Crystallization Behavior and Spherulite Growth Rate of Isotactic Polypropylene in Isotactic Polypropylene/Natural Rubber Based Thermoplastic Elastomers

Aju Joseph,[1] T. Koch,[2] S. Seidler,[2] S. Thomas,[3] K. Joseph[1]

[1]Department of Chemistry, St. Berchmans College, Changanacherry, Kerala 686101, India
[2]Institute of Material Science and Technology, Vienna University of Technology, Favoritenstrasse 9-11, Vienna A-1040, Austria
[3]School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala 686560, India

ABSTRACT: The melting and crystallization behavior of isotactic polypropylene/natural rubber (PP/NR) based thermoplastic elastomers (TPEs) were investigated using differential scanning calorimetry. The samples were scanned at a heating rate of 10°C/min under nitrogen atmosphere. The effects of blend ratio on the melting and crystallization characteristics of the blends were analyzed. Normalized crystallinity is unchanged by the addition of small amount of NR, but as the amount of rubber increases crystallinity increased for the 30/70 NR/PP and lowered for the 50/50 NR/PP blend system. Morphology of the blend was analyzed using scanning electron microscopy (SEM). Blend ratio showed a pronounced influence on the phase morphology of the NR/PP TPEs. As the amount of NR increases more than 50 wt % the system changes from dispersed to cocontinuous structure. Hot-stage polarizing optical microscopy (POM) was used to study the radial growth of spherulite as a function of blend ratio, cooling rate, and crystallization temperature. Spherulite growth rate is marginally influenced by the rubber inclusions. The spherulite morphology observed under polarized optical microscopy is influenced by the blend morphology. It was found that for the cocontinuous 50/50 blend system, spherulites are much different from the usual appearance under polarized light. Attempts have been made to correlate the crystallization behavior with the morphology of the blend. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1714–1721, 2008

Key words: blends; morphology; crystallization; spherulites

INTRODUCTION

The properties of a polymer can be extensively modified by blending with another polymer. The properties of the resulting polymer blend depend not only on the composition and processing condition but also on the physical state of each component at the temperature of application of the blend. Most of the theoretical and experimental investigation of the properties of polymer blends concern mainly on the systems containing amorphous component.[1]

Thermoplastic natural rubber (TPNR) could be produced by blending thermoplastics with natural rubber (NR).[2,3] Polypropylene (PP) is considered to be the best choice for blending with NR for the production of high performance TPNR.[4,5] At the molecular level, NR and PP are incompatible which will give rise to a two-phase blend, but their solubility parameters are fairly similar and thus a stable dispersion of NR particles in a PP matrix or vice versa is possible.[6,7] PP/NR thermoplastic blend compositions can be varied to give materials of different mechanical properties ranging from a soft elastomer to a semirigid plastic. The soft grade TPNR is produced by blends with compositions richer in rubber while the harder grades contain up to about 30% NR. Tailoring a TPNR to meet the requirements of certain mechanical and physical specifications can be done by optimizing the blend composition.[8] Rubber-toughened PP is a heterophasic system in which discrete elastomer particles are dispersed in a PP matrix. The rubbery phase enhances the impact resistance by initiating highly dissipative deformation mechanisms.[9–12]

In the case of blends of amorphous/semicrystalline polymers, the mechanical properties of the system are strongly related to the properties of the crystalline phase including the overall crystallinity, crystalline morphology, and the size of the crystallites and their aggregate such as spherulites. Although a large number of articles have been published on the morphology, mechanics, and rheology of thermoplastic elastomers (TPEs) based on NR/PP blends,[13–16]

Correspondence to: K. Joseph (kuruvillajoseph@sancharnet.in) or (kuruvillajoseph@sify.com).

TABLE I
Melting Behavior of the PP/NR Blend

Blend ratio PP/NR	T_m onset (°C)	T_m endset (°C)	T_m (°C)	ΔH_f (J/g)	X_c (%)
100/0	136.3	173.1	158.7	99.3	47.51
98/02	135.8	172.7	159.0	88.3	43.10
95/05	135.8	171.6	159.8	90.5	45.61
90/10	133.9	171.8	159.4	87.3	46.41
80/20	133.9	172.2	159.0	78.9	47.18
70/30	134.3	172.6	159.3	76.4	52.21
50/50	135.3	172.7	158.0	44.0	42.1

no detailed investigations have been performed on the crystallization behavior of these blends. Additionally, in practical processing, crystallization usually proceeds under either isothermal or nonisothermal conditions. Therefore, it is important to investigate both the isothermal and nonisothermal crystallization of these blends. In view of this, a detailed study has been undertaken to analyze the influence of blend ratio, crystallization temperature, and cooling rate on the crystallization behavior of PP/NR blends.

