Journal of Thermal Analysis, Vol. 54 (1998) 637-650

ANNEALING OF POLYPROPYLENE/POLYETHYLENE BLENDS NEAR TO THE MELTING POINTS IN TMDSC

F. Cser[*] *and R. A. Shanks*[**]

CRC for Polymers Pty. Ltd. 32 Business Drive, Notting Hill, VIC 3168 Australia

Abstract

Annealing experiments have been carried out just below the melting temperature of both polyethylene (LLDPE) and polypropylene (PP) and their blends. The total melting enthalpy measured after the annealing cycle was greater by 10–15% with respect to the value having been measured before it. During the annealing period the heat capacity decreases to a lower value within the first 2–3 min. Heat capacities of PP (either in pure form or in the blends) measured during the heating cycle following the annealing cycle have the same value as during the cooling section. The heat capacities of the LLDPE in the heating cycle following the annealing were those of the preceding heating cycle. The total heat flows in the cooling section following the annealing cycle were greater than those in another cooling cycle at the same temperatures indicating that the crystallisation takes place during the cooling rather than during the annealing periods.

The presence of LLDPE decreases the crystallisation temperature of PP. The presence of SEBS in the blend results in a greater crystallisation temperature than that of pure PP. The crystallisation temperature of LLDPE increases with increasing levels of PP.

Keywords: blends, crystallisation, TMDSC, melting, polyethylene, polypropylene, reversibility

Introduction

The phase relationship of polyethylene (PE) and polypropylene (PP) in their blends is a problem of industrial interest. They form individual crystalline phases in their processed and cooled systems [1]. The problem to be studied is whether the phase separation occurred only during the crystallisation or whether it was already present in the liquid state, i.e. the system was also partly or completely immiscible in the liquid phase. PP and PE are generally considered to be immiscible in the liquid state [2].

---

[*] Author to whom all correspondence should be addressed: c/o Department Materials Engineering, Monash University, Clayton, VIC 3168 Australia

[**] Postal address: Applied Chemistry, RMIT University, Melbourne VIC 3001, Australia.

1418-2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

In one of our previous studies on the structure and properties of PP/linear low density polyethylene (LLDPE) blends [3] we found that LLDPE and PP did not form separate spherulites. There are individual PP and LLDPE lamellae within the spherulites of PP. This is an indication, that PP and LLDPE crystallise from a solution of each other, i.e. they were miscible, at least in the time frame of the mixing and the injection moulding. Recently Long, Shanks and Stachurski [4] studied the isothermal crystallisation of PP from its blends with PE. They showed that there was a difference in the crystallisation kinetics of PP depending on the type of PE in the blends. Most of the PEs blended with PP did not modify the crystallisation kinetics of PP, but some types of LLDPE (the same ones that we have used in our experiments) dramatically reduced the rate of crystallisation. Microscopic studies (polarising microscopy and scanning electron microscopy) showed that when PP crystallised according to its original crystallisation rate, it formed separated phases from the PE and when the PE reduced the rate of crystallisation the PP crystallised from a homogeneous mixture with PE.

In this work, temperature-modulated DSC (TMDSC) is used to study the melting and crystallisation behaviour of PP and LLDPE blends prepared with and without hydrogenised poly(styrene-*b*-butadiene-*b*-styrene) (SEBS) which is supposed to be a compatibiliser for the system. It has been shown that SEBS is not a true compatibiliser of the system as it isolates in the two phases [3]. SEBS could be found mainly in the PP phase as well as at the interphase between the two phases in the form of droplets with an average diameter of 60–120 nm.

TMDSC has been shown to give reproducible heat flow and heat capacity data for samples over a fairly great range of parameters such as modulation period and amplitude, rate of purge gas [5]. The curves showed differences in the melting range of the samples, and the heating and the cooling rates also influenced this range. The heat capacities, and consequently the reversing heat flow data measured with constant underlying heating and cooling rates, could have been obtained as they would have been measured by a hypothetical zero frequency modulation [5] using a frequency dependent cell constant.

Thermal behaviour of the components has also been investigated and discussed in [6] and [7]. The measured heat capacities under the melting peak decreased by increasing modulation frequency, but there was always an excess heat capacity indicating a reversible melting of the polymeric crystals [7–11]. Wunderlich suggested [10, 11] that melting of some so-called 'condis crystals' is responsible for the excess heat capacities i.e. the difference between the measured heat capacities and those calculated from lattice vibrations.

