

Isothermal Crystallization Behavior and Properties of Polypropylene/EPR Blends Nucleated with Sodium Benzoate

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ABSTRACT: The effect of sodium benzoate on the isothermal crystallization behavior of isotactic polypropylene (iPP)/ethylene-propylene rubber (EPR) blends was investigated using differential scanning calorimetry. Dynamic mechanical and physical properties of the iPP/EPR blends nucleated with sodium benzoate were also measured. It was found that the crystallization behavior and physical properties such as heat deflection temperature (HDT), flexural modulus, and impact strength were strongly affected by the competition between the nucleating effect of EPR attributed to its partial compatibility with iPP and the simple addition of the amorphous component, as well as the nucleating effect of sodium benzoate. High impact strength was achieved by addition of EPR and sodium benzoate to iPP. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 201–211, 2002

Key words: crystallization behavior; polypropylene; EPR; sodium benzoate; nucleating agent

INTRODUCTION

As a general purpose resin, isotactic polypropylene (iPP) has various excellent properties such as mechanical rigidity, thermal and chemical resistance, and so forth.¹ However, its great disadvantage is poor impact strength at low temperature.^{2–4} One method to solve this problem is to blend iPP with a rubber, such as ethylene-propylene rubber (EPR) or ethylene-propylene-diene terpolymer (EPDM).^{5–7}

Given that the trend in current processing techniques is toward shorter cycle times and therefore higher cooling rates, the addition of an external nucleating agent to iPP/EPR or iPP/EPDM blends as well as iPP enables fast cycle times in iPP processing.^{8,9} Although a variety of nucleating agents are known for iPP, dibenzylidene sorbitol (DBS) has been found to be useful thus far.^{10,11}

In our previous work, sodium benzoate, which has been used, for example, as an antimicrobial agent, a flavoring agent, and an acid acceptor, was found to work as a nucleating agent for iPP.¹² Sodium benzoate with fine particle sizes was selected because it meets several requirements as a nucleating agent in that it possesses a polar group, is insoluble in a polymer, and is crystal-


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Table I Properties of Materials Used in This Work

	Melt Index (MI) (g/10 min, 230°C, 2.16 kg)	Catalyst Residue (wt ppm) Ti/Al/Cℓ	Density (g/cm ³) Solid/Melt	Molecular Weight $M_n/M_w/$ M_z/Q	T_g (°C)	
H540	10	2.4/48/42	0.903/0.734	108/360/1179/3.3	9	
	Melt Index (g/10 min, 230°C, 2.16 kg)	Mooney Viscosity (ML(1 + 4), 100°C)	Density (g/cm ³)	C ₃ Content (wt %)	T_g (°C)	Crystallinity (%)
KEP-020P	3.2	24	0.86	26	-52	3
	Formula	Molecular Weight	Type	Melting Point	Density (g/cm ³)	
Nucleating agent	Sodium benzoate <chem>C6H5COONa</chem> 	144.1	Fine powder	>300°C	1.44	

lized before the crystallization of its matrix polymer on cooling, and so forth.^{13–15}

This study focuses on the effect of sodium benzoate as a nucleating agent in the isothermal crystallization kinetics of iPP/EPR blends. Crystallization kinetics, such as crystallization peak temperature, isothermal crystallization half-time (ICHT), and spherulitic growth rate, were measured by differential scanning calorimetry (DSC) and polarizing optical microscopy. Dynamic mechanical and physical properties of the iPP/EPR blends nucleated with sodium benzoate were also measured.

EXPERIMENTAL

Materials

A commercial grade of iPP, H540 homopolymer, produced by LG-Caltex Oil Co. (Korea) was used. A commercial ethylene-propylene rubber (EPR), KEP-020P [ethylene content 74 wt %, MI 3.2 g/10 min (at 230°C, 2.16 kg)], supplied by Kumho Polychem Co. (Korea), was used to blend with iPP. Blending was performed in an 30-mm Φ twin-screw extruder (APV, South Plainfield, NJ; m.p. 2030). Compositions of iPP/EPR blends were 100/0, 95/5, 90/10, 85/15, and 80/20 by weight. Sodium benzoate (as a nucleating agent) was obtained from the Fluid Energy Processing Equip-

ment Co. (Hatfield, PA). The properties of materials used in our study are shown in Table I.

Measurements

Specimens for measurements were prepared by an injection-molding machine (Gold Star, Korea; IDE 75EN) at a melt temperature of 220°C, a molding temperature of 50°C, an injection time of 2 s, an injection pressure of 70 kg_f/cm², a holding time of 13 s, a holding pressure of 50 kg_f/cm², and a cooling time of 30 s.

Dynamic mechanical properties were determined by a Rheometrics dynamic spectrometer (model RDS 2) with a 2-mm-thick specimen. The heating rate was 5°C/min in the temperature range of -100 to 40°C, and the amplitude vibration was 0.2 mm.

Flexural modulus (FM) was measured according to ASTM D-790 using an Instron universal testing machine. Izod impact strength (IZOD) was tested by ASTM D-256. Heat distortion temperature (HDT) was measured by ASTM D-648.

