Cold-Crystallisation of Polyphenylene Sulphide, Studied by Measuring the Electrical Resistance of a Carbon-Fibre Polyphenylene-Sulphide-Matrix Composite

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SUMMARY

Cold-crystallisation of polyphenylene sulphide (PPS) was studied by measuring the electrical resistance of a continuous-carbon-fibre PPS-matrix composite in the fibre direction during heating after cold-crystallisation. Melting of PPS caused a peak in the plot of resistance vs. temperature. Cold-crystallisation was found to cause an extra peak at a lower temperature in this plot, due to the melting of the portion of PPS that had undergone cold-crystallisation. The resistance results are supported by calorimetry.

INTRODUCTION

Polyphenylene sulphide (PPS) is a high-temperature thermoplastic having a thermosetting/thermoplastic character[1-10]. Upon heating a PPS amorphous polymer below the ideal melting temperature (T_m), partial melting and subsequent crystallisation (known as cold-crystallisation) occurs. Cold crystallisation is an exothermic process which results in a part of the polymer exhibiting increased structural order. The higher the annealing temperature during cold-crystallisation, the greater the degree of structural order and the higher the T_m for the regions of increased structural order. This T_m is approximately equal to the annealing temperature. Hence, after cold-crystallisation, PPS exhibits two values of T_m, i.e., the ideal value and the extra value, which is lower[6,11-13].

Knowledge of the cold crystallisation behavior is valuable for the processing and use of PPS. Such behavior is most commonly studied by differential scanning calorimetry (DSC)[6,11-20], 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 cold-crystallisation behavior. This paper provides a relatively 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[21]. 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 crystallisation. 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 fibres such as continuous carbon fibres. The resistance is in the fibre direction. The polymer molecular movements that occur at the glass transition and melting disturb the carbon fibres, which are much more conducting than the polymer matrix, and affect the electrical resistance of the composite in the fibre 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) 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.

The DC electrical resistance method has been previously used to observe the glass transition and melting behavior of Nylon-6[20].

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 PPS reinforced with unidirectional continuous carbon fibres. In addition, comparison is made between resistance and DSC results.

EXPERIMENTAL METHODS

The thermoplastic material used was polyphenylene sulphide (PPS), which had a glass transition temperature (T_g) of 90 °C and a melting temperature (T_m) of 280 °C. The material was in the form of continuous unidirectional carbon fibre (CF) prepreg, supplied by Quadrax Corp. (Portsmouth, Rhode Island; Product QLC4164). The thickness of the prepreg was 250 μm. The carbon fibre was AS-4C, from Hercules Advanced Materials and Systems Company (Magna, Utah), with a diameter of 8 μm. The fibre weight fraction in the prepreg was 64%.

A Keithley (Cleveland, Ohio) 2001 multimeter was used to measure the DC electrical resistance of the prepreg (single ply) in the fibre direction before and after annealing, which was conducted in air at 120 and 150 °C for 30 h, at 180 °C for 5, 15 and 30 h and at 220 °C for 5 h, followed by furnace cooling to room temperature. In order to study the glass transition and melting behavior, the DC electrical resistance measurement was carried out during heating in air from 25 to 380 °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 polytetrafluoroethylene (PTFE) film for electrical insulation. The DC electrical resistance of the prepreg strip in the fibre 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 fibre direction of the composite. The four contacts were positioned symmetrically relative to the mid-point of the length of the rectangular sample.

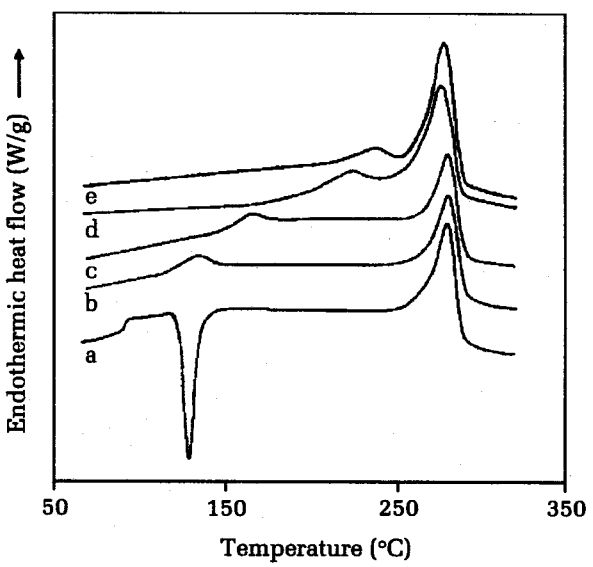
A Perkin-Elmer (Norwalk, Connecticut) DSC-7 differential scanning calorimeter was used. About 10 mg of each sample before and after cold-crystallisation was weighed and placed in standard aluminum DSC pans. DSC scans were conducted in air at a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