EXPERIMENTAL

Materials

Isotactic polypropylene, (PP, Koylene M3060) having melt flow index (MFI) of 3 g/10 min was kindly supplied by Indian Petro Chemical, Vadodara, India. Natural rubber (NR, ISNR-5) was supplied by Rubber Research Institute of India, Kottayam, India.

Blend preparation

PP/NBR blends were prepared by melt mixing PP with NR in a Rheocord at 180°C. The rotor speed was optimized as 60 rpm. In the case of the uncompatibilized blend, PP was first melted for 3 min followed by the addition of NR and the mixing continued for another 6 min.

Scanning electron microscopy

The morphology of the blends was analyzed by electron microscopy, using a scanning electron microscopy (SEM) Philips microscope on cryogenically fractured surfaces of the samples. The SEM samples were prepared as follows: the compression molded blends were fractured in liquid nitrogen, the fractured surfaces were cryotomed using a microtome to achieve smother surface, and then the NR phase was extracted in benzene at 50°C for 12 h. After etching, the samples were dried in a vacuum oven at 70°C for 12 h and were coated with gold using sputter coater.

Differential scanning calorimetry analysis

A TA DSC-3 apparatus was used to determine the melting and crystallization behavior of PP and PP/NR blends (Table I). The following conditions were applied for the study of the melting and crystallization behavior of PP/NR blends.

Stage 1: Heating of the sample in the calorimeter at a rate of 10°C/min from −20 to 220°C.

Stage 2: Isothermal annealing at 220°C for 5 min; this was done to remove any crystalline nuclei if present.

Stage 3: Cooling of the sample in the calorimeter to −20°C at the rate of 10°C/min.

Stage 4: Heating the sample in the calorimeter again to 220°C at a rate of 10°C/min.

From the heating and cooling curves the melting and crystallization parameters were estimated. These include:

(a) Onset of melting (Tm$_{onset}$)
(b) Melting point (T_m)
(c) Onset of crystallization (Tc$_{onset}$)
(d) Crystallization temparature (T_c)
(e) Endset of crystallization (Tc$_{endset}$)
(f) Normalized value of heat of fusion (ΔH_f)
(g) Normalized value of heat of crystallization (ΔH_c)
(h) Percentage crystallinity (X_c)

The percentage crystallinity was calculated using the expression,

$$\% \, \text{Crystallinity} = \Delta H_f \times \frac{100}{\Delta H_f^0} \qquad (1)$$

Here ΔH_f was the heat of fusion of the sample and ΔH_f^0 is that of 100% pure crystalline PP, which is taken as 209 J/g.[16]

Hot stage-polarizing optical microscopy

The morphology and the isothermal spherulite growth rate were studied by using a Zeiss Axioscope polarizing optical microscope, fitted with a Linkam
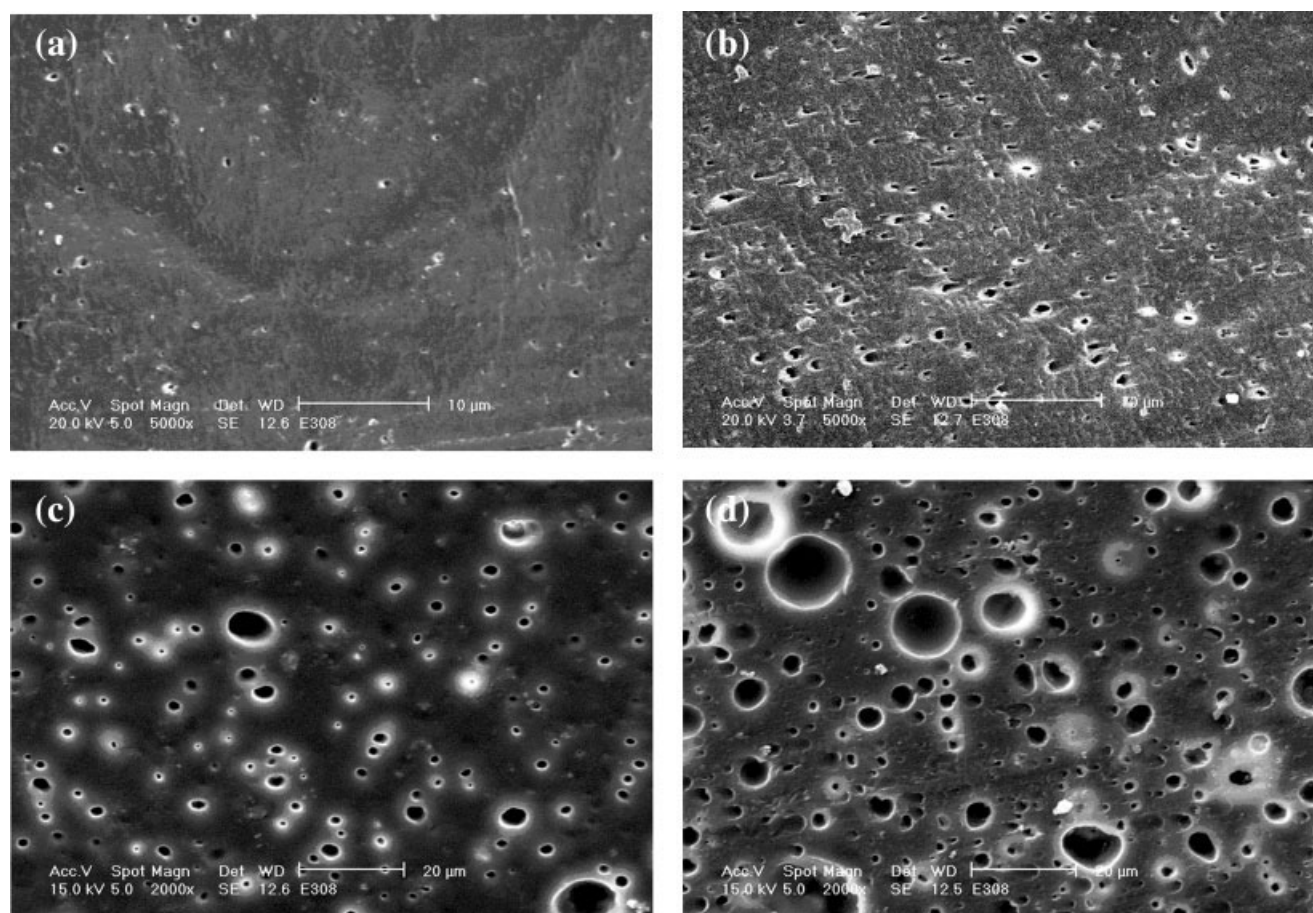
Figure 1 (a–e) SEM micrographs showing how the phase morphology is changing with blend ratio, where (a) NR/PP 02/98, (b) NR/PP 05/95, (c) NR/PP 20/80, (d) NR/PP 30/70, and (e) NR/PP 50/50.

