Multiple crystallization behaviour of polypropylene/thermoplastic rubber blends and its use in assessing blend morphology

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Blends of polypropylene (PP) and thermoplastic rubber (TR) have been studied using differential scanning calorimetry (d.s.c.). For blends with PP as the dispersed phase, a multiple crystallization behaviour was observed; two low-temperature crystallization exotherms at about 75° and 45°C were found in addition to the amount PP crystallization exotherm at about 106°C. The occurrence of the crystallization exotherm at 75°C was explained by a homogeneous nucleation mechanism. It is shown that this multiple crystallization behaviour can be utilized in assessing the morphology of the blends, such as the type of the dispersion (phase continuity) and the degree of the dispersion (PP particle size). The d.s.c. approach is not necessarily restricted to PP/TR blend systems, but can also be applied to other blend systems.

Keywords Blends; crystallization; differential scanning calorimetry; morphology; polypropylene; nucleation mechanism

INTRODUCTION

Differential scanning calorimetry (d.s.c.) has been extensively used for characterizing polymer blend systems. Glass transition (T_g) measurements, for instance, have frequently been employed to determine the state of compatibility of the amorphous phases of the blend[1]. For blend systems containing at least one crystallizable component, both the crystallization and melting characteristics have also frequently been utilized for blend characterization, for instance in terms of polymer compatibility[2], blend composition, interfacial adhesion[3] and the state of mixing[4]. Recently, the d.s.c. technique was applied to the binary blend system polypropylene (PP)/thermoplastic rubber (TR). The present paper describes a multiple crystallization behaviour observed for PP/TR blends and its use in assessing blend morphology such as the degree and type of dispersion.

EXPERIMENTAL

Materials

The materials studied were blends of Shell polypropylene HY-6100(hereafter:PP) and CARIFLEX TR-1102 thermoplastic rubber, a styrene–butadiene–styrene block copolymer manufactured by Shell (hereafter: TR). The blends were prepared by melt-mixing PP granules and TR crumbs in a 64 mm Henschel single screw extruder (L/D ratio of screw = 25) at a mass temperature of 230°C. Different PP/TR blend ratios were used, viz. 75/25, 50/50 and 25/75 %w, as well as a few intermediate compositions.

Crystallization experiments

The crystallization experiments were performed with a Perkin-Elmer differential scanning calorimeter, model DSC-2. The samples, varying in mass from 10 to 12 mg, were run in standard aluminium sample pans, with an empty sample pan as the reference. All scanning was conducted in a helium atmosphere. The temperature calibration of the instrument was carried out at a heating rate of 20°C/min using pure substances with well-known transition temperatures like indium and cyclohexane. For the energy calibration high-purity indium was used.

For the crystallization experiments the following procedure was used: first, the samples were preheated at 220°C for 1 minute to destroy prehistory effects and then cooled at a rate of 20°C/min to record the PP crystallization behaviour; thereafter they were reheated at a rate of 20°C/min to detect PP melting behaviour. The heats of crystallization and that of fusion were obtained from the d.s.c. thermograms by measuring the area under the crystallization and melting peaks by planimetry. The values for the heat of crystallization and the heat of fusion were usually calculated per gram of total sample; in a few cases the heat of crystallization values were calculated per gram of PP.

Electron microscopy

The microphase structure of the PP/TR blends was examined by transmission electron microscopy. Ultrathin sections were cut parallel and perpendicular to the extrusion direction using a cryo-ultramicrotome. Selective staining of the sections by osmium tetroxide vapour was applied to enhance the contrast between the phases[5]. In all cases the dispersed particles were slightly elongated in the extrusion direction, the more so when TR was the dispersed phase.

Particle size measurements on the electron micrographs were performed with a Quantimet 720 image analyser (Cambridge Instrument Ltd.). The size of the domains is expressed in terms of an average diameter; here the second moment of the number distribution was taken as the average value.

