Thermochimica Acta, 144 (1989) 165–172
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

STUDIES OF THE THERMAL AND CRYSTALLIZATION BEHAVIOUR OF POLYPHENYLENE SULPHIDE/POLYCARBONATE BLENDS

I.S. BHARDWAJ, VIJAI KUMAR and ANIL DAS

Central Institute of Plastics Engineering and Technology (CIPET), Guindy, Madras - 600 032 (India)

(Received 10 August 1988)

ABSTRACT

Blends of polycarbonate (PC) and polyphenylene sulphide (PPS) of five different ratios were prepared and the thermal properties of these blends were studied using differential calorimetry (DSC) and thermogravimetry (TG). It was found that PC was partially miscible with PPS as evidenced by the decrease in the melting point of PPS and the glass transition temperature of PC. The other thermal properties such as the onset of melting temperature, the heat of fusion and the heat of crystallization were also studied. The density and melt flow index (MFI) of all the blends were studied to determine their processibility. Degradation kinetics and activation energies were computed by the Broido method.

INTRODUCTION

The technique of blending one polymer with another is an effective way of achieving suitable combinations of physical properties [1–3], better processing characteristics and, ultimately, of making it cost-effective for wider applications [4–6]. PPS is a high performance engineering plastic with excellent thermal, mechanical and chemical properties. However, due to its high cost and high flow, it has limited applications. Its end-use potential can be improved by blending it with another amorphous and/or crystalline polymer which has low flow characteristics. A good number of papers have been published on crystalline/amorphous polymer blends [7–11]. The present investigation was undertaken to determine the optimum blend composition of PPS/PC having better thermal characteristics and a higher degree of compatibility, using DSC and TG techniques.

0040-6031/89/$03.50

EXPERIMENTAL

Materials

Polyphenylene sulphide (Ryton R 9 901) and Polycarbonate (Merlon AL-400) from Philips Chemicals Co., U.S.A., and Mobay Chemicals Corporation, U.S.A., respectively, were used in this study.

Blending

The melt blending was carried out at 297 °C and 30 rpm on a Brabender plasticorder (model PLV 330). Five compositions of blends were prepared in the ratios of 90/10, 60/40, 50/50, 40/60 and 10/90 of PPS/PC, by weight.

Density and melt flow index

The density of each set of blends, as well as the pure material, was measured as per ASTM D 792. The melt flow index of all blends was measured at 300 °C and 1.08 kg load in order to determine the processability of the blends.

Thermal analysis

The Dupont thermal analyser (model 1090) with differential scanning calorimeter (model 910) and thermogravimetric analyser (model 950) were used to study the thermal behaviour of the blends. For calorimetric analysis, the samples were heated at the rate of 10 °C min^{-1} up to 300 °C under a nitrogen blanket, and subsequently cooled at a rate of 10 °C min^{-1} to 60 °C.

The thermal parameters obtained from the heating and cooling scans include the glass transition temperature (T_g), the onset of melting, the heat of fusion and the heat of crystallization. Thermogravimetric analysis was carried out at a heating rate of 10 °C min^{-1} in nitrogen medium to determine the degradation behaviour and the energy of activation of the blend compositions.

RESULTS AND DISCUSSIONS

Density and melt flow index

The results of the density and melt flow index measurements of the different blends are listed in Table 1. The results show that when the percentage of PPS increases, the overall density of the blend increases. The

TABLE 1

Density and melt flow index

Blend compositions (%) PPS/PC	Density ($g\ cm^{-3}$)	MFI (300 °C and 1.08 kg load) (gf/10 min)
100/0	1.380	32.34
90/10	1.317	28.24
60/40	1.264	20.40
50/50	1.242	18.40
40/60	1.222	16.35
10/90	1.220	12.51
0/100	1.200	Not measurable [a]

[a] Very high flow because of high temperature.

melt flow index plays a vital role in predicting the processability of the material. The results reveal that the MFI of pure PPS is 32.34 gf/10 min when it is measured at 300 °C and 1.08 kg load. But the melt flow index decreases significantly with increase in the percentage of PC. Therefore, it is clear that the melt flow of PPS in blends of PPS/PC have decreased, making it more easily processable.

