Studies on Dynamically Vulcanized Polypropylene (PP)/Butadiene Styrene Block Copolymer (SBS) Blends: Crystallization and Thermal Behavior

MADHUMITA SAROOP,¹ G. N. MATHUR²

¹ Shriram Institute for Industrial Research, 19, University Road, Delhi-110007, India

² Defence Materials Stores Research and Development Establishment, G.T. Road, Kanpur, India

Received 10 November 1997; accepted 5 January 1998

ABSTRACT: Crystallization of polypropylene (PP) in unvulcanized blends of PP with the butadiene–styrene block copolymer (SBS) was studied through differential scanning calorimetry (DSC) and X-ray diffraction measurements in the composition range of 0-40 wt % SBS content. Analysis of the crystallization exotherms revealed variation in the crystallization behavior, crystallinity, and crystalline morphology of the PP component in the blends at various levels of SBS concentration. The crystallinity determined by X-ray diffraction and DSC showed identical variations with the blend composition. The tensile and thermal properties of the blends were studied in the entire composition range. Correlations of the tensile properties with the crystallization parameters of the PP component in the blends are also presented. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 151–161, 1999

Keywords: polypropylene; butadiene-styrene block copolymer; dynamic vulcanization; crystallinity; thermal stability

INTRODUCTION

The melt blending of isotactic polypropylene (PP) with different elastomers and rubbers such as butyl rubber, ethylene-propylene copolymers (EPM), ethylene-propylene-diene terpolymers (EPDM), polyisobutylene, and styrene-butadiene block copolymers is widely used for increasing the impact strength of PP, especially at low temperatures.¹⁻⁴ An approach to improve upon the performance and properties of rubber-modified PP is to develop the blends by dynamic vulcanization wherein the elastomeric phase is cured under shear while melt mixing with PP.^{5,6} A number of

research articles have been published on the mechanical and morphological properties of dynamically vulcanized PP/elastomer blends.^{7,8} Studies on the crystallization behavior of unvulcanized PP/elastomer blends have also been reported,^{9–11} but not much work has been carried out to study the effect of the elastomeric component on the crystallization behavior of PP in dynamically vulcanized blends.

In this article, a study of the crystallization behavior of PP in unvulcanized and dynamically vulcanized PP/SBS blends and their thermal properties in the composition range of 0-40 wt % SBS content is presented. The crystallization behavior and the degree of crystallinity were determined through differential scanning calorimetry (DSC) and X-ray diffraction measurements. An attempt was made to correlate the crystallization

Correspondence to: M. Saroop

Journal of Applied Polymer Science, Vol. 71, 151-161 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/010151-11

behavior and the mechanical and thermal properties of the blends.

EXPERIMENTAL

Materials

Isotactic polypropylene (PP), Koylene S-3030 (MFI 3 g/10 min at 230°C and 2.16 kg/cm²) was obtained from Indian Petrochemicals Corp., Ltd., Vadodara, India. The butadiene–styrene block copolymer (SBS), Cariflex-1101 (30% styrene content), was procured from Shell Chemical Co. (USA) A modified phenolic resol resin, Hylak HR-6415 from Bakelite Hylam, India, and zinc oxide (LR) from Qualigens were used as the curing agent and accelerator, respectively, for the vulcanization.

Preparation of Blends

The unvulcanized PP/SBS blends of compositions of 10, 20, 30, and 40 wt % SBS were prepared by melt mixing at a rate of 60 rpm at 180°C for 10 min in the internal mixer of a torque rheometer, a HAAKE Rheocord RC-90, using roller rotors. The charge weight taken was 200 g. The corresponding dynamically vulcanized blends were also prepared under identical conditions, except that after the initial mixing for 5 min a mixture of the curing agent and accelerator (10 and 1 wt %, respectively, on the basis of the SBS content in the blend) was introduced in the cavity of the mixer, while mixing which was further continued for 5 min until an equilibrium torque was reached after curing. The molten mass from the mixer was cooled and cut into fine granules. These were then compression-molded at 190°C and 30 MPa pressure for tensile testing. DSC and X-ray diffraction measurements were done on a ground powder of the blends.