Kinetic thermal analysis was carried out using a Perkin-Elmer DSC-7 calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT). About 5 mg of sample pellets were heated to 200°C and kept for 10 min to remove the thermal history before cooling it to a predetermined crystallization temperature. For isothermal crystallization the cooling rate to a given crystallization temper-

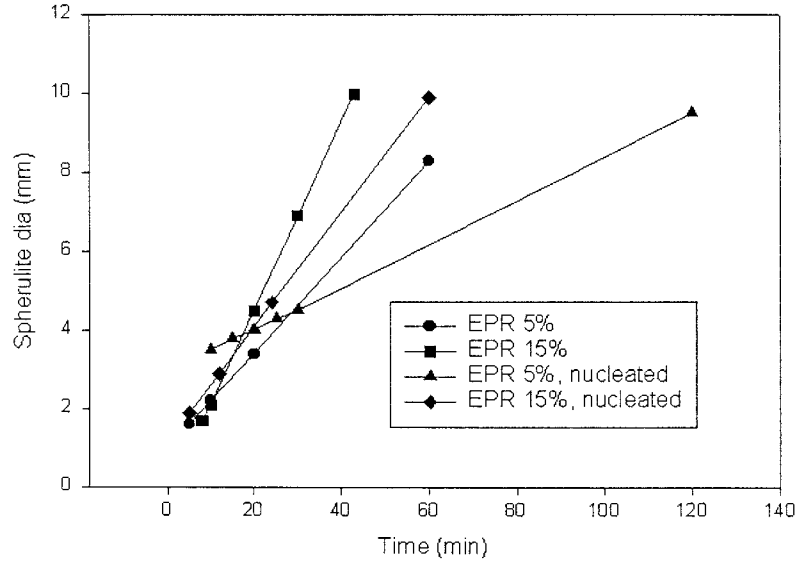


Figure 1 Spherulite diameter as a function of time at the crystallization temperature of 138°C for both the un-nucleated and the nucleated blends.

ature was adjusted to be faster than 80°C/min. The isothermal recrystallization thermograms were obtained as a function of time at several temperatures.

The nucleation and growth rates of iPP crystallization under various crystallization conditions were determined by the aid of micrographs taken successively by polarizing optical microscopy. Samples of thin film were sandwiched between microscope coverslips, melted at 200°C for 10 min to destroy any trace of crystallinity (as for DSC), and then rapidly cooled to a predetermined crystallization temperature.

The heat of crystallization on cooling was recorded during DSC measurements. The isothermal crystallization behaviors were constructed by integrating the area under the exothermic peak according to the following equation:^{10,16,17}

$$X_t = \frac{Q_t}{Q_\infty} = \frac{\int_0^t (dH/dt) dt}{\int_0^\infty (dH/dt) dt}$$

where dH/dt is the rate of heat evolution.

The degree of crystallinity (X_c) was determined from the heat evolved during crystallization using the following equation:

$$X_c (\%) = \frac{\Delta H_c}{\Delta H_m^\circ} \times 100$$

where ΔH_c is the heat of crystallization and ΔH_m° is the heat of fusion for 100% crystalline (209 J/g for α -PP).^{16,18,19}

Crystallization kinetics were analyzed by evaluating X_c as a function of time at a constant temperature for the isothermal mode.

RESULTS AND DISCUSSION

Effect of EPR Contents on the Crystallization of iPP

Figure 1 shows the growth of spherulite diameter, measured by optical microscopy, as a function of time at the crystallization temperature of 138°C, where larger spherulites are observed at higher EPR contents for both blends with and without sodium benzoate. The concentration of the nucleating agent was fixed at 450 ppm for the nucleated blends throughout the study, unless otherwise specified. It is also seen that blends without sodium benzoate (i.e., un-nucleated blends) exhibit larger spherulites than those of nucleated blends. As EPR content increases in the iPP/EPR blends, it seems to increase the spherulite growth rate rather than the nucleation rate. Careful inspection of Figure 1, however, indicates that the spherulite diameters of the nucleated blends are larger than those of un-nucleated blends at the earlier crystallization times, regardless of the EPR contents, and that the trend is more clearly

Table II Effect of EPR Content on the Crystallization Behavior and Properties of iPP

Item	EPR Content (wt %)				
	0	5	10	15	20
(a) Unnucleated Blend					
T_c (°C)	114.3	112.9	114.9	112.1	112.6
X_c (%)	66.2	58.4	55.0	52.1	47.6
Izod (kg cm ⁻¹ cm ⁻¹)	2.4	3.2	3.8	4.2	6.0
FM (kg/cm ²)	15,300	14,200	13,000	11,800	10,700
HDT (°C)	111	106	102	99	94
(b) Nucleated Blend					
T_c (°C)	125.6	118.4	116.8	114.7	113.5
X_c (%)	69.6	61.1	55.1	53.4	51.8
Izod (kg cm ⁻¹ cm ⁻¹)	3.6	4.0	4.2	4.4	6.6
FM (kg/cm ²)	17,300	16,600	14,200	12,300	10,800
HDT (°C)	125	122	106	102	94

seen when the EPR contents are 5 wt % compared to that at 15 wt %. The initial larger iPP spherulites for the nucleated blends compared to those for the unnucleated blends should be related to the nucleation effect of sodium benzoate, as shown in Table II.