DSC Analysis

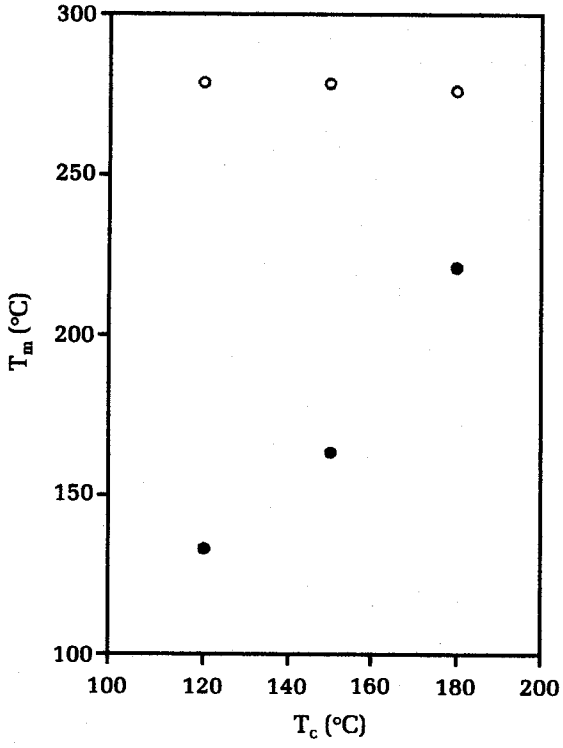
The DSC thermograms of PPS/CF composite before and after cold-crystallisation from the rubbery amorphous state are shown in Figure 1(a) and Figure 1(b)-1(e) respectively. Figure 1(a) reveals three transitions for the as-received composite: the glass transition, then the exothermic crystallisation and finally the endothermic melting peak. The glass transition temperature (T_g) was 90.7 °C, the crystallisation temperature (as indicated by the

Figure 1 DSC thermograms of PPS/CF composite before and after cold-crystallisation at the temperatures and for the times shown.
a. As-received.
b. 120 °C, 30 h.
c. 150 °C, 30 h.
d. 180 °C, 30 h.
e. 220 °C, 5 h.



peak temperature) was 126.5 °C and the melting temperature (T_m, as indicated by the peak temperature) was 277.5 °C. Figures 1(b), 1(c), 1(d) and 1(e) show the effect of the cold-crystallisation temperature (T_c). Figure 1(b) (cold-crystallized at 120 °C for 30 h) reveals two melting peaks with peak temperatures 132.9 and 278.7 °C. Neither the glass transition nor the crystallisation peak was observed. Two melting peaks were also observed for other cold-crystallisation temperatures (Figure 1(b)-1(e)). The presence of two melting peaks is often observed in polymers such as PEEK and PPS upon cold-crystallisation or melt-crystallisation (crystallisation from the melt)[6, 11-14]. Typically the lower melting peak is attributed to the melting of the portion that had reorganized during annealing. The relationship between T_m and T_c for both melting peaks is shown in Figure 2. The lower melting temperature (T_{m1}) was dependent on the cold-crystallisation temperature, and the upper melting temperature (T_{m2}) occurred at about 277 °C. The T_{m1} increased as T_c increased, whereas T_{m2} slightly decreased as T_c increased.

Figure 2 Plots of T_{m1} (●) and T_{m2} (O) of cold-crystallised PPS/CF composite vs. cold-crystallisation temperature, T_c, determined by DSC.