Thermal properties of PPS in PPS / PC blends

The thermal analysis of PPS in blends has been analysed in order to determine the thermal parameters such as the onset of melting, the fall in the melting point, the heat of fusion and the heat of crystallization (Table 2).

It can be seen in Fig. 1 that the onset melting temperature of the blends varies between 260.8 °C and 276.0 °C, whereas it is 285.2 °C for pure PPS. It

TABLE 2

Thermal behaviour of PPS in PPS/PC blends

Blend composition PPS/PC (%)	T_g of PC (°C)	PPS melting		Heat of fusion (ΔH_1) ($J\ g^{-1}$)	PPS crystallization		Heat of crystallization (ΔH_c) ($J\ g^{-1}$)
		Onset (°C)	Peak (°C)		Onset (°C)	Peak (°C)	
100/0	—	285.2	294.7	57.6	257.8	252.1	38.8
90/0	146.0	267.8	277.9	19.0	250.3	245.6	19.2
60/40	145.0	260.8	275.8	18.2	245.7	239.6	17.0
50/50	147.0	267.8	278.1	17.5	249.5	243.3	16.8
40/60	146.0	270.2	280.5	14.5	254.5	249.5	13.5
10/90	146.0	276.0	280.8	10.7	255.1	250.0	10.5
0/100	152.0	—	—	—	—	—	—

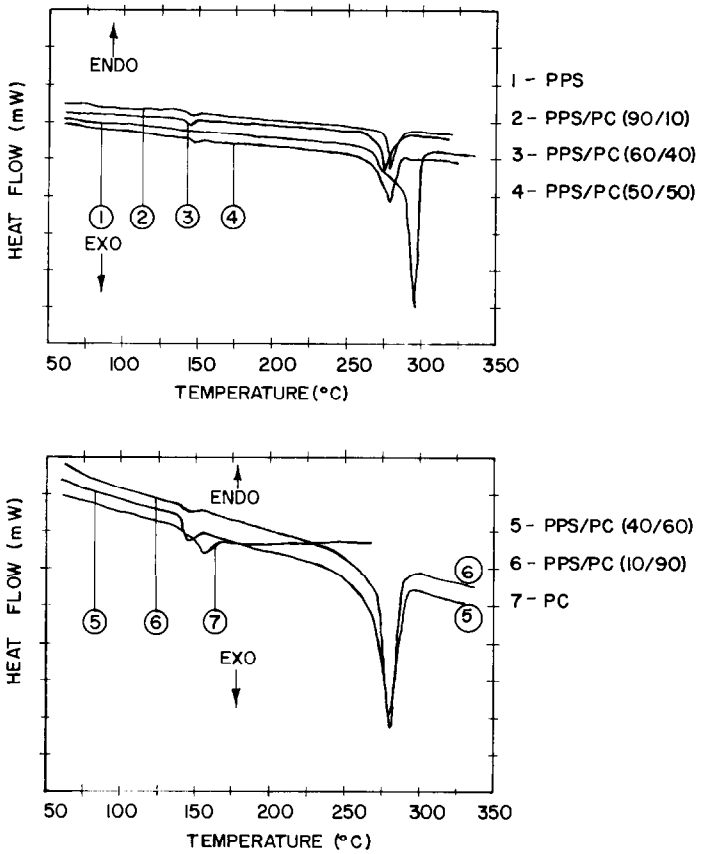

Fig. 1. DSC curves of PPS, PC and their blends.

is observed that for the 60/40 ratio of PPS/PC blend, the onset melting temperature has decreased to the maximum extent, i.e. 260.8 °C. This decrease in onset melting in the blends may be due to the small size of the crystallites of PPS in the blends relative to that in pure PPS.

The melting peak analysis reveals that there is a remarkable decrease in the melting point of PPS from 294.7 °C to 275.8 °C (i.e. in the 60/40 blend of PPS/PC). This shows that PPS has a higher compatibility in the 60/40 ratio blend of PPS/PC than in other compositions.