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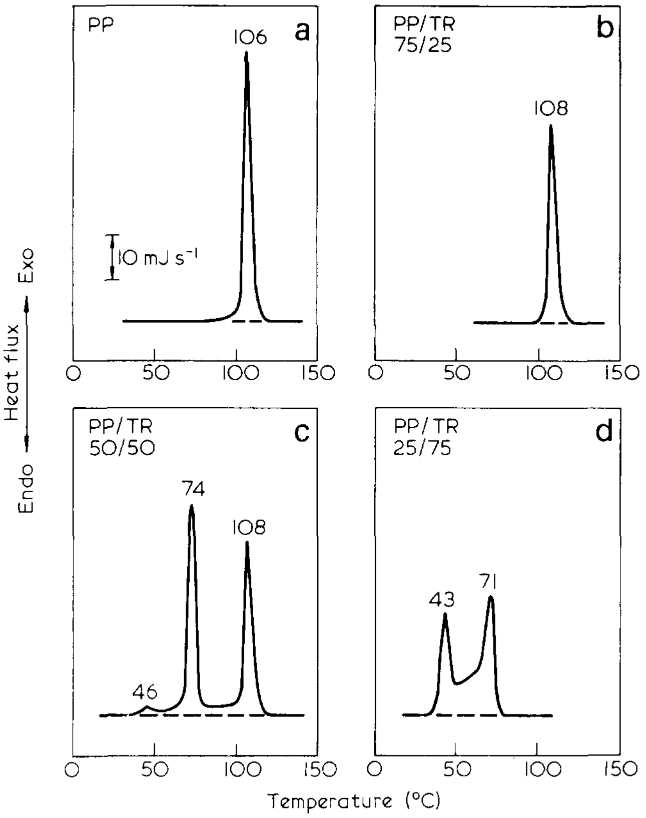

Figure 1 Typical d.s.c. crystallization exotherms of PP and PP/TR blends of different composition. Bottom thermograms (c) and (d) were run at a sensitivity 4 times (c) and 8 times (d) higher than the top thermograms (a) and (b)

RESULTS

Figure 1 shows typical d.s.c. thermograms of PP and of PP/TR blends of different blend composition obtained during cooling from the molten state. From these thermograms it follows that pure PP crystallizes at a temperature of 106°C (peak temperature) when a cooling rate of 20°C/min is being used. The 75/25 PP/TR blend also exhibits a single crystallization exotherm but crystallizes at a slightly higher temperature. Similar small shifts of the crystallization peak to higher temperatures were reported by Karger-Kocsis *et al.*[6] for 95/5 and 90/10 PP/TR blends also based on CARIFLEX TR-1102. It was suggested in their work that the TR block copolymer acts as a weak nucleating agent in such blend systems. What is much more striking, however, is the completely different crystallization behaviour of TR-rich PP/TR blends. The 50/50 PP/TR blend even shows three distinct crystallization exotherms instead of a single one; the normal crystallization exotherm at 108°C, a second at 74°C and a very small one at 46°C. In the 25/75 PP/TR blend the crystallization exotherm at 108°C is no longer present but the exotherm at 43°C is now of considerable size.

The crystallization exotherm observed at 74°C is attributed to crystallization by homogeneous nucleation rather than by heterogeneous nucleation. In TR-rich PP/TR blends, homogeneous nucleation can occur when polypropylene forms the dispersed phase and the number of isolated PP domains is greater than the number of heterogeneous nuclei, i.e. when some of the domains present are free from active heterogeneities. Upon cooling, such PP domains do not crystallize at the normal crystallization temperature of about 106°C, but at the (lower) temperature region where homogeneous nucleation is active.

Electron micrographs and d.s.c. thermograms on several PP/TR blends have confirmed that the crystallization exotherm at 74°C is present only when PP forms the dispersed phase and that blends with PP present as the continuous phase always exhibit a normal crystallization behaviour. *Figure 2* shows, as an example, the electron micrographs of the 50/50 and 25/75 PP/TR blends of this study.

Analogous crystallization behaviour was reported by Hay and co-workers for the blend system high density polyethylene/polystyrene[7] and for phase-separated ethylene block copolymers[8] and by O'Malley *et al.*[9] for phase-separated ethylene oxide/styrene block copolymers. Homogeneous nucleation mechanisms were proposed for the observed low temperature polyethylene (PE) and polyethylene oxide (PEO) crystallization exotherms. Close analogy also exists with the results of droplet crystallization experiments of polymers in inert liquid media[10-13]. With optical microscopy techniques it was found that fine droplets of PE[10], PEO[11] and also PP[12,13] free from heterogeneities crystallized at much higher degrees of supercooling than the corresponding bulk polymers. Binsbergen[12], for instance, reported that fine PP droplets crystallized between 75° and 70°C, the same temperature range as observed for the crystallization exotherm in this work. Similarly, Burns and Turnbull[13] have reported that small PP droplets (diameter <6 μm) crystallized in the temperature range 82.5 to 76.5°C, while the larger droplets (diameter about 20 μm) crystallized at around 105°C. The very high degrees of supercooling observed for small polymer droplets were also interpreted in terms of homogeneous nucleation by the researchers in this field.

As to the crystallization exotherm at about 45°C, additional work was carried out by one of the authors to elucidate its origin; results of this later work will be reported in a separate article[14].

Some other crystallization and melting characteristics of the blends are summarized in *Table 1*. It can be seen that the values for the total heat of crystallization are lower than expected on the basis of blend composition, especially for the blend having the lowest PP content. The same effect is found for the heat of fusion, albeit to a lesser extent. The melting temperatures of the blends have been found to be independent of blend composition and 2°C lower than that of the bulk PP.