The thermograms of cold crystallized PPS/CF composites before and after cold-crystallisation at 180 °C for different times are shown in Figure 3(a) and Figure 3(b)-3(d) respectively. The relationship between T_m and time for both melting peaks is shown in Figure 4. Figure 3(b) shows the DSC thermogram of the sample cold-crystallized at 180 °C for 5 h. It reveals two melting peaks with

Figure 3 DSC thermograms of PPS/CF composite before and after cold-crystallisation at 180 °C for the times shown.

a. As-received.
b. 5 h.
c. 15 h.
d. 30 h.

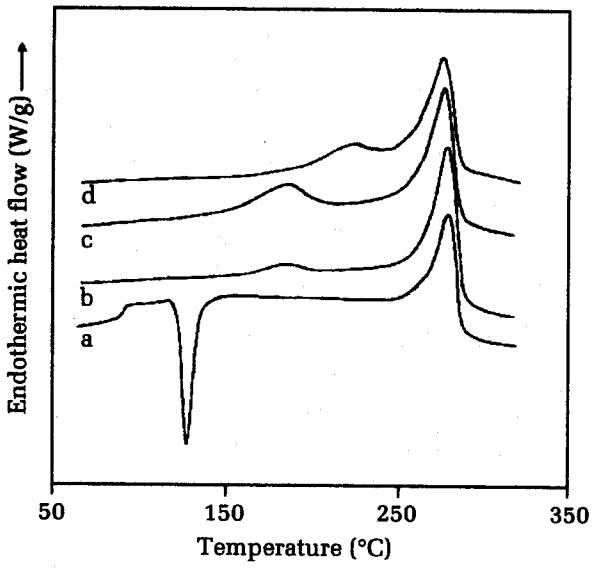
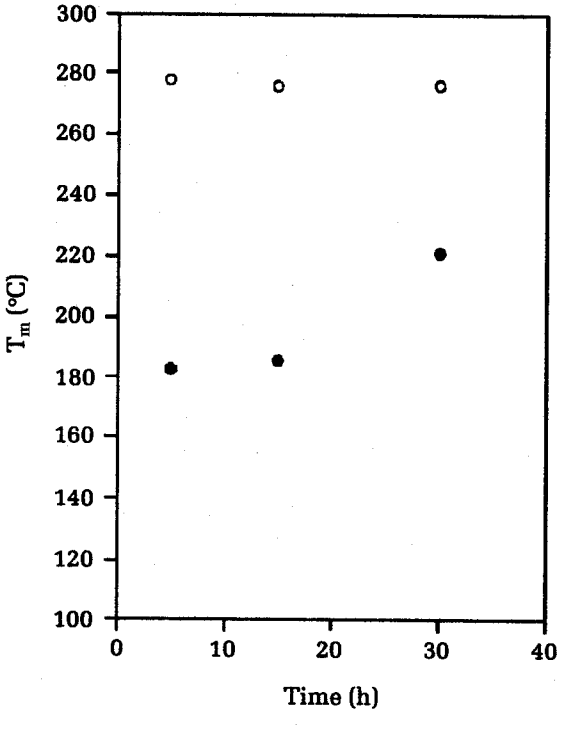


Figure 4 Plots of T_{m1} (●) and T_{m2} (O) of cold-crystallised PPS/CF composite vs. cold-crystallisation time, t_c, based on DSC.