hot stage. The radial growth rate, G (dr/dt where r is the radius of the spherulites and t the time), was calculated by measuring the size of iPP spherulites during the isothermal crystallization process. The standard procedure adopted was given later. Thin films having a thickness of 30 μm were trimmed using a Leica microtome. Then, the thin film was sandwiched between two microscope slides, heated at 220°C for 10 min, then cooled to T_c, and allowed to crystallize. The entire procedure was done in flowing dry nitrogen atmosphere. The radial growth rate of a spherulite under careful observation using polarizing optical microscope was finally monitored during crystallization by taking photomicrographs automatically at appropriate intervals of time with cross-polarized light. From the plots of r against the time, G was calculated as the slope of the resulting straight lines.

RESULTS AND DISCUSSION

Influence of the blend ratio on the morphology

The blend ratio has a pronounced impact on the morphology development during melt mixing. Scan-

ning electron micrographs of the cryogenically cut and selectively extracted (NR phase of the blend was extracted using benzene) surfaces of the blend samples are given in Figure 1(a–e), where the holes represent the NR phase which has been removed by the solvent. The SEM of NR/PP 02/98 blend given in Figure 1 shows that submicron NR domains are dispersed in the continuous PP matrix. SEM micrograph of NR/PP 10/90 blend system is shown in Figure 1(b). It is clear from the Figure 1(b) that as the amount of NR increases, the number of NR domains in the PP matrix also increased. Both the blend systems showed a relatively uniform size distribution of the NR domains. The change in the morphology by further increase in the NR content is shown in the Figure 1(c), where this SEM picture corresponds to a NR/PP 20/80 blend system. It is quite interesting to see that NR/PP 20/80 blend showed a dispersed morphology with a broad distribution of domain size. Also, the number of domains in unit volume is much higher than those of the NR/PP blend with 02/98 and 10/90 blend ratios. It is clear from the Figure 1(d) that, as the amount of NR in the blend reaches 30 wt %, size of the NR
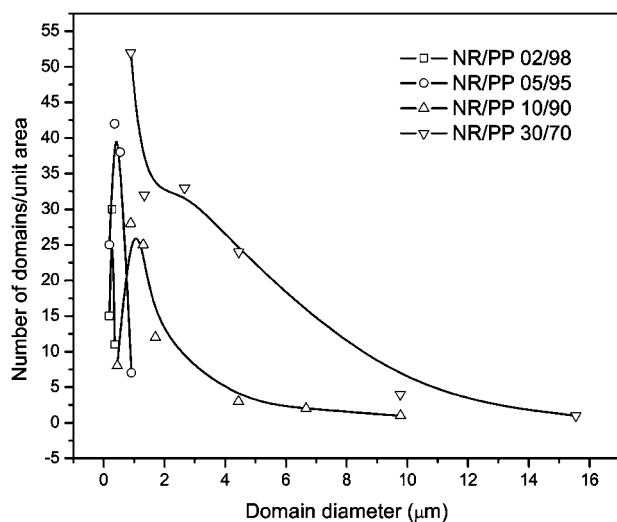
Figure 2 Influence of blend ratio on the domain size distribution of NR/PP blends.