Annealing experiments have been performed on semi-crystalline polymers using TMDSC and reported in our previous work [7, 9]. It has been shown that during the annealing within the range where excess heat capacity is present (i.e. in the range of the existence of condis crystal according to Wunderlich [10]) the heat capacity falls to a lower value and crystallisation takes place during the cooling cycle following the annealing cycle. The extent of decrease in heat capacities depended on the type of the polymer. PP, HDPE showed greater decreases in heat capacities compared to branched PE showed and the greater the degree of branching the less the decrease. The reversing melting enthalpy data were interpreted as the reversible melting of the crystals and a fringed micelle type of model was presented as an explanation for the phenomenon.

Okazaki and Wunderlich studied the reversible melting of polymeric crystals in their recent work [12]. They also found that there is a reversible component of the melting of polymeric crystals, at least over a small temperature range, but they did not give a reasonable explanation for its origin.

In this paper we present data obtained during the annealing of blends of PP and LLDPE with and without SEBS. The structure and properties of the materials used have been reported previously [3]. Both crystalline components were studied just below the melting temperatures of the blend samples which had already been heated and cooled using 2 K min^{-1} rates. A comparison of these data with those obtained on the same basic polymers [7] will also be made.

Experimental

Materials and sample preparation

The following materials have been used for the study:

LLDPE	Produced by ICI; an injection moulding grade polymer containing hexane comonomer, MFI: 1 g (10 min)$^{-1}$, density: 922 kg m^{-3}.
PP	Produced by ICI, an injection moulding grade polymer, MFI: 4 g (10 min)$^{-1}$
SEBS	Produced by Shell; (Kraton G 1652), $\langle M_w \rangle$–43000 g mol^{-1}, with 25% styrene.
Blend#1:	60% PP and 40% LLDPE.
Blend#2:	80% PP and 20% LLDPE.
Blend#3:	60% PP, 35% LLDPE and 5% SEBS.
Blend#4:	80% PP, 15% LLDPE and 5% SEBS.

The composition of the blends is given in mass%. Blends were mixed in a Brabender twin screw extruder. All of the samples were cut from injection moulded test bars prepared using a Johns injection moulding equipment. The details of the experimental conditions are given in our previous papers [5, 6].

TMDSC

TA Instrument TMDSC equipped with a liquid nitrogen cooling device was used for the experiments using β=2 K min^{-1} heating and cooling rates with p=40 s as modulation periodicity and A_T=0.6 K as modulation amplitude. This is a heating/cooling type modulation [5]. The heating/cooling type of modulation was selected to reduce the reversing component of the heat flow with respect to the total heat flow. Therefore its remaining amount (excess reversibility) reflects the thermodynamic reversibility of the system in a greater manner [5]. The modulation periodicity (40 s) was selected to be a small value in order to assure at least three complete modulation cycles during the crystallisation. Helium was used as purge gas with 100 mL min^{-1} flow rate. Flat samples of 6–10 mg have been cut from the inner portion of the injection moulded test bars and encapsulated in sample pans supplied by TA.

Annealing experiments were carried out as follows: The samples were initially brought to a reference state (defined as heating at least 20°C above the melting temperature i. e. to 190°C and then cooling by β=2 K min^{-1} to room temperature) followed by another complete cycle to show the curves of the material in its reference state (standard cycle). The temperature was raised to 2–3°C below the peak melting temperature of the corresponding blend component and the system was annealed for 10 min. Then the sample was cooled to 40°C (annealing cycle). The following heating cycle was an analysing cycle for the component having been annealed at the previous annealing cycle and at the same time it was the annealing cycle for the second component. Another heating/cooling cycle was applied to show the effect of the annealing (second analysing cycle). A supplementary heating/cooling cycle of the blends showed that the system did not change and the curves were exactly the same as those of the reference state. The heat capacities and the total heat flow were recorded during the complete experiment. Reversing heat flow and kinetic heat flow were also calculated and supplied by the equipment. For clarity, the standardising and the final analysing cycle are generally not shown on the Figures. The total heat flow curves and the heat capacity curves are shown in this paper, but all of the heat flow curves have been analysed.