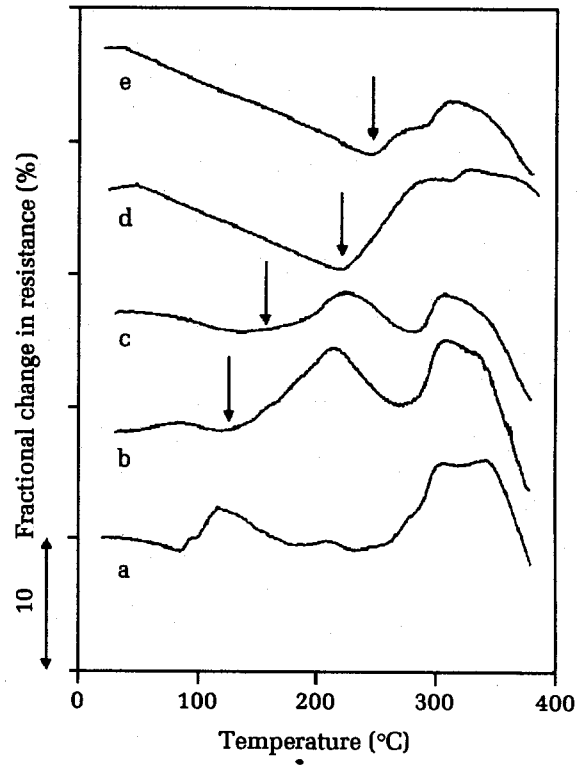
peak temperatures 182.7 and 278.0 °C. As the cold-crystallisation time (t_c) increased, T_{m1} shifted to a higher temperature and T_{m2} shifted to a lower temperature (Figure 4). These trends as a function of cold-crystallisation time are consistent with those as a function of cold-crystallisation temperature (Figure 2). The effects are probably due to the reorganization and thermal oxidative linkage, as explained below. When t_c increased, the perfection of the crystalline phase formed by cold-crystallisation increased, so T_{m1} shifted to higher temperature. However, at the same time, the high-temperature exposure of the PPS matrix involved chain extension and branching through thermal oxidative linkages. The extent of chain extension and branching is increased by either increasing the cold-crystallisation time or raising the cold-crystallisation temperature. These changes in the chemical structure would inhibit chain packing in the crystalline phase formed by reorganization, thus resulting in a lower T_{m2}.

DC Electrical Resistance Analysis

Figure 5(a) shows the fractional change in resistance of 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 280°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. The onset temperature (280°C) of the second peak (Figure 5(a)) is higher than the onset temperature (T_{onset} = 264.1°C) of the DSC melting peak (Figure 1(a)) and is close to the peak melting temperature (T_m = 277.5°C) indicated by DSC (Figure 1(a)). The matrix molecular movement at T_{onset} is less intense than that at T_m, thereby having 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 5(b), 5(c), 5(d) and 5(e) show the effect of the cold-crystallisation temperature. Comparison of Figure 5(a) and 5(b) shows that the peak due to molecular movement above T_g disappeared after cold-crystallisation at 120°C for 30 h. A new peak (arrow) with the onset temperature 130°C was observed. This is consistent with the DSC results (Figure 1(a) and 1(b)). This new peak is attributed to the melting of the crystalline phase formed from

Figure 5 Effect of cold-crystallisation temperature on the variation of the electrical resistance with temperature. Arrows indicate T_{m1}.
a. As-received.
b. 120 °C, 30 h.
c. 150 °C, 30 h.
d. 180 °C, 30 h.
e. 220 °C, 5 h.



the rubbery amorphous state. Because the crystalline portion constrains the molecular mobility, the molecular movement above T_g is inhibited by the crystalline phase formed during cold-crystallisation. The double melting peaks were observed in all the plots of the fractional change in resistance of the samples cold-crystallized at different temperatures (Figure 5(b), 5(c), 5(d) and 5(e)). This is consistent with the DSC results (Figure 1(b), 1(c), 1(d) and 1(e)). The relationship between the onset temperature of the first resistance peak and T_c is shown in Figure 6. The onset temperature of the first peak increased with T_c. Comparison of Figure 2 and 6 shows that the onset temperature of the first resistance peak was almost equal to T_{m1} based on the DSC thermogram for the same T_c. This result supports the conclusion that the first resistance peak is attributed to the melting of the crystalline phase formed from the rubbery amorphous state during cold-crystallisation.

Figure 7(a) shows the fractional change in resistance for the as-received sample during heating, in which

Figure 6 Plot of T_{m1} (●) based on resistance measurement of cold-crystallised PPS/CF composite vs. cold-crystallisation temperature, T_c.