Figure 3 Effect of blend ratio on the number average, weight average, and volume average diameters of NR/PP blend.

domains further increases with a broader size distribution. The increase in size of the domains and broadness of the distribution is associated with coalescence. Totally different phase morphology is shown by 50/50 NR/PP blend as given in Figure 1(e). In this case both NR and PP exist as cocontinuous interpenetrating phases. The domain size distribution of NR/PP blend is shown in Figure 2. It is clear from the Figure 2 that lower amount of NR in the blend showed a narrow domain size distribution. NR/PP blend with 02/98 and 05/95 show a narrow distribution curves and hence the domains having almost uniform domain size. As the amount of NR in the blend increases, the domain distribution becomes broader. NR/PP 30/70 blend shows a broader size distribution.

The domain diameter Dn, Dv, and Dw as a function of composition is shown in Figure 3. From the Figure 3, it is clear that the amount of NR having a profound influence on the Dn, Dv, and Dw values. All the three diameters of the NR calculated from the SEM [Fig. 1(a–d)] showed a increase with the NR content.

Melting behavior of the TPEs: Influence of blend ratio

Influence of blend ratio on the melting behavior of TPEs is shown in the Figure 4. Processing history could influence the melting behavior of the blends; therefore second heating endotherm is selected for the evaluation of the melting behavior. It is interesting to note that T_m onset, T_m endset, and T_m of the TPEs were unaffected by the presence of NR. This proves that these systems are incompatible in the molecular level. The single melting peak shows that there is no reorganization during melting.[17] Normal-
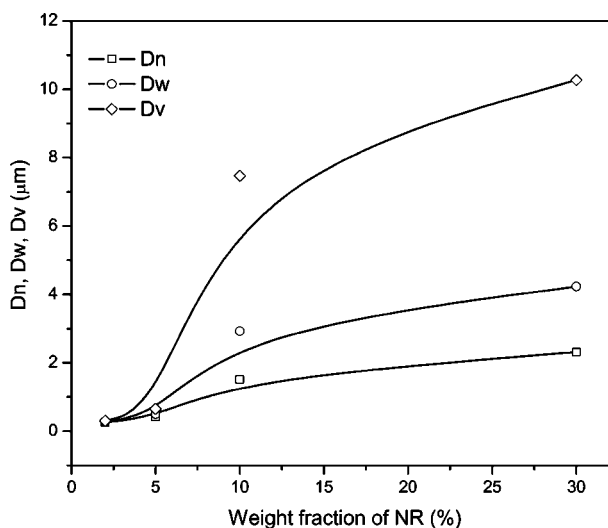
ized crystallinity values calculated from the enthalpy of crystallization showed that in the presence of lower amount of NR (2% of NR), X_c values showed a 4.4% decrease from the value shown by the neat PP. It may be due to the presence of submicron NR domains which could be rejected or engulfed from the growing crystal front and this will reduce the final crystallinity. However, the crystallinity is unaffected on further increase of rubber content upto 20%. But 70/30 wt % PP/NR TPEs showed an increase in the normalized X_c values. The reasons for the higher X_c values shown by this system needs further investigations. However, we believe that this could be due to the nucleation effect from the NR phase. NR contains lower molecular mass substances like proteins and other impurities; this could be
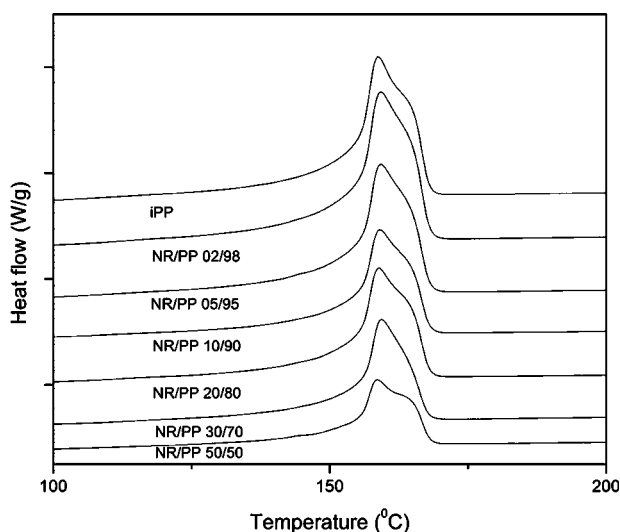