Melting enthalpies have been calculated by integrating the area under the peaks. The starting temperature for integration of the total transition enthalpies (that is the sum of the melting of all of the crystalline phases) was accepted as the temperature at which the heat capacities measured on heating started to deviate from the values having been measured on cooling. This temperature was in the range 40–60°C for LLDPE and for its blends and 90–110°C for pure PP. Melting curves of LLDPE are superposed on that of PP. Melting enthalpies of the PE are calculated by integration of the first peak only while the melting enthalpies of the PP component were calculated by subtraction of the melting enthalpy of PE from that of the total transition enthalpy. This way of calculating the melting enthalpy of PP does not include its total value, as the PP starts to melt at 90–110°C, but there is no precise way to separate the two peaks under the melting process of the PE phase.

Enthalpies of crystallisation were determined similarly. The enthalpy of crystallisation of PE is highly underestimated in this way as there is a long lag associated with post-crystallisation which could not be separated from the enthalpy of crystallisation of PP, neither from the total heat flow nor on kinetic heat flow. Therefore the sum of the enthalpies are given for the total and kinetic heat flows, respectively. The melting and the crystallisation enthalpy data are collected in Table 1.

Results and discussion

Noncompatibilised blends

Figure 1 shows the total heat flow curves for Blend#1 before, during and after annealing while, Fig. 2 shows the heat capacity curves of Blend# 1 in the annealing experiment as a function of the temperature. In the first annealing cycle (LLDPE) only a small portion of the LLDPE crystals were molten. Crystallisation is observed in the cooling cycle. There is a drop in the absolute value of heat flow in the first analysing cycle at the temperature of annealing then a double peak appears with the same total melting enthalpy (within experimental error) as that measured in the standard cycle (Table 1). The same behaviour was observed for LLDPE when it was studied [7].

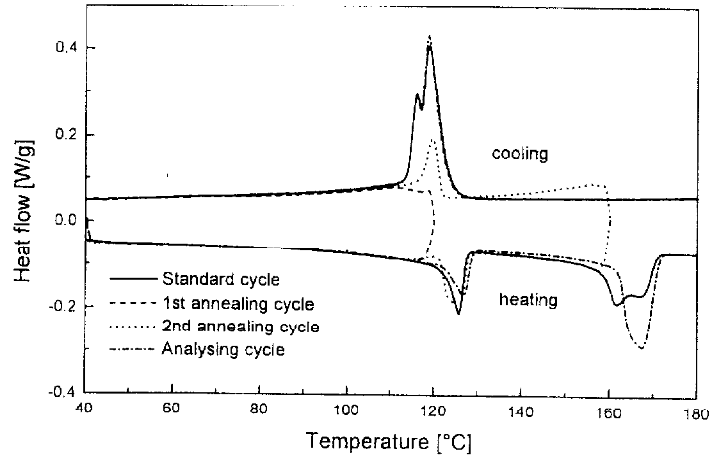

Fig. 1 Total heat flow of PP:LLDPE blend (60:40) before, during and after annealing at 120 and at 160°C

PP was annealed in the second annealing cycle just below the temperature of the first peak of the double melting peak. There is an additional exothermic heat flow in the cooling cycle following the annealing, indicating a crystallisation of PP in this section. As the heat capacities are much lower on cooling in the annealed system (Fig. 2), this exothermic heat flow is not a reversing one, it is a kinetic heat flow. LLDPE crystallised at nearly the same temperature than PP previously crystallised. This means the crystallisation temperature of LLDPE is

Table 1 Transition enthalpies of the melting and crystallisation of PP and PE in the blends/J g^{-1}