Table II shows that the crystallization temperature (T_c) and the degree of crystallinity (X_c) of nucleated blends, compared to those of the unnucleated blends, are higher; these determinants are related to higher nucleation rates of the iPP spherulites at a given crystallization

resulting from the initial nucleation effect. It is seen from the larger differences in T_c or X_c between the nucleated blends and the unnucleated blends at lower EPR contents that the nucleation effect is more clearly observed as the EPR content is lower in the blends.

The effect of EPR contents on the spherulite growth rate is shown in Figure 2. The spherulite growth rate shows a maximum value at certain contents of EPR (10 to 15 wt % for unnucleated blends, and 15 to 20 wt % for nucleated blends). This result suggests that EPR itself can play a

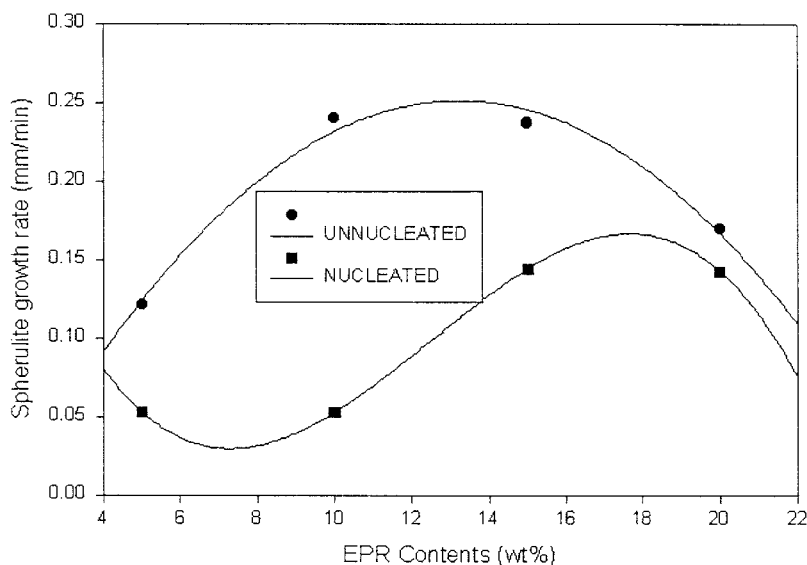


Figure 2 Spherulite growth rate (G) versus EPR contents at the crystallization temperature of 138°C for both the unnucleated and the nucleated blends.

role as a nucleating agent for iPP at lower EPR contents because of the partial compatibility between EPR and iPP. It is not surprising, however, that the spherulite growth rate of iPP decreases with further increases of EPR content because of the amorphous nature of EPR.

It is also seen that the blend without a nucleating agent exhibits a higher growth rate than that of the nucleated blend at the same EPR contents. The result means that the effect of the nucleating agent on the spherulite growth rate of iPP is not predominant in comparison to the partial compatibility effect of EPR and iPP.

In the primary nucleation phenomenon in a polymer, three paths for nucleation can be distinguished: (1) homogeneous nucleation, which takes place if no preformed nuclei or foreign surfaces are present; (2) heterogeneous nucleation, in which the nuclei form on foreign surfaces, often reducing the nucleus size needed for stable crystal growth and thus enhancing the nucleation process; and (3) self-seeding nucleation, unique to polymers, in which nucleation is caused by small polymer crystals that survived the melting of the polymer samples.^{20,21}

The primary nucleation of iPP crystallization in the iPP/EPR blend was studied for isothermal crystallization at a high undercooling condition, that is, 138°C as above. Such a condition was usually applied to study the homogeneous case of primary nucleation as well as heterogeneous nucleation.²²

Figures 3 and 4 show, respectively, the polarizing optical micrographs of unnucleated and nucleated iPP/EPR blends with 15 wt % of EPR at the crystallization temperature of 138°C, taken at various crystallization times. It seems that the nucleating sites may be mostly the nucleating agents, that is, sodium benzoate, in part with EPR.

Generally, at a higher crystallization temperature, heterogeneous nucleation is predominant over homogeneous nucleation.²² Homogeneous nucleation has too low a rate to influence the average size of spherulites at this temperature. The further rapid increase of the homogeneous nucleation rate with the decrease of crystallization temperature leads to a significant decrease in the average spherulite radius. At a given temperature, the rate of homogeneous nucleation in the iPP/EPR blend decreases with increasing EPR concentration in the blend.²²