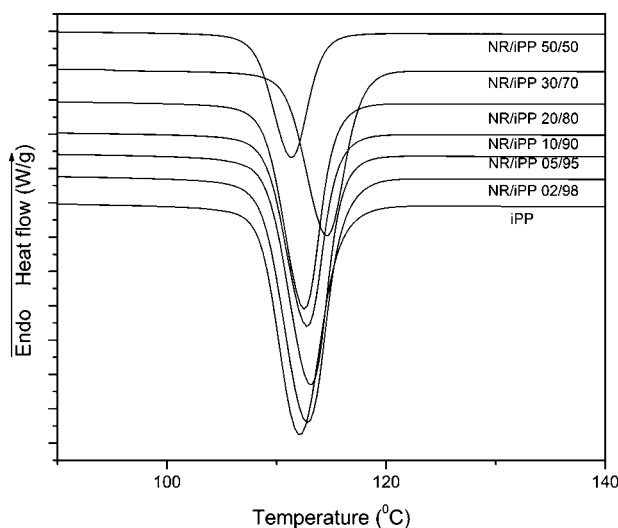**Figure 4** Melting behavior of PP/NR blends.

Figure 5 Crystallization behavior of PP/NR blends.

migrated to the PP phase during the melt mixing and can enhance the crystallization process, resulting in the higher amount of crystallinity. Since NR/PP 30/70 has a large number of NR domains distributed in the PP matrix, the migration is much more efficient in this blend than the other systems. While the NR content increases to 50 wt % the phase morphology changes from dispersed to cocontinuous. This cocontinuous morphology will slow down the crystal growth front and ultimately, normalized X_c value showed a lower crystallinity.

Influence of blend ratio on the crystallization behavior of NR/PP

Effect of NR content on the crystallization behavior of PP is given in Figure 5. It is clear from the Figure 5 that T_c onset of PP is influenced by the blending with NR. The values calculated from the DSC exotherms are shown in Table II. The values of T_c onset are unaffected by the addition of NR except 50/50 blend where onset temperature showed a decrease indicating hindrance by the continuous rubber phase. Interestingly, T_c values of PP were unaffected by the addition of rubber except 30/70 NR/PP which showed an increase possibly by the nucleating effect of impurities form the rubber phase. The T_c endset are marginally increased for 20/80 and 30/70. For other blend systems the values are unaffected.

Influence of blend ratio on the spherulite growth rate

Optical micrographs of spherulites grown at 136°C at a cooling rate of 10°C/min in neat PP and NR/PP blend were shown in Figure 6(a–g). All micrographs were taken under reflection mode with 100× magni-

fication. The crystallization of PP, which amounts to a transition from a fully amorphous to an amorphous/crystalline state, proceeds through the free growth of the spherulites from a homogeneous melt. All the spherulites display the characteristic ''Maltese Cross'' extinction pattern. The ''Maltese Cross'' arises from the coincidence of the principal axis of the crystal with the extinction direction of the polarizer or analyzer.[17]

The image clearly taken by optical microscopy [Fig. 6(b–e)] supports the observation of formation of well-organized spherulites by the presence of lower amount of NR, and allows an even more accurate determination of the maltase cross in the spherulite.[17] It is clear from the micrographs [Fig. 6(b–f)] that lower amount of NR does not change the texture of the PP spherulite.

Spherulite developed for the 50/50 NR/PP blend shows a difference in the spherulite morphology, which is given in Figure 6(g). NR cocontinuous phase totally affects the spherulite morphology under polarized light, especially for the NR/PP 50/50 blend systems. Maltase cross is totally vanished for the spherulite grown in the NR/PP 50/50 blend system.

Crystallization of PP could be followed by monitoring the spherulite growth rate. In this method, the radial growth rate of the spherulite was determined by measuring the spherulite radius ''R'' as a function of time during isothermal crystallization in the hotstage of a polarizing microscope. From the Figure 7, radial growth of PP spherulite in NR/PP 10/90 blend at T_c 124°C is given (the melt was brought to the crystallization temperature of 124°C at a cooling rate of 10°C/min). Four independent measurements from the different samples were shown in Figure 7. From this measurement it is clear that the growth rate measurements were reproducible. Also it is well understood that the spherulite growth of PP in the blend is linear.