	PP	LLDPE	Blend#1	Blend#3	Blend#2	Blend#4
PP %	100	–	60	60	80	80
LLDPE %	–	100	40	35	20	15
SEBS	–	–	–	5	–	5
Standard cycle, heating						
Total PP	126.5		62.4	62.5	83.9	92.0
PE		112.9	40.9	37.1	18.4	11.9
Revers PP	72.9		41.2	23.3	41.9	82.45
PE		83.9	26.8	24.7	8.75	13.83
Kinetic PP	51.4		36.7	36.8	44.5	42.09
PE		28.9	23.6	18.0	5.06	1.41
Standard cycle, cooling						
Total sum	–117.4		–120.2	–114.3	–118.1	–115.6
PE		–116.0	–5.5	–17.6	?	–4.72
Revers PP	–2.24		?	–0.22	–4.83	–1.04
PE		–20.1	–10.84	–8.2	?	–3.99
Kinetic sum	–116.6		–106.6	–108.7	–114.1	–108.7
PE		–95.0	–5.02	–16.6	?	–4.69
1st analysing cycle, heating PE						
Total		113.4	42.5	38.1	15.6	12.7
Revers		81.1	27.5	23.8	8.48	6.51
Kinetic		34.6	16.42	14.7	5.69	3.00
1st analysing cycle, cooling PE						
Total		–114.1	–48.9	–43.5	–16.8	–15.9
Revers		–20.6	–8.24	–7.17	–4.41	–5.43
Kinetic		–94.7	–40.8	–36.8	–13.9	–11.3
2nd analysing cycle, heating						
Total PP	145.5		78.9	79.0	112.6	114.5
PE		113.4	47.9	41.0	19.6	15.0
Revers PP	43.9		14.1	17.7	25.7	30.7
PE		81.1	31.2	27.3	14.9	13.0
Kinetic PP	101.7		58.8	58.2	23.2	65.7
PE		34.6	19.9	17.4	7.34	5.28
2nd analysing cycle, cooling						
Total sum	–120.0		–119.7	–114.2	–114.0	–118.1
PE		–114.1	–4.78	–16.8	?	–4.00
Revers PP	–2.42		?	–0.34	?	–0.94
PE		–20.6	–9.54	–8.9	–5.25	–4.95
Kinetic sum	–116.7		–110.5	–107.8	–110.9	–114.4
PE		–94.7	–4.33	–15.6	?	–4.04

shifted by a few degree to higher temperatures with respect to that of the standard; however crystallisation of molten PP still precedes that of LLDPE.

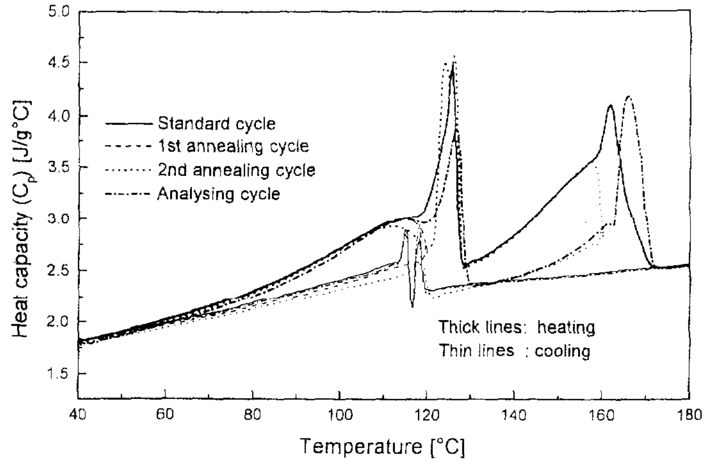

Fig. 2 Heat capacities of PP:LLDPE blend (60:40) before, during and after annealing at 120 and at 160°C

The analysing cycle shows that the first melting peak (~160°C) of PP disappeared, while the second peak increased, resulting in an increased melting enthalpy for the total heat flow with respect to that of the standard cycle (Table 1).

The heat capacities of the LLDPE in the blend after the annealing and analysing cycle behaved the same as those for the pure polymer [7]. This means, they decreased down to the values of the standard cooling cycle after crystallisation and then in the next heating cycle they followed the heat capacities of the standard cycle on heating.

The heat capacity of the PP portion dropped during annealing and it decreased with cooling up to the crystallisation temperature of LLDPE at 120°C, where a step can be seen. In the analysing cycle the heat capacities are higher at temperatures before the melting of LLDPE than those in the preceding cooling cycle but they are the same as those of the preceding annealing cycle. After the melting of LLDPE the heat capacities dropped to that value of the preceding cooling cycle and followed that function up to the temperature of the annealing. Above the annealing temperature they increased sharply to a value which was much greater than before the annealing. Then they formed a sharp peak with a shoulder before melting. Similar behaviour has been observed for pure PP [7] in these type of annealing experiments. The reversible component of the melting enthalpy of LLDPE and PP decreased during annealing (Table 1).