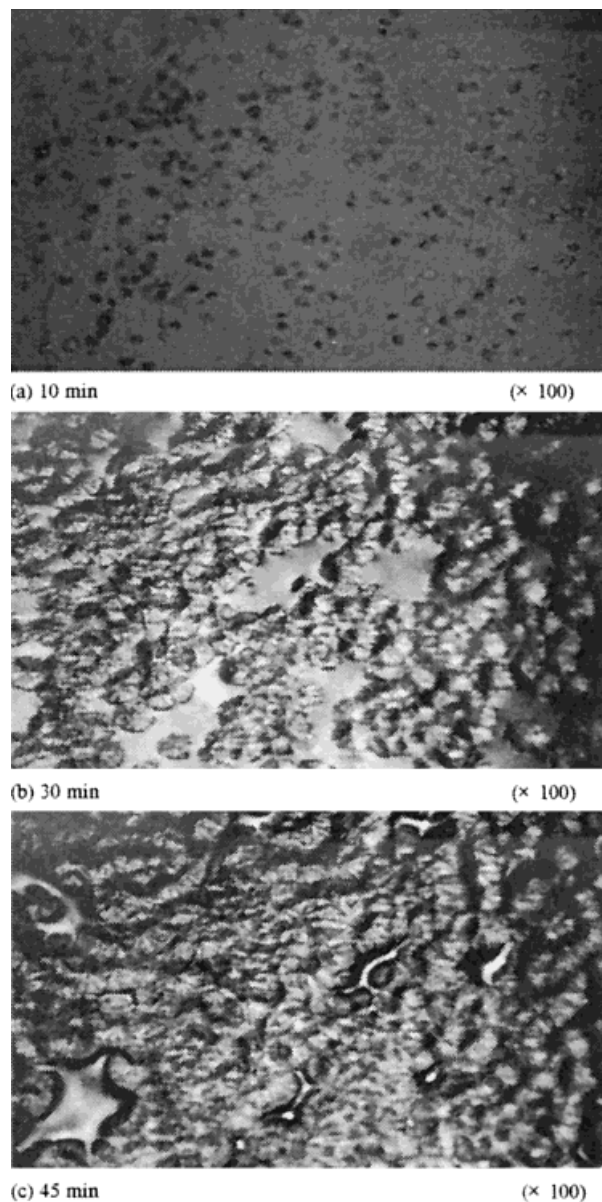


Figure 3 Polarized optical micrographs of unnucleated iPP/EPR blends with 15 wt % of EPR at the crystallization temperature of 138°C, taken at various crystallization times.

Figure 5 shows the crystallization temperature and ICHT of blends as a function of EPR contents. The ICHT was obtained from the exothermic heat of crystallization curve on DSC thermograms as a function of time, when quenching to a desired temperature after completely melting.

The crystallization temperature was not significantly dependent on the EPR contents for the unnucleated blends, whereas the crystallization

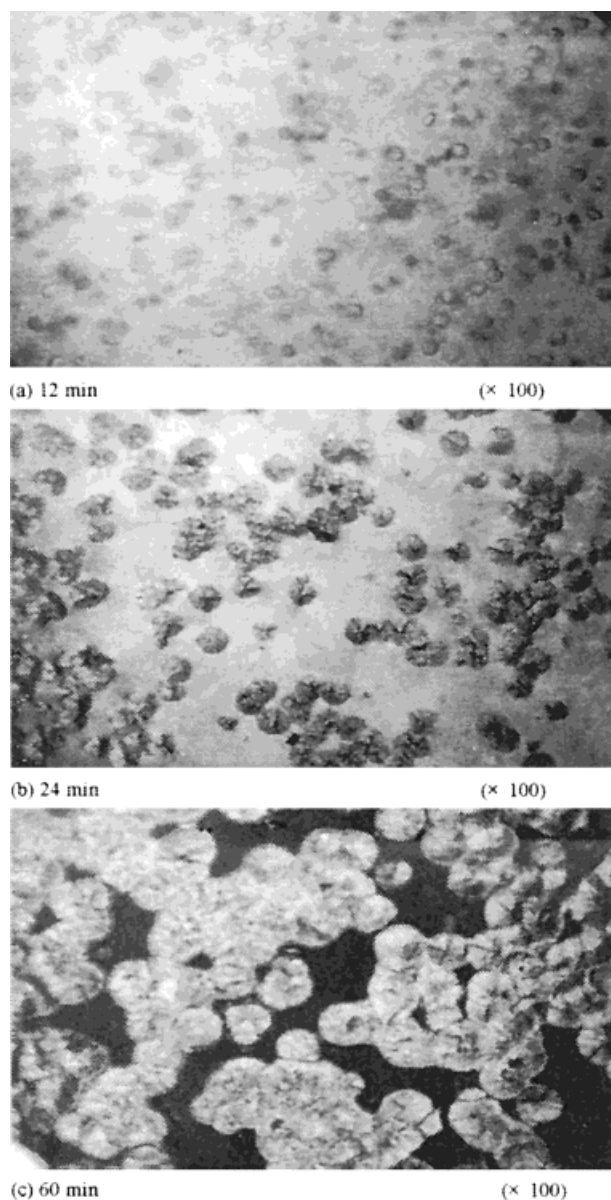


Figure 4 Polarized optical micrographs of nucleated iPP/EPR blends with 15 wt % of EPR at the crystallization temperature of 138°C, taken at various crystallization times.

temperature was dramatically decreased with EPR contents for the nucleated blends. The result clearly shows the nucleating effect of sodium benzoate for the nucleated blends, as seen for iPP homopolymer in our previous work.²² The trend for un-nucleated iPP/EPR blends may be ascribed to the competition between the nucleating effect of EPR attributed to the partial compatibility between the components and the simple addition of amorphous component, as explained for Figure 2.