DISCUSSION

From the preceding results it becomes clear that the crystallization behaviour might provide useful information about the type and degree of dispersion of PP/TR blends. Both the presence and intensity of the crystallization exotherms at 108° and 75°C can be utilized in this respect.

The type of dispersion can easily be determined by inspecting the d.s.c. thermograms of the blends for the presence of crystallization exotherms at 108° and 75°C. When only one single crystallization exotherm at 108°C is present in the thermogram, then PP most probably forms the continuous phase. Another possibility is that PP

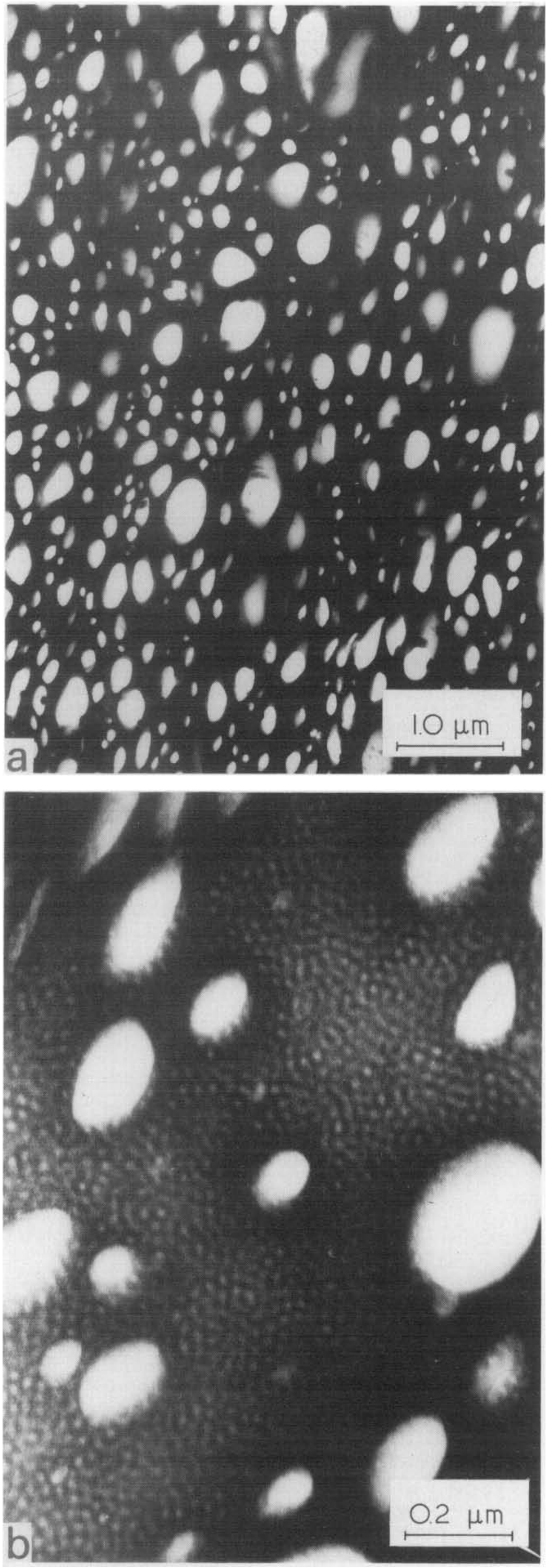

Figure 2 Electron micrographs of PP/TR blends (a) PP/TR 50/50, (b) PP/TR 25/75 (sections were cut perpendicular to extrusion direction)

Table 1 Crystallization and melting characteristics of PP/TR blends

PP content of blend, (%w)	H_c* (J/g)	H_m** (J/g)	T_m*** (°C)
25	15.3	19.7	163
50	40.0	45.2	163
75	73.3	71.1	163
100	98.5	96.0	165

* Total heat of crystallization, expressed in joules per gram of total sample
** Heat of fusion, same units as above
*** Melting temperature (d.s.c. peak value)

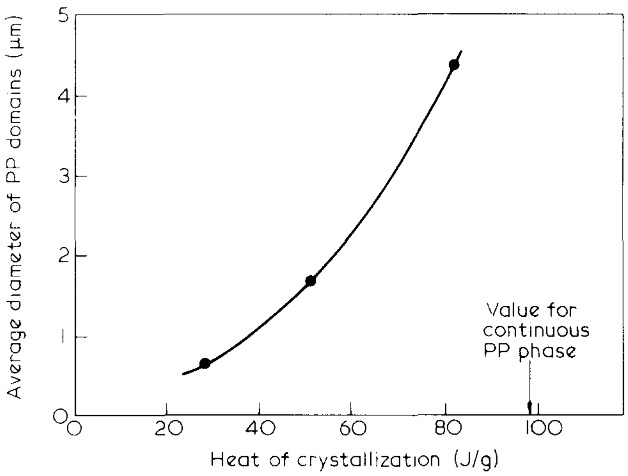

Figure 3 Dependence of the average diameter of PP domains on the intensity of the PP crystallization exotherm at 108°C (in joules per gram PP)

forms a semi-continuous phase or even the dispersed phase with very large PP domains (of size say >10 μm). Such coarse PP dispersions, however, do not usually occur in practice. When the low temperature crystallization exotherm at 75°C is present in a thermogram, alone or together with other crystallization exotherms, then PP forms the dispersed phase.