For the crystallization of PP in the 10/90 blend crystallized at 124°C, ''R'' was found to increase linearly with time up to the point of impingement, indicating a constant growth rate throughout the crystallization process (Fig. 7). Similar observations were

TABLE II
Crystallization Behavior of the Blend

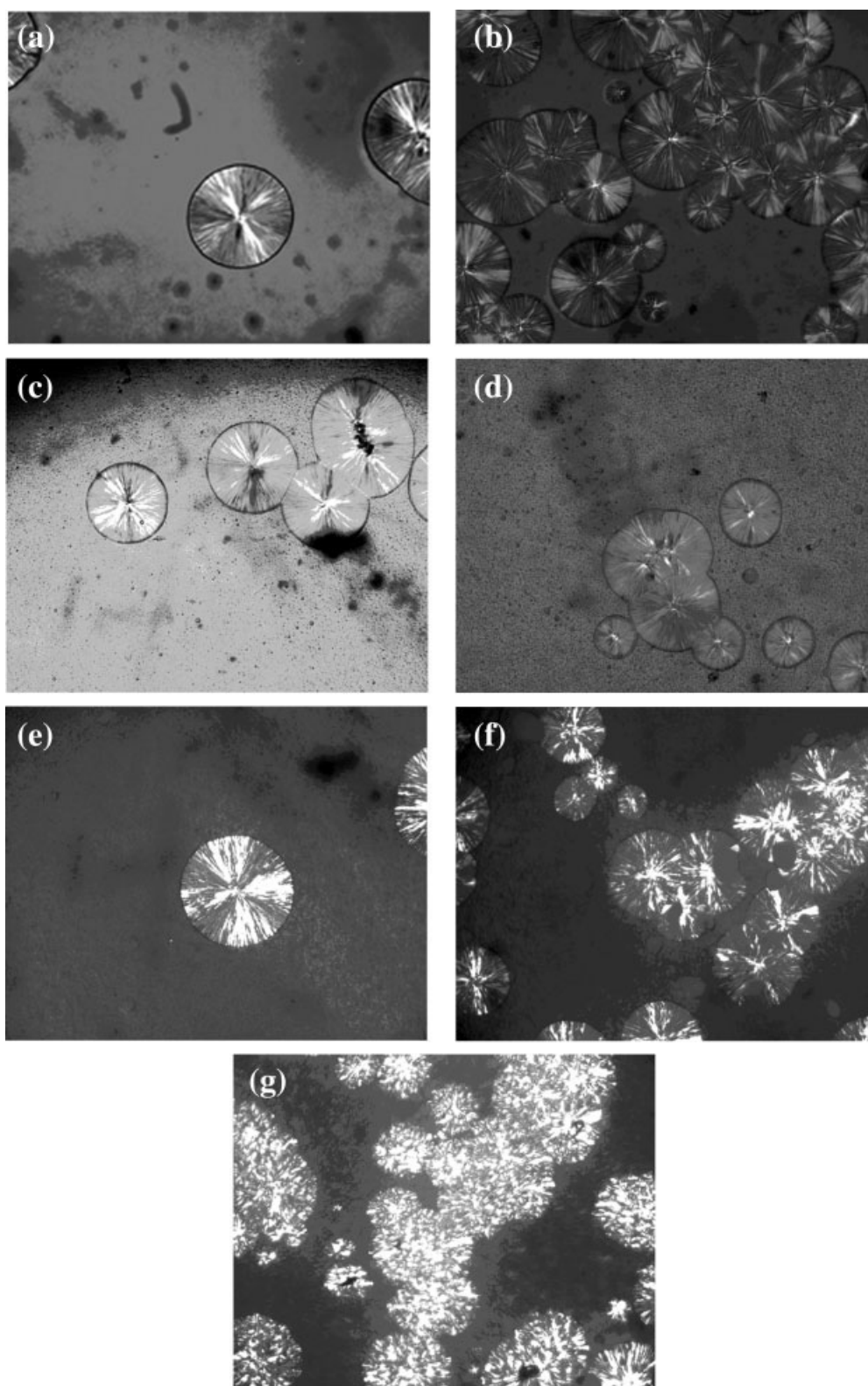| Blend ratio PP/NR	T_c endset (°C)	T_c onset (°C)	T_c (°C)	ΔH_c (J/g)
100/0	92.4	123.4	112	99
98/02	93	124.5	112.8	88
95/05	93.9	123.3	113.2	99
90/10	94.2	122.3	112.5	97
80/20	97.5	121	114.7	99
70/30	107	122	114	99
50/50	98.2	118.7	111.2	97

Figure 6 (a–g) Micrographs showing spherulite developed in the iPP and its different NR/PP blend at 136°C at a cooling rate of 10°C/min. All micrographs were taken under reflection mode with 100 times magnification where (a) iPP 6, (b) NR/PP 02/98, (c) NR/PP 05/95, (d) NR/PP 10/90, (e) NR/PP 20/80, (f) NR/PP 30/70, and (g) NR/PP 50/50.