This compatibility of PPS with PC in PPS/PC blends is also confirmed from the glass transition (T_g) analysis of PC. The 60/40 ratio blend of PPS/PC is more compatible than any other composition. The decrease in onset melting and melting point temperatures makes the blend processable at lower temperatures than pure PPS.

The heat of fusion (ΔH_f) was determined from the area under the fusion peak. The heat of fusion of PPS in the blends decreases significantly compared to that of pure PPS.

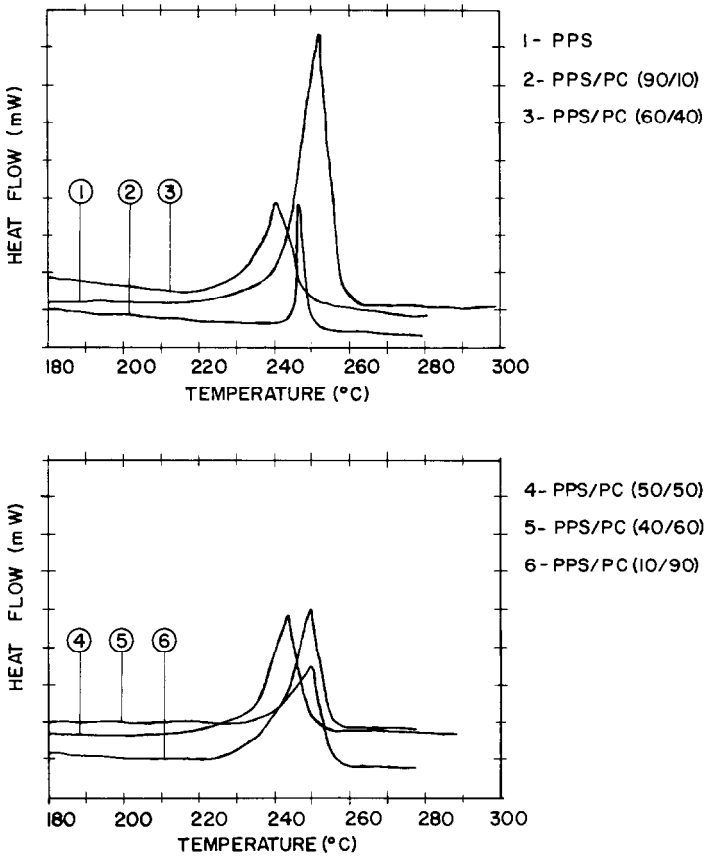

Fig. 2. Crystallization curves of PPS and blends of PPS/PC.

The DSC cooling scans (Fig. 2) of the blends were analysed in terms of the onset of crystallization peak and the heat of crystallization. It was found that the temperature at the onset of crystallization of the blends varied between 255.1° C and 245.7° C compared to 257.8° C for pure PPS. This indicates that the crystallizability is affected by the presence of PC. Moreover, the crystal growth of PPS in the blends takes place at lower temperatures which may be due to smaller crystallite size.

The heat of crystallization of PPS has been found to decrease with increase in PC content. This sharp drop in heat of crystallization indicates the retarding character of crystallizability of PPS in PPS/PC blends. Hence, it can be concluded that the presence of PC adversely affects the crystallizing ability of PPS and retards the homogeneous nucleation process.

Thermogravimetric analysis plots of the blends are given in Fig. 3 and Table 3. Thermogram analysis reveals that the initial decomposition temperature of the blends is lower than that of pure PPS. But, among all the blend ratios, the 60/40 ratio of PPS/PC shows a higher initial decomposition temperature (i.e. 440° C) than the other blend ratios.