Figures 3 and 4 show the total heat flow and the heat capacity charts for Blend#2 in the annealing experiment. The same features as in Blend#1 can be seen here. As the amount of LLDPE here is half that which it is in Blend#1, the behaviour of LLDPE is much less visible. The crystallisation of LLDPE is cov-

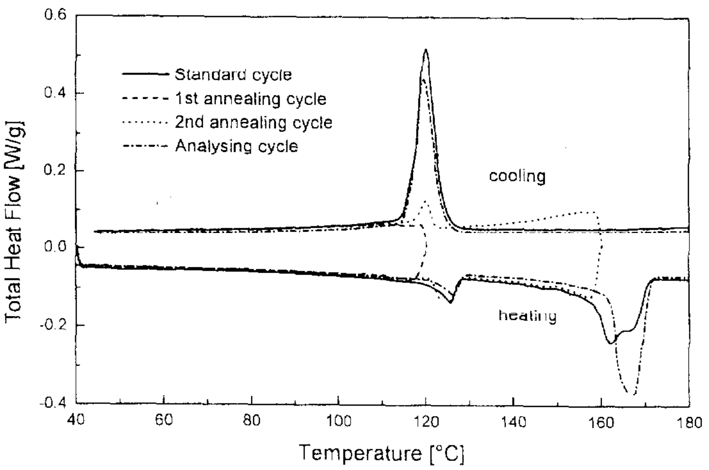

Fig. 3 Total heat flow of PP:LLDPE blend (80:20) before, during and after annealing at 120 and at 160°C

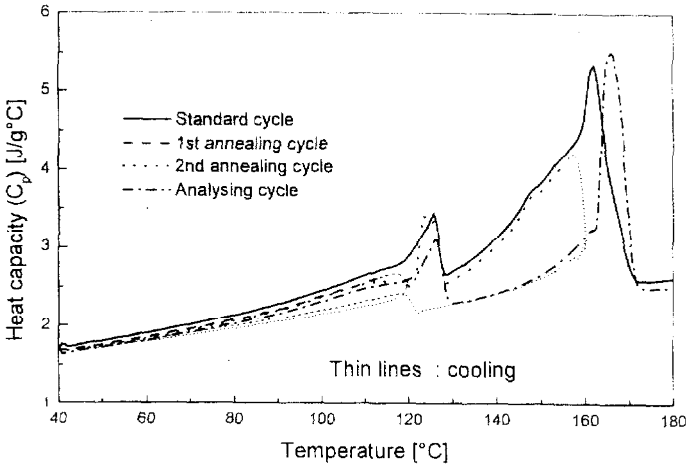

Fig. 4 Heat capacities of PP:LLDPE blend (80:20) before, during and after annealing at 120 and at 160°C

ered by that of PP, and appears as a slightly visible shoulder at the lower temperatures of the crystallisation peak in the total heat flow curves (Fig. 3).

Blends 'compatibilised' by SEBS

Figures 5–8 show the total heat flow and heat capacity curves of Blend#3 and Blend#4. Comparing Figs 5–8 with Figs 1–3 it can be seen, that the blends with SEBS behave similarly to the blends without SEBS. It is worth mentioning that the separation of the crystallisation peak of LLDPE from that of PP is more distinct in Blend#3 and Blend#4 than in Blend#1 and Blend#2. The crystallisation temperature of PP was increased and this is an indication that SEBS forms a nucleating surface for PP crystals.

The melting enthalpy of the LLDPE component in the blends depends on the presence or absence of SEBS. It is less than the expected value in the non-compatibilised blends but it is greater in the presence of SEBS. The smaller the volume of LLDPE with respect to the SEBS the smaller is this increase. The melting enthalpy of PP in the blend decreased with respect to the value expected for the composition but it did not depend on the presence or absence of SEBS (Table 1).

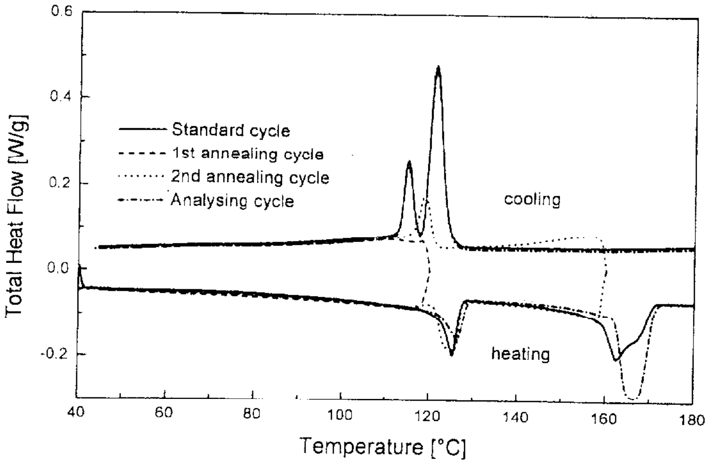

Fig. 5 Total heat flow of PP:LLDPE:SBS blend (60:35:5) before, during and after annealing at 120 and at 160°C