When PP forms the dispersed phase, the degree of dispersion can be derived from the intensities of the crystallization exotherms. In such blends, PP domains that are free from heterogeneities give rise to the exotherm at 75°C (homogeneous nucleation) and those with heterogeneities present to the exotherm at 108°C (heterogeneous nucleation). As the number of PP domains that are free from heterogeneities increases as the size of the domains decreases, the intensity of the crystallization exotherm at 75°C will increase and that of the exotherm at 108°C will decrease. As the dispersions become very fine (of size say <0.2 μm; see the 25/75 blend in *Figure 2b*), the number of isolated PP domains ultimately becomes much greater than the number of heterogeneous nuclei and thus the crystallization exotherm at 108°C will even disappear.

Thus, for a relatively wide range of particle sizes (say between 0.2 and 10 μm), the intensity of one of the two crystallization exotherms (expressed in joules per gram PP) or its intensity ratio can be used as a measure of the size of the PP domains. As an example, *Figure 3* shows the relationship between the average diameter of the domains and the intensity of the crystallization exotherm at 108°C for PP/TR blends. The average diameter values were obtained from the electron micrographs of the blends using the Quantimet image analyser. Relationships like those presented in *Figure 3* can also be produced for blends of unknown composition, but in that case the intensity ratio has to be used rather than the intensities themselves.

When the present d.s.c. method is used for determining the PP particle size, some limitations should be borne in mind, however. The method, for instance, is not able to differentiate between different particle sizes in the case of very fine and very coarse PP dispersions. Furthermore, erroneous results may be obtained when the blends have quite different particle size distributions or when the polypropylenes used in the blending studies have different nucleation densities.

Despite these limitations, d.s.c. is a rapid and sensitive method for assessing the type and degree of dispersion in PP/TR blends.

CONCLUSIONS

The multiple crystallization behaviour of PP/TR blends as observed by differential scanning calorimetry can be exploited to provide useful information about the morphology of the blends. The type of dispersion can be established by inspecting the d.s.c. thermograms for the presence of the crystallization exotherms at 108° and 75°C. It is very easy to distinguish polymer blends in which PP forms the continuous phase from those in which it forms the dispersed phase. In the latter case, the degree of dispersion (the PP particle size) can be assessed from the intensities of the crystallization exotherms at 108° and 75°C.

This approach is not necessarily restricted to PP/TR blend systems, but can also be applied to other blend systems; the only proviso is that one of the components of the blend should be a crystalline polymer.

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REFERENCES

1 Paul, D. R. and Newman, S. Polymer Blends, Vol. I, Academic Press, New York, 1978

2 Imken, R. L., Paul, D. R. and Barlow, J. W. *Polym. Eng. Sci.* 1976, **16**, 593

3 Parasiewicz, W. and Gaczynski, R. *Int. Polym. Sci. Technol.* 1979, **6**, 95

4 Ghijsels, A. *Rubber Chem. Technol.* 1977, **50**, 278

5 Kato, K. *Polym. Eng. Sci.* 1967, **7**, 38

6 Karger-Kocsis, J., Kallo, A., Szafner, A. and Bodor, G. *Polymer* 1979, **20**, 37

7 Aref-Azar, A., Hay, J. N., Marsden, B. J. and Walker, N. *J. Polym. Sci. Polym. Phys. Edn.* 1980, **18**, 637

8 Hay, J. N. and Wiles, M. to be published

9 O'Malley, J. J., Crystal, R. G. and Erhardt, P. F. 'Block Copolymers', (Ed. S. L. Aggarwal) Plenum Press, New York, 1970

10 Cormia, R. L., Price, F. P. and Turnbull, D. *J. Chem. Phys.* 1962, **37**, 1333

11 Price, F. P. Abstracts of IUPAC Symposium on Macromolecules, Wiesbaden, 1959

12 Binsbergen, F. L. 'Nucleation in the Crystallisation of Polyolefins', Thesis, Groningen, 1969

13 Burns, J. R. and Turnbull, D. *J. Appl. Phys.* 1966, **37**, 4021

14 Yip, C. W. to be published