There are drastic changes of nucleation density at the nucleation process of the iPP/EPR blend, at which nucleation density significantly increases with increasing concentration of EPR by up to around 10 wt % and levels off with further increases of EPR contents, as reported by Martuscelli et al.^{23,24} Therefore, the ICHT related to the nucleation density as a function of EPR contents showed the same trend as the nucleation density behavior. On the contrary, for the nucleated blends, the ICHT reaches a minimum at 10 wt % EPR and increases with further increases of EPR contents. It may not be caused by the nucleation activity of EPR on the iPP crystallization but, rather, by the increased number of heterogeneous nuclei. Such impurities as catalyst residues and additives (nucleating agent, etc.), which act as heterogeneous nuclei, migrate from the EPR phase into the iPP phase during preparation of the blend by melt mixing.^{21,25} This unexpected crystallization behavior may be caused by a significant depression of the self-seeding nucleation mode in the blend attributed to the partial miscibility of components and an increase in the number of heterogeneous nuclei.²⁵

In the case of a binary blend, if the second polymer dispersed in a crystallizable matrix crystallizes under conditions similar to those of the matrix polymer, the crystals of a second polymer can grow at interfaces²⁶ and may act as a nucleating agent for crystallization of the matrix. Such behavior may be caused in the blend of iPP and EPR of ethylene-rich contents as the iPP/HDPE blend because EPR shows some degree of crystallinity according to its composition of ethylene/propylene ratios, that is, a solid PP phase for higher propylene content and a polyethylene (PE) phase for higher ethylene content.²⁷

Actually, for EPR (ethylene, 74% content) used in our work, the DSC thermogram exhibits some crystalline structure. When sodium benzoate was added to EPR, the crystallization behavior of the nucleated EPR was similar to that of iPP, sustaining a crystallinity of about 10%.

A small ethylene fraction in EPR of the iPP/EPR blend will be crystallized at a temperature below 125°C with a rate close to that of crystallization of iPP.²⁸ The crystalline HDPE inclusions dispersed in iPP matrix induce additional nucleation of a number of iPP spherulites. As a result, the nucleation density of iPP spherulites in the iPP/EPR blends increases with increasing EPR content in the blend during crystallization below 125°C.²⁸

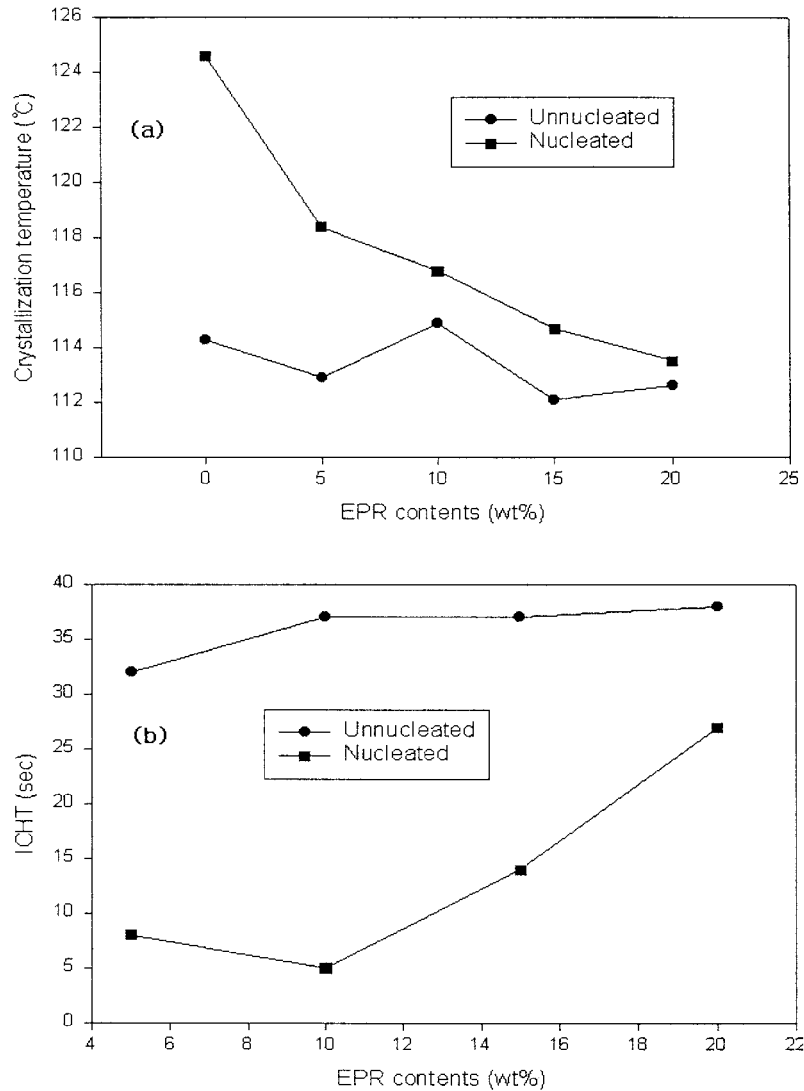


Figure 5 Effect of EPR contents on the crystallization temperature at the cooling rate of 10°C/min (a) and ICHT at 120°C for both the un-nucleated and the nucleated blends.