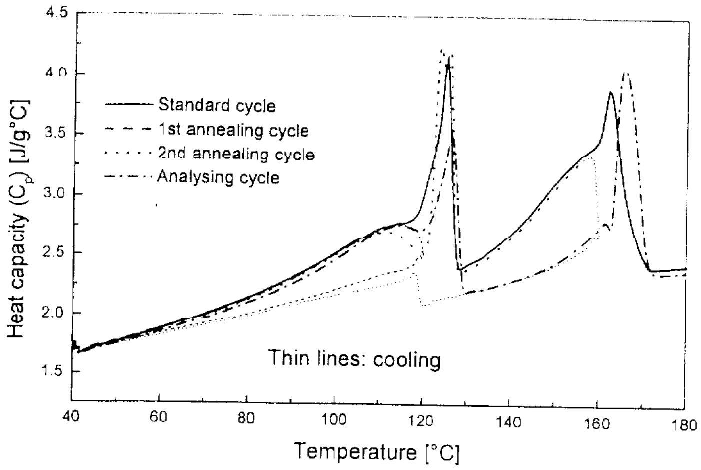

Fig. 6 Heat capacities of PP:LLDPE:SBS blend (60:35:5) before, during and after annealing at 120 and at 160°C

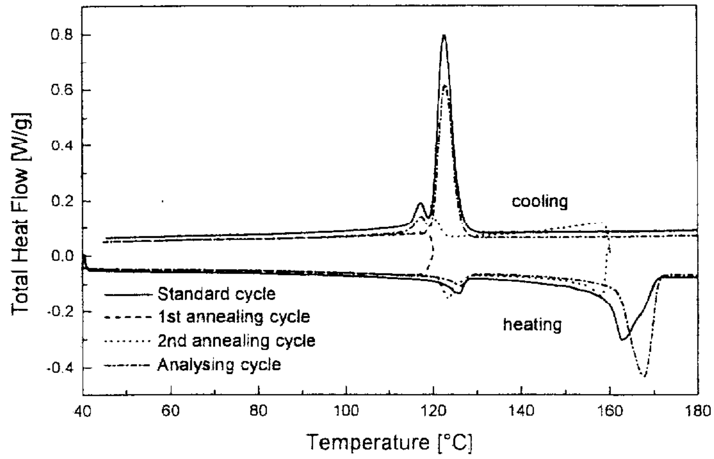

Fig. 7 Total heat flow of PP:LLDPE:SBS blend (80:15:5) before, during and after annealing at 120 and at 160°C

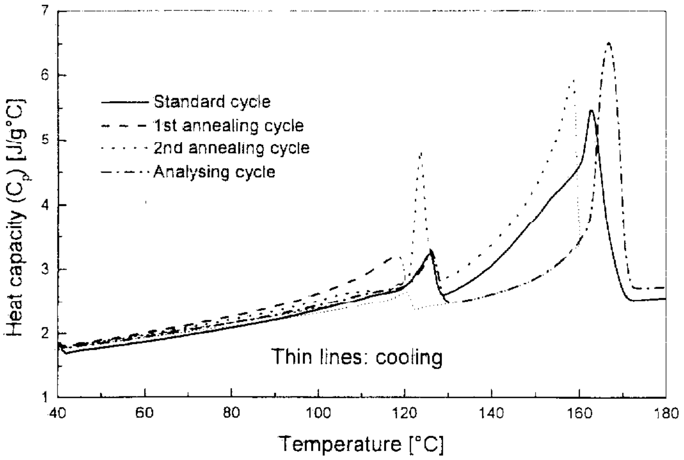

Fig. 8 Heat capacities of PP:LLDPE:SBS blend (80:15:5) before, during and after annealing at 120 and at 160°C

The reversible portion of the melting enthalpy of PP decreased in the blends during annealing. It is either unchanged for LLDPE or it slightly increased with respect to the standard state.

Figure 9 shows the change of the heat capacities of the PP or of PP components within the blends during the annealing. The heat capacities fall rapidly (in 2 min time) to a smaller value. This value was reproduced by the analysing cycle upon heating.

Figure 10 shows the change of the heat capacities of LLDPE in its pure state as well as in blends. Pure LLDPE has been annealed at 121°C in its pure state and it was annealed at 120°C in its blends. The fall of the heat capacities to the lower level also occurs within several minutes.

