylon-6/CF) composite along the fiber direction is governed by the 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 thermal history. Therefore, the DC electrical resistance measurement is useful for studying the thermal history and thermal properties of thermoplastic/carbon-fiber composite.

Comparison of resistance, DSC and TMA data shows consistency among these results. The electrical resistance measurement gave more information on the melting of the polymer matrix than TMA. In particular, the melting of the reorganized crystalline phase and that of the original crystalline phase were more clearly distinguished by resistance measurement than by TMA. The electrical resistance measurement is more sensitive to the glass transition of the polymer matrix than DSC.

After annealing at 250°C for 30 h, melting of the nylon-6 matrix was not observed by DSC, TMA or electrical resistance measurement. This is due to the thermal oxidative degradation of the nylon-6 matrix.

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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