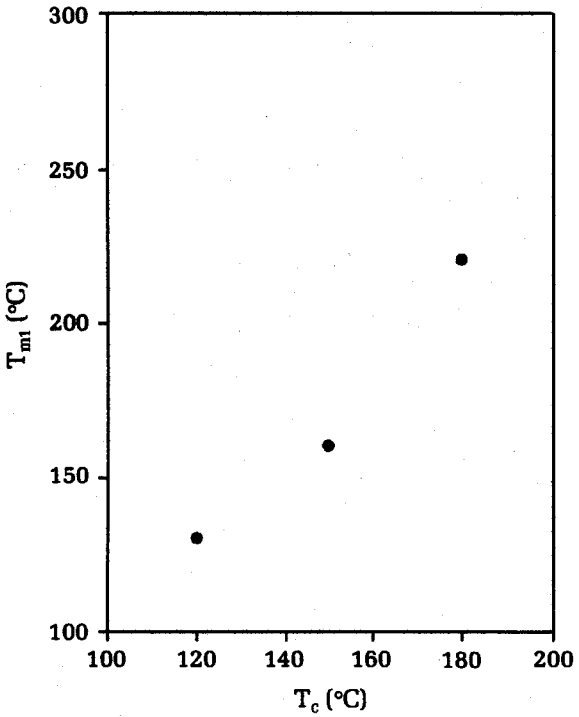
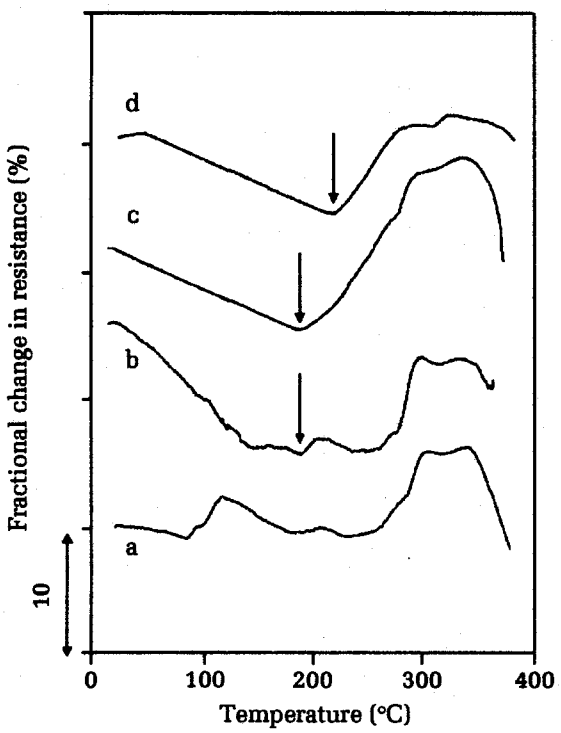


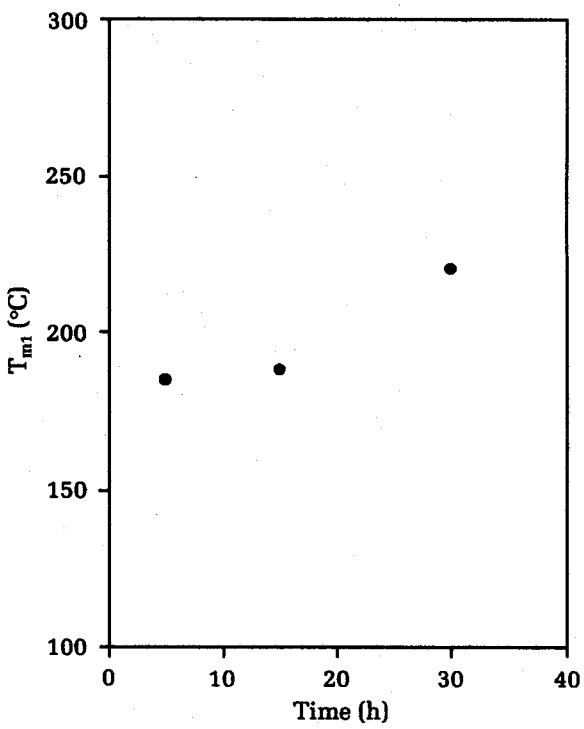
Figure 7 Effect of cold-crystallisation time on the variation of the electrical resistance with temperature. Arrows indicate T_{m1}.

a. As-received.
b. 5 h.
c. 15 h.
d. 30 h.



the temperature was raised from 25 to 350°C at a rate of 0.5°C/min. Figure 7(b), obtained after cold-crystallisation at 180°C for 5 h, shows two peaks. The onset temperature of the first peak (arrow) was 185°C and that of the second peak was 280°C. The first peak is attributed to matrix molecular movement above T_{m1}; the second peak is attributed to matrix molecular movement above T_{m2}. Figures 7(b)-7(d) show the effect of cold-crystallisation time. As the cold-crystallisation time increased from 5 h to 15 h (Figure 7(c)), the onset temperature of the first peak slightly increased, while the peak itself shifted to a higher temperature and converged with the second peak. As the cold-crystallisation time increased to 30 h (Figure 7(d)), the onset temperature of the first peak increased to 220°C. The relationship between the onset temperature of the first resistance peak and t_c is shown in Figure 8. The onset temperature of the first resistance peak was almost equal to T_{m1} based on DSC (Figure 4).