Figures 9 and 10 show also the change of the temperature during this period (lines). The fall of the heat capacities takes place in parallel with the increase in the temperature, nevertheless this increase too, should result in an increase of the heat capacities. This is an indication again, that a transition takes place parallel with heating and the heat capacities are a result of the two competitive process: heating increases the heat capacities, annealing decreases them.

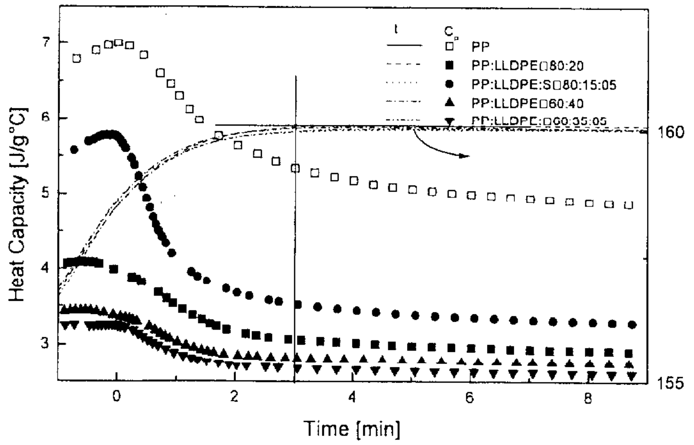

Fig. 9 The change of the heat capacities of PP and the temperature by annealing time

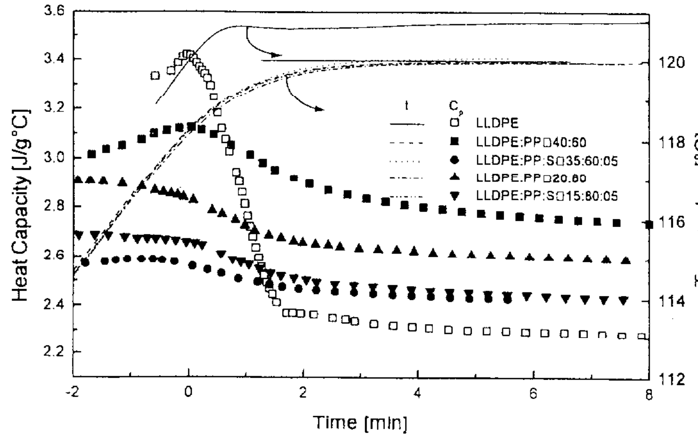

Fig. 10 The change of the heat capacities of LLDPE and the temperature by annealing time

Figure 11 shows the crystallisation curves of the blends to compare the effect of the individual components (Blend#1-4) on the crystallisation of PP and PE. The crystallisation curves of the pure components are shown in Fig. 12.