In the iPP/EPR (with ethylene-rich content) blend, major factors influencing the crystallization behavior such as spherulite density or crystallization temperature will be a combination of not only the migration of impurities including nucleating agent to iPP but also the crystallization of HDPE fraction in EPR in the blend.^{17,18,23,24} In fact, the latter compared to the former will not be large, as expected, because of small HDPE content generated by the ethylene-rich content.

Figure 6 indicates that the flexural modulus was decreased but Izod impact strength was increased with the addition of EPR for both nucleated and un-nucleated blends, as expected. It is interesting to note that the Izod impact strength

remarkably increases with EPR contents when the contents are above 15 wt %. This effect may be attributed to the crystallizable PE segments of the EPR of high ethylene content acting as reinforcing nodes in the physical network structure.²⁹

The nucleated blends showed higher flexural and Izod impact strength than that of un-nucleated blends. The higher impact strength of the nucleated blends compared to that of the un-nucleated blends was already explained in more detail, in our previous work, for iPP when sodium benzoate was used as a nucleating agent.¹³

Spherulites controlled by a nucleating agent have many nuclei and microcrystal impingement between neighboring spherulites by their growth

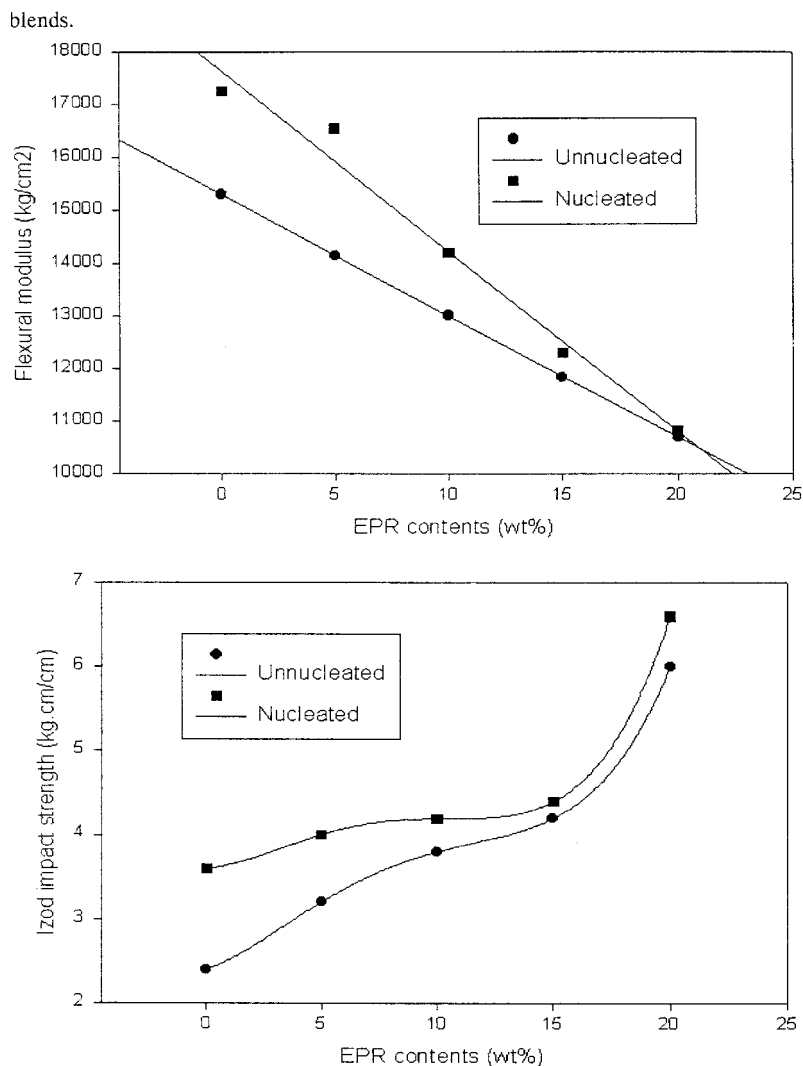


Figure 6 Flexural modulus (a) and Izod impact strength (b) of blends as a function of EPR contents for both the unnucleated and the nucleated blends.

sites.³⁰ Nomura et al.^{31,32} reported that the introduction of microcrystals with talc or a blend in amorphous and crystalline phases generates an interpenetrating polymer network (IPN)-like structure, which leads to improvement of mechanical properties such as hardness and modulus, for example.

Tjong et al.³³ also reported that a distinct spherulitic morphology results in a substantial improvement in the falling weight impact resistance. They explained that the greater impact toughness observed in the nucleated β -form PP specimen is attributed to the large energy dissipation associated with the formation of microfibrils.

Table II summarizes the mechanical properties such as HDT, flexural modulus, and Izod impact strength as well as the thermal properties according to EPR contents with or without sodium benzoate, respectively. It is clearly seen that the HDT and the flexural modulus and impact strength as well as T_c and X_c for the nucleated blends were higher than those of unnucleated blends, regardless of EPR contents, indicating the nucleating effect of sodium benzoate.