Figure 8 Plot of T_{m1} (●) based on resistance measurement of cold-crystallised PPS/CF composite vs. cold-crystallisation time, t_c.



CONCLUSIONS

The dual melting behavior of the cold-crystallized thermoplastic matrix (PPS) of thermoplastic/carbon-fibre (PPS/CF) composite was investigated by DSC and electrical resistance measurements. It

was found that (a) T_{m1} increased as the cold-crystallisation temperature increased, while T_{m2} slightly decreased; (b) T_{m1} increased as the cold-crystallisation time at 180°C increased, while T_{m2} slightly decreased. The DC electrical resistance of PPS/CF composite along the fibre direction was governed by the carbon fibre ordering, which was affected by the matrix molecular movement above T_g and above T_m. The molecular movement was affected by the crystalline perfection, the degree of crystallinity and the extent of thermal oxidation, which were in turn affected by the cold-crystallisation conditions. The DC electrical resistance measurement is useful for studying the thermal history and thermal properties of thermoplastic/carbon-fibre composites. Comparison of resistance and DSC data shows consistency between these results.

REFERENCES

1. **Hill H.W. and Brady D.G.**, in Encyclopedia of Chemical Technology, 18 (1982), Wiley, New York.
2. **Jog J.P.**, Advances in Polymer Technology 12(3) (1993), 281-289.
3. **Jog J.P., Lodha A. and Nafkarni V.M.**, Advances in Polymer Technology 11(1) (1991/1992), 41-52.
4. **Hawkins R.T.**, Macromolecules 9(2) (1976), 189-194.
5. **Short J.N. and Hill H.W.**, CHEMTECH August (1972), 481-485.
6. **Chung J.S. and Cebe P.**, J. Polym. Sci., Part B: Polym. Phys. Ed. 30(2) (1992), 163-176.
7. **Scobbo J.J. Jr.**, J. Appl. Polym. Sci. 48(11) (1993), 2055-2061.
8. **Mai K., Mei Z., Xu J. and Zeng H.**, J. Appl. Polym. Sci. 63(8) (1997), 1001-1008.
9. **Mai K., Mei Z., Xu J. and Zeng H.**, J. Appl. Polym. Sci. 69(4) (1998), 637-644.
10. **Lu S.X., Cebe P. and Capel M.**, Macromol. 30(20) (1997), 6243-6250.
11. **Chung S. and Cebe P.**, Polymer Preprints, Division of Polymer Chemistry, American Chemical Society, ACS Books & Journals Division, Washington, D.C. 31(1), p. 253-245.
12. **Deporter J. and Baird D.G.**, Polymer Composites 14(3) (1993), 201-213.
13. **Cheng S.Z.D., Wu Z.Q. and Wunderlich B.**, Macromolecules 20 (1987), 2802-2810.
14. **Kuphal J.A., Sperling L.H. and Robeson L.M.**, J. Appl. Polym. Sci. 42 (1991), 1525-1535.
15. **Simal A.L. and Martin A.R.**, J. Appl. Polym. Sci. 68 (1998), 453-474.
16. **Davis Ch.R.**, J. Appl. Poly. Sci. 62 (1996), 2237-2245.
17. **Risch D.G. and Wilkes G.L.**, Polymer 34 (1993), 2330-2343.
18. **Oswald H.J., Turi E.A., Harget P.J. and Khanna Y.P.**, J. Macromol. Sci. Phys., B13(2) (1977), 231-254.
19. **Otaigbe J.U. and Harland W.G.**, J. Appl. Polym. Sci. 36 (1988), 165-175.
20. **Mei Zhen and Chung D.D.L.**, Polymer Composites, in press.
21. **Brown M.E.**, Introduction to Thermal Analysis: Techniques and Application, Chapman and Hall, New York (1988), pp. 25.