found for other TPEs too. The linearity of ''R'' implies that NR domains that are rejected from the growing PP crystal front do not accumulate at the spherulite boundary, but rather become trapped within the interlamellar or interfibrillar regions of the growing spherulite.[18] It should be mentioned
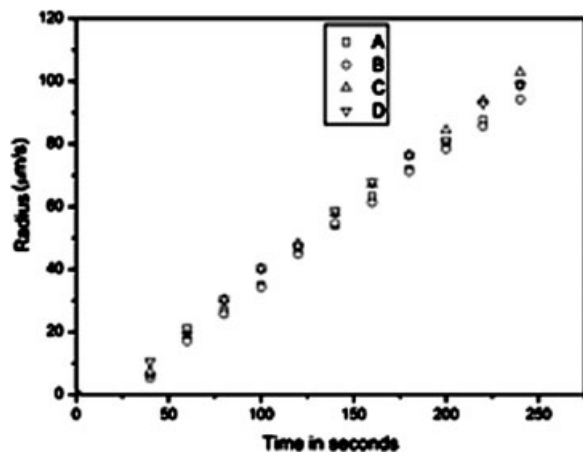
Figure 7 Radial growth of PP spherulite in NR/PP 10/90 blend at T_c 124°C (the melt was brought to the crystallization temp at cooling rate of 10°/min).

Figure 9 The relation between G and blend ratio at different T_cs.

that the crystallinity within the spherulite remains constant during the isothermal crystallization if there is no change in the concentration of crystallizable elements at the crystal growth front.[19,20]

Impact of T_c on the "G" value of NR/PP blend with varying NR content is given in Figure 8. And from the Figure 8, it is seen that as the T_c showing a depressing effect on the "G" as the T_c increases. This may be due to the fact that at higher T_c, the activation energy for the nuclei for the crystallization is higher. Therefore, at higher T_c the growth rate will be slow. However, when the T_c becomes very high the growth rate shows a tendency for leveling off since the molecules have high degree of mobility.

Influence of the blend ratio on the "G" at different T_c is given in Figure 9. At lower T_c (less than 128°C),

the spherulite growth rate decreases with very small amount of rubber phase (10 wt % of rubber followed by a leveling off). This could be due to the rejection of the extremely small rubber particle by the growing crystal front. However, at higher T_c (132–136°C), the "G" is unaffected by composition because of the extremely slow growth rate on account of the high molecular mobility.

Influence of cooling rate on the spherulite growth rate of PP and its TPEs

Figure 10 shows the influence of spherulite growth rate as a function of T_c at different cooling rate (10 and 50°C) of neat PP. It can be seen that cooling rate has no effect on growth rate. It is seen that "G"
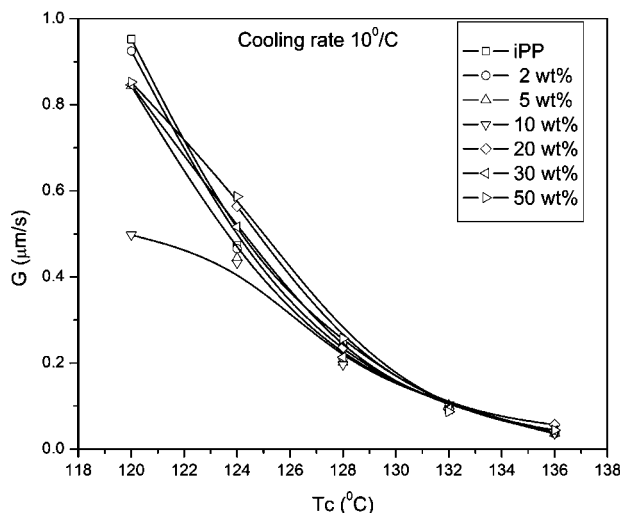

Figure 8 The relation between T_c and spherulite growth rate of PP having different weight percentage of NR at cooling rate of 10°C/min.

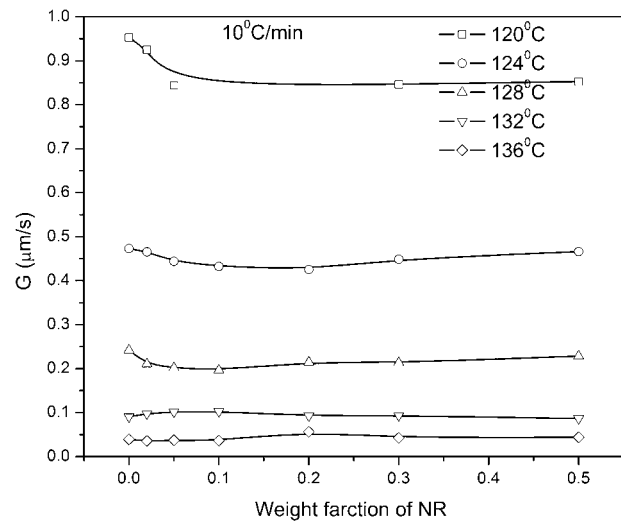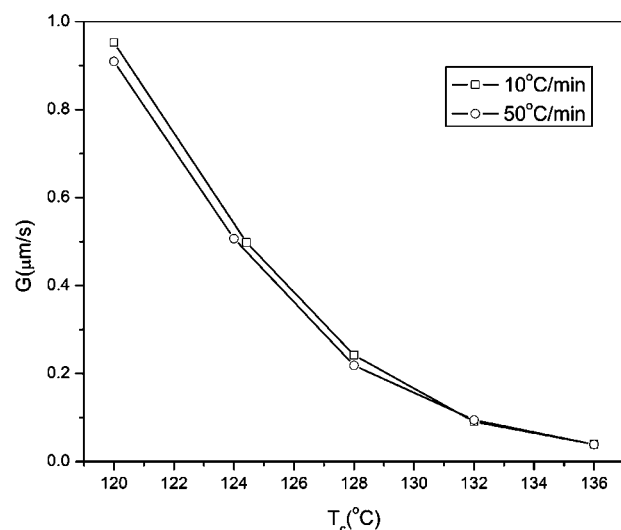**Figure 10** The influence of cooling rate on the spherulite growth rate of neat PP at different T_c.