Dynamic Mechanical Properties

For the iPP/EPR blend, the dynamic mechanical data showed that there are three transitions at

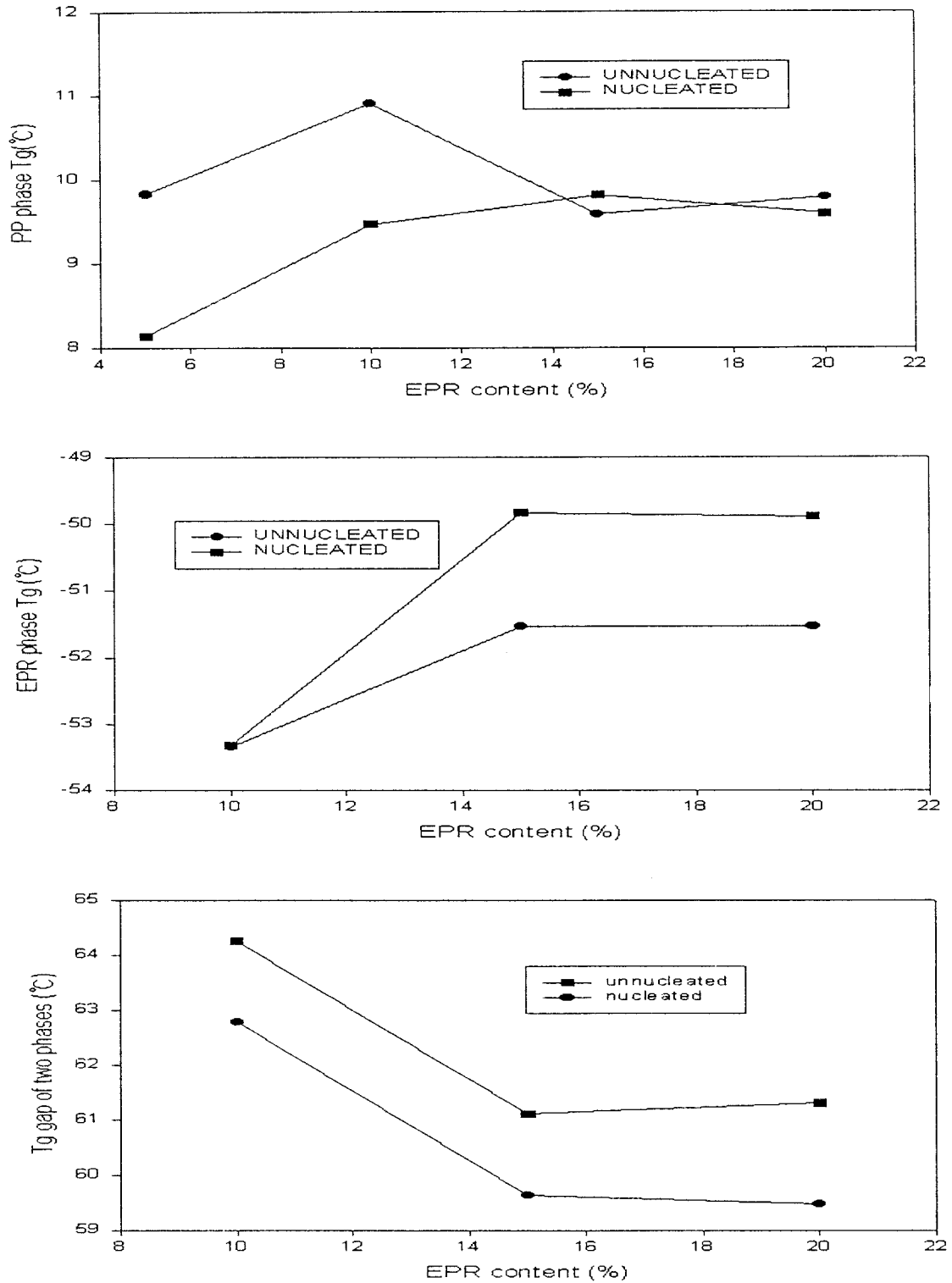


Figure 7 Transition temperature of PP (a) and EPR (b) phases and T_g gap of two phases of both the un-nucleated and the nucleated blends as a function of EPR contents.

about 10°C, -50 to -53°C, and around -80°C. The three transitions indicate the existence of three phases in the iPP/EPR blend, suggesting a PP phase, an EPR phase, and a PE phase, respectively. Each transition is illustrated in Figure 7 as a function of EPR contents for both un-nucleated and nucleated blends.

Figure 7 shows that for the un-nucleated blends, the β -transition (T_g) for the PP phase increases with increasing EPR content, shows a maximum, decreases, then levels off, whereas for the nucleated blends the T_g increases with increasing EPR content and levels off with further increases of EPR content. The T_g was almost the same for both nucleated and un-nucleated blends when the EPR content is above 15 wt %. On the other hand, the T_g of the EPR phase increased with an increase of EPR content for both un-nucleated and nucleated blends. It is very interesting that the T_g of the nucleated blend is lower than that of the un-nucleated blend for the PP phase but is reversed for the EPR phase. This may correspond to the result that the nucleated blends obtain a higher Izod impact strength as well as higher flexural modulus than that of the un-nucleated blends, regardless of EPR contents, as mentioned previously.