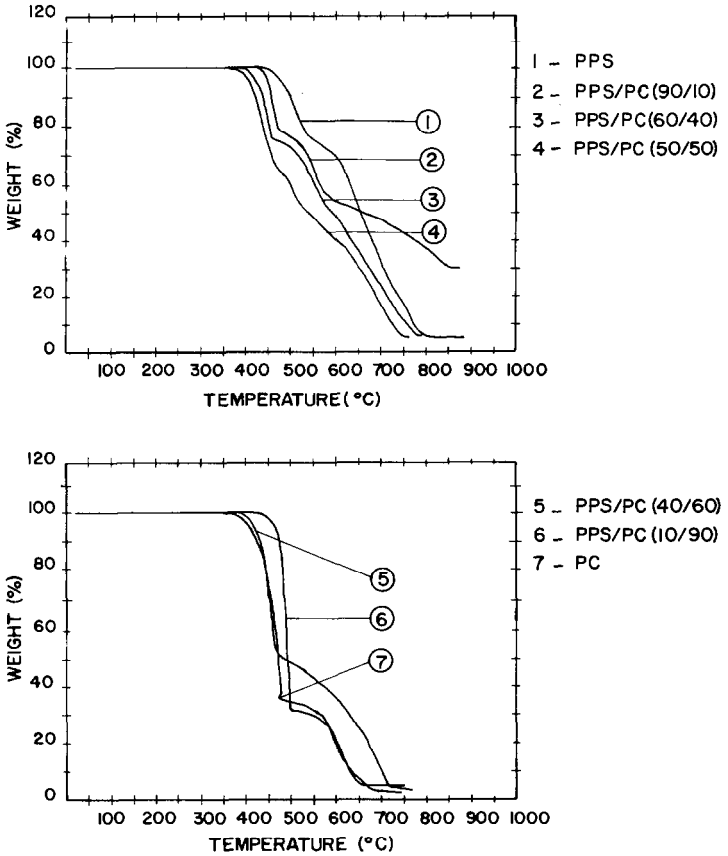

Fig. 3. Thermogravimetric curves of PPS, PC and their blends.

TABLE 3

Thermogravimetric analysis

Blend compositions PPS/PC (%)	Temperature for initial decomposition (°C)	Temperature of half decomposition (°C)	Temperature of maximum decomposition (°C)	Activation energy (E^*) (kcal mol^{-1})
100/0	460.0	680.0	880.0	5.99
90/10	400.0	680.0	880.0	5.26
60/40	440.0	600.0	800.0	4.82
50/50	420.0	520.0	740.0	6.90
40/60	240.0	480.0	700.0	7.26
10/90	300.0	490.0	740.0	9.21
0/100	400.0	470.0	700.0	16.70

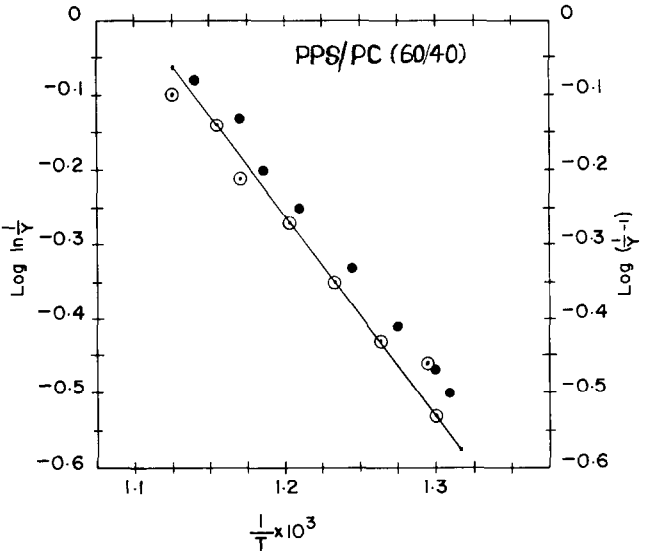

Fig. 4. Typical Broido plots for determination of the activation energy (E^*).