value shows a analogous trend as that of the result observed with 10°C/min cooling rate.

CONCLUSIONS

The relationship between the phase morphology and crystallization behavior of TPEs made from NR/PP blends has been analyzed. The morphology of the blend showed at lower content of NR phase, the NR is dispersed in the continuous PP phase. The NR/PP 50/50 blend showed a cocontinuous morphology. At very low concentration of NR (2% wt/wt), the normalized crystallinity values showed a decrease in account of the rejection of the very small NR domains by the growing crystallizing front. A 50/50 composition also showed a decreased crystallinity value. The T_c values of the blends are unaltered by the composition except the 50/50 NR/PP system where the morphology is cocontinuous. All the blend showed linear spherulite growth rate decreased with increasing T_c followed by a leveling off. The growth rates were unaltered by the blend ratio at high crystallization temperature (132 and 136°C). Interestingly, at very low concentration NR phase the growth rate showed a decrease at lower crystallization temperature (120, 124, and 128°C). This could be due to the rejection of the rubber phase at the crystal front.

The growth rates were unaltered by the cooling rate. Polarized optical microscopy picture showed that when the rubber phase becomes continuous, highly imperfect spherulites were developed. This could be associated with the hindrance from the rubber phase.

References

1. Paul, D. R.; Newman, S., Eds. Polymer Blends; Academic Press: New York, 1978.
2. Coran, A. Y.; Patel, R. Rubber Chem Technol 1981, 14, 141.
3. Tinker, A. J. Plast Rubber Int 1986, 11, 24.
4. Elliott, D. J.; Tinker, A. J. In Proceedings of International Rubber Conference 1985, Vol. II; Rajarao, J. C.; Amin, L. L., Eds.; RRIM: Kuala Lumpur, Malaysia, 1986.
5. Tinker, A. J.; Icenogle, R. D.; Whittle, I. Rubber World 1989, 199, 25.
6. Paul, D. R. In Polymer Blends and Mixtures; Walsh, D. P.; Higgins, J. S.; Maconnachie, A., Eds.; Martinus Nijhoff: Dordrecht, 1985; p 1.
7. Pyne, J. R. Consice Encyclopedia of Polymer Science and Engineering; Wiley Interscience: New York, 1990; p 914.
8. Perkins, W. G. Polym Eng Sci 1999, 39, 2445.
9. Walker, I.; Collyer, A. A. In Rubber Toughened Engineering Plastics; Collyer, A. A., Ed.; Chapman & Hall: London, 1994; Chapter 29, p 161.
10. Bucknall, C. B.; Gaymans, R. J. In Polymer Blends, Vol. 2; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, 2000; p 177.
11. Christelle, G. Adv Polym Sci 2005, 188, 43.
12. Nakason, C.; Saiwari, S.; Kaesaman, A. Polym Test 2006, 25, 413.
13. Nakason, C.; Wannavilai, P.; Kaesaman, A. Polym Test 2006, 25, 34.
14. Azman, H.; Mat, U. W.; Ching, Y. C. Polym Test 2003, 22, 28.
15. Ismail, H.; Suryadiansyah, R. Polym Test 2002, 21, 389.
16. Braun, D.; Fischer, M.; Hellmannt, G. P. Polymer 1996, 37, 3871.
17. Androsch, R. Eur Polym J 2007, 43, 93.
18. Penning, J. P.; Manley, R. S. J. Macromolecules 1996, 29, 84.
19. Lee, J. K.; Choi, M. J.; Im, J. E.; Hwang, D. J.; Lee, K. H. Polymer, to appear.
20. Wang, Z. G.; Phillips, R. A.; Hsiao, B. S. J Polym Sci Part B: Polym Phys 2000, 38, 2580.