The locations of relaxation transitions for each phase are similar to those of their pure components (iPP, EPR, PE) except for a small change in their T_g 's, demonstrating that they are partially miscible. As a measure of degree of miscibility, we used the temperature difference between T_g for the PP phase and T_g for the EPR phase; the smaller the difference, the closer to their peaks and the better the miscibility. Figure 5 shows that in the iPP/EPR blend the nucleated blend has a lower gap than that of the un-nucleated blend and both blends have a critical point at the same EPR content (i.e., 15 wt %).

CONCLUSIONS

In this work, the effect of sodium benzoate on the isothermal crystallization behavior of isotactic polypropylene (iPP)/ethylene-propylene rubber (EPR) blends was investigated using differential scanning calorimetry. Dynamic mechanical and physical properties of the iPP/EPR blends nucleated with sodium benzoate were also measured.

High impact strength was achieved by adding EPR with high ethylene composition and sodium benzoate to iPP. EPR itself also played a role as a

nucleating agent for iPP at lower EPR contents because of the partial compatibility between EPR and iPP. The sodium benzoate acted as a nucleating agent in the iPP/EPR blend as well as iPP. It was found that the isothermal crystallization behavior and physical properties such as HDT, flexural modulus, and impact strength were strongly affected by the competition between the nucleating effect of EPR, because of its partial compatibility with iPP, and the simple addition of the amorphous component.

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REFERENCES

- Ito, J.; Mitani, K.; Mizutani, Y. *J Appl Polym Sci* 1992, 46, 1221.
- Bartczak, Z.; Galeski, A.; Martuscelli, E.; Janik, H. *Polymer* 1985, 26, 1843.
- Coppola, F.; Greco, R.; Martuscelli, E.; Kammer, H. W.; Kummerlowe, C. *Polymer* 1987, 28, 47.
- Bartlett, D. W.; Barlow, J. W.; Paul, D. R. *J Appl Polym Sci* 1982, 27, 2351.
- Wenig, W.; Asresahegn, M. *Polym Eng Sci* 1993, 33, 877.
- Karger-Kocsis, J. *Polypropylene: Structure, Blends and Composites*; Academic Press: New York, 1980; Vol. 2, pp 103-125.
- Moore, E. P. *Polypropylene Handbook* (Montell); Hanser: New York, 1996; pp 149-164, 215-225.
- Pillips, R.; Manson, J. E. *J Polym Sci Part B Polym Phys* 1997, 35, 875.
- Kim, Y. C.; Kim, C. Y.; Kim, S. C. *Polym Eng Sci* 1991, 31, 1009.
- Dogopolsky, I.; Silberman, A.; Kenig, S. *Polym Adv Technol* 1995, 6, 653.
- Technical Manual Vol. IV, Product Technology, Union Carbide Corp., 1986.
- Jang, G. S.; Cho, W. J.; Ha, C. S. *J Polym Sci Part B Polym Phys* 2001, 39, 1001.
- Milliken Chemicals, Technical Materials—Nucleating Agent Bulletin, 1989.
- Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1976; Vol. 2, pp 43-52.
- Zhang, R.; Zheng, H.; Lou, X.; Ma, D. *J Appl Polym Sci* 1994, 51, 51.
- Avalos, F.; Lopez-Manchado, M. A.; Arroyo, M. *Polymer* 1996, 37, 5681.
- Yokoyama, Y.; Ricco, T. *J Appl Polym Sci* 1997, 66, 1007.
- Dorazio, L.; Mancarella, C.; Martuscelli, E.; Sticotti, G. *J Mater Sci* 1991, 26, 4033.

19. Tjong, S. C.; Xu, S. A. *Polym Int* 1997, 44, 95.
20. Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1976; Vol. 2, pp 1–105.
21. Karger-Kocsis, J. *Polypropylene: Structure, Blends and Composites*; Academic Press: New York, 1980; Vol. 2, pp 25–46.
22. Bartzak, Z.; Galeski, A. *Polymer* 1990, 31, 2027.
23. Martuscelli, E.; Silvestre, C.; Abate, G. *Polymer* 1982, 23, 229.
24. Martuscelli, E.; Silvestre, C.; Bianchi, L. *Polymer* 1983, 24, 1458.
25. Bartzak, Z.; Galeski, A.; Martuscelli, E.; Janik, H. *Polymer* 1985, 26, 1843.
26. Duvall, J.; Sllitti, C.; Hiltner, A.; Baer, E. *J Appl Polym Sci* 1994, 52, 207.
27. Greco, R.; Mancarella, C.; Martuscelli, E.; Ragosta, G.; Hua, Y. J. *Polymer* 1987, 28, 1929.
28. Bartzak, Z.; Galeski, A.; Pracella, M. *Polymer* 1986, 27, 537.
29. Canevarolo, S.; De Candia, F. *J Appl Polym Sci* 1995, 57, 533.
30. Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1976; Vol. 2, pp 43–52, 135, 147, 216, 217, 236.
31. Nomura, T.; Nishio, T.; Sato, H.; Sano, H. *Kobunshi Ronbunshu* 1993, 50,19.
32. Nomura, T.; Nishio, T.; Sato, H.; Sano, H. *Kobunshi Ronbunshu* 1993, 50,87.
33. Tjong, S. C.; Shen, J. S.; Li, R. K. Y. *Polymer* 1996, 37, 2309.