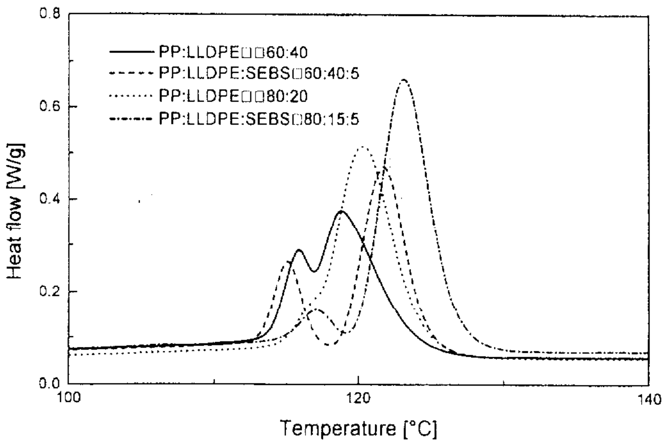

Fig. 11 Total heat flow of PP:LLDPE(:SBS) blends in cooling cycle

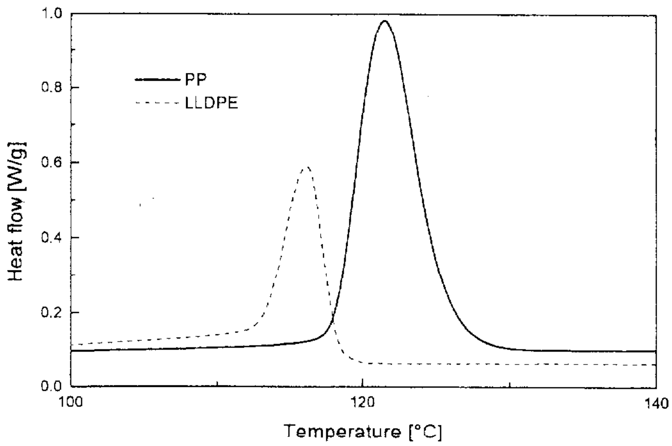

Fig. 12 Total heat flow of PP and LLDPE in cooling cycle

The crystallisation temperature of LLDPE is increased with its decreasing concentration and it slightly increases in the presence of SEBS. The crystallisation temperature of PP decreases with increasing content of LLDPE in the blend, but it is increased dramatically by adding SEBS. SEBS serves as nucleating agent for PP resulting in a more separated crystallisation process for PP and LLDPE. PP crystallises at temperatures in between that of the compatibilised and non-compatibilised blends. LLDPE crystallises in its pure state at lower temperatures than in its blends with PP. As there is a shift in the crystallisation temperature of PP in the presence of LLDPE this indicates some kind of miscibility of the two materials in the liquid state. The presence of SEBS decreases this shift what is an indication of an interphase between the two materials, i.e. of phase separation in the liquid state.

Conclusions

The individual components in the blends in the annealing process respond indepedently and similarly to those in their pure state [7, 9].

Annealing effected the overall crystallinity of the individual components differently. It increased the crystallinity of PP, but this increase did not occur during the annealing itself, it was visible on the curves in the cooling period. The overall crystallinity of LLDPE was not increased by the annealing but the crystallisation following the melting up to the annealing temperature could be seen again on cooling. There was a considerable amount of reversibility in the melting and in the crystallisation processes. The reversible portion of the melting enthalpy of PP was decreased by the annealing while that of LLDPE was not changed or only slightly increased.

As the crystallisation temperatures of both components depended on the composition a close contact of the individual crystalline phases (PP and PE) has occurred. This means, the blend is not a mixture of separated spherulites, but it might be a mixture of individual crystallites. Consequently the associated amorphous phases (~50%) might also be mixed at a finer structural level (below the micrometer scale).

As SEBS influences the crystallisation behaviour of PP to a greater level than that of LLDPE we can conclude that the SEBS is associated with the PP phase to a greater degree than with the LLDPE phase. This conclusion fits our previous observation of the same blends by TEM [7] as well as the results of Long *et al.* [4]. It is also an indication of at least a partial miscibility of LLDPE and PP in the liquid state. Further experiments should be done to prove or to disprove this result.

The data support our conclusion given in [7, 9] that the excess reversibility of the melting process cannot be explained by the so called condis crystal model [10], it is rather an indication of the fringed micelle portion of the crystalline lamellae.

* * *

The authors are indebted to F. Rasoul (Chiron Mimotopes, Australia) for his participation in the experimental work and to E. Kosior for managing the project.

References

1 J. W. Teh, A. Rudin and J. C. Keung, Advances in Poly. Technol., 13 (1994) 1.

2 R. D. Deanin and Ch-H. Chuang, in Handbook of polyolefins: synthesis and properties, Ed. C. Vasile and R. B. Seymour, M. Dekker Pub., New York 1993, p. 779.

3 F. Cser, F. Rasoul and E. Kosior, Polym. Eng. Sci., In print (1998).

4 Y. Long, R. A. Shanks and Z. H. Stachurski, J. Mat. Sci. Letters, 15 (1996) 610.

5 F. Cser, F. Rasoul and E. Kosior, J. Thermal Anal., 50 (1997) 727.

6 F. Cser, F. Rasoul and E. Kosior, J. Thermal Anal. Cal., 52 (1998) 293.

7 F. Cser, J. Hopewell and E. Kosior, J. Thermal Anal. Cal., 53 (1998) 493.

8 F. Cser, Reversible melting and crystallisation of semi-crystalline polymers; Poster presented at RACI 10. Nat. Conv. of Australian Chemists, Adelaide, 27 September–2 October 1995, p. 99.

9 F. Cser, F. Rasoul and E. Kosior, Reversible melting and crystallisation of semi-crystalline polymers. Paper presented at 22nd Australasian Polymer Symposium, Auckland, 3–5 October 1997, p. 213.

10 B. Wunderlich, Macromol. Symp., 98 (1995) 1069.

11 B. Wunderlich et al., Modulated Differential Scanning Calorimetry; Summary of Eqs and Derivations Needed for the Understanding of MDSC, for internal use of the ATHAS Group, November 8, 1995.

12 I. Okazaki and B. Wunderlich, Macromolecules, 30 (1997) 1758.