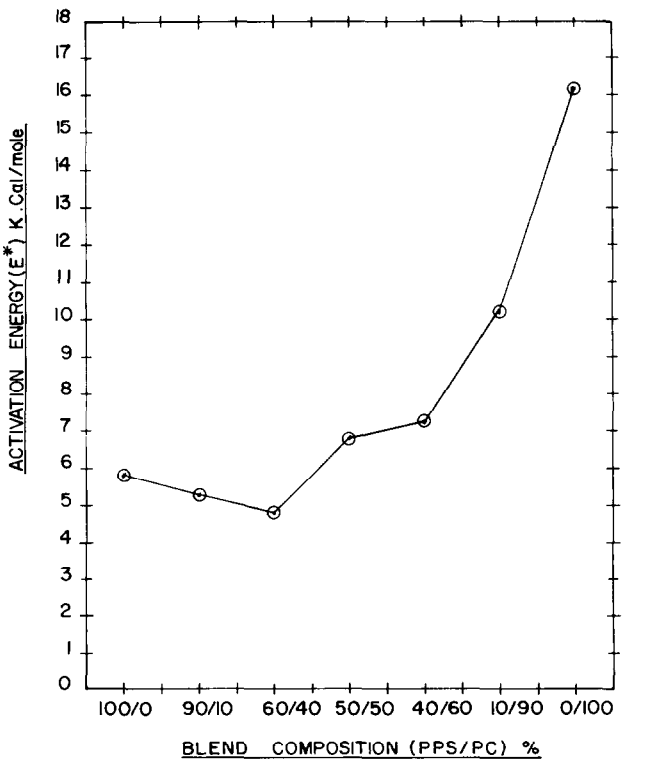

Fig. 5. Activation energy of blends.

In order to understand the mechanism of decomposition, the kinetic parameters have been evaluated using the Broido [12] method. For first-order reaction ($n = 1$)

$$\lg\left[\ln\left(\frac{1}{Y}\right)\right] = -\frac{E^*}{2.303R}\frac{1}{T} + \text{constant}$$

For second-order reaction ($n = 2$)

$$\lg\left(\frac{1-Y}{Y}\right) = -\frac{E^*}{2.303R}\frac{1}{T} + \text{constant}$$

$Y = W_t/W_0$ and the ratio is termed the normalized weight, where W_t and W_0 are the weights of the material not decomposed at time t and the initial weight of the material, respectively. Figure 4 represents a plot of $\lg[\ln(1/Y)]$ and $\lg[(1-Y)/Y]$ for $n = 1$ and $n = 2$, respectively. The activation energy, E^*, has been calculated from the slope of the plot and is presented in Table 3.

It can be seen in Fig. 5 that the activation energy changes with change in the composition of the blends. The minimum activation energy is observed for the (60/40) PPS/PC blend ratio which indicates that this composition is the optimum in terms of the interaction and miscibility of the two components. This reinforces our observation from the calorimetric data on the suppression of the melting point of this blend and the improved processability characteristics for this blend ratio.

REFERENCES

1 B. Ke and A.W. Sisho, J. Polym. Sci., 50 (1961) 87.
2 B. Ke, J. Polym. Sci., 42 (1960) 15.
3 V.M. Nadkarni and J.P. Jog, J. Appl. Polym. Sci., 32 (1986) 5817
4 Chi-Kai Shih, Polym. Eng. and Sci., 27, No.6 (1987) 458.
5 K.S. Shih and C.L. Beatly, Polym. Eng. Sci., 27, No. 20 (1987) 1530.
6 D.V. Howe and M.D. Wolkowicz, Polym. Eng. Sci., 27, No. 21 (1987) 1582.
7 V.M. Nadkarni and J.P. Jog, Int. Polym. Processing, 2 (1987) 1.
8 D.R. Worton and A.J. Keller, Mater. Sci., 19 (1984) 447.
9 Z. Bartczak, A. Galeski and M. Pracella, Polymer, 27 (1986) 537.
10 C.A. Craz, J.W. Barlow and D.R. Paul, Macromolecules, 12 (1979) 726.
11 V.M. Nadkarni and J.P. Jog, J. Appl. Polym. Sci., 32 (1986) 3817.
12 A. Broido, J. Polym. Sci., Part A-2, 7 (1969) 1761.