Measurements

DSC measurements were undertaken on a Du-Pont 2200 thermal analysis system. The sample size used was 10 mg and was first heated to 200°C (i.e., above the melting point of PP) and kept at that temperature for 5 min so as to eliminate the effect of the previous history of the crystallization. Thermograms were recorded during the cooling cycle at a constant cooling rate of 5°C/min at identical settings of the instrument and almost equal sample weights.

X-ray diffraction measurements were done on Philips Noreleco X-ray diffraction equipment provided with a scintillation counter and recorder. Radial scans of intensity (*I*) versus the diffraction angle (2θ) were recorded in the range of $10^{\circ}-40^{\circ}$ of 2θ using CuK α radiation. Diffractograms of all the samples were recorded at identical settings of the instrument.

Thermal degradation of the PP and PP/SBS blends were analyzed on a thermal analysis instrument SDT-2960 in the dynamic mode. The kinetic parameters of degradation such as the activation energy (E_a) , preexponential factor (log z), and 60-min half-life temperature were determined by an instrument software program using a multiple heating rate kinetics method at a 10% constant conversion under the assumption that reaction follows first-order kinetics. About 6-12 mg of the powdered samples were used. Each sample was subjected to multiple heating rates of 5, 10, and 15°C/min under a nitrogen atmosphere. Thermogravimetric analysis in an inert atmosphere is used as a method for empirically assessing the thermal stabilities of experimental polymers. The available information can be summarized in a consistent manner in a single comprehensive index of thermal stability under the procedural conditions employed. This index, the integral procedural decomposition temperature (IPDT), was devised as a means of summing up the whole shape of the normalized data curve and is a reproducible datum having practical significance. The IPDT was calculated¹² from the thermal curves, obtained at a heating rate of 10° C/min according to eq. (1):

$$IPDT = (T_2 - T_1)A^* - T_1 \tag{1}$$

where T_1 and T_2 denote the initial and final temperature and A^* is the ratio of the area under a primary thermogram with respect to the whole of the rectangular plotting area.

Tensile testing was carried out at $25 \pm 2^{\circ}$ C on an Instron universal testing machine (Model 4302) on compression-molded dumbell-shaped samples according to ASTM D-638 at a strain rate of 50 mm/min with an initial gauge length of 2.5 cm.



Figure 1 DSC exotherms representing crystallization of PP in unvulcanized PP/SBS blend at various SBS contents (wt %): (1) 0; (2) 10; (3) 20; (4) 30; (5) 40.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry

DSC thermograms of PP and its blends in the region of crystallization, recorded during the cooling cycle, are shown in Figures 1 and 2. All thermograms showing prominent crystallization exotherms are presented at the same temperature scale for comparison. To study the crystallization behavior, these thermograms were analyzed in terms of the following parameters defined below and are illustrated in Figure 3. These parameters have also been used to study the crystallization behavior of PP by other authors:^{9,13}



Figure 2 DSC exotherms representing crystallization of PP in dynamically vulcanized PP/SBS blend at various SBS contents (wt %): (1) 0; (2) 10; (3) 20; (4) 30; (5) 40.



Figure 3 Typical crystallization exotherm, recorded during cooling cycle, and the illustration of the various parameters used in the analysis.

- T_p : exotherm peak temperature. Addition of a nucleating agent increases the peak temperature.¹⁴
- Si: Slope of initial portion of the exotherm. The faster the nucleation, the greater will be the initial slope.
- Δw : Width at half-height of the exotherm peak determined after normalization of the peak to constant mass of the PP component in the sample. The narrower the crystallite size distribution, the smaller will be Δw .
- $T_c T_p$: The inverse measure of the overall rate of crystallization where T_c is the tem-

perature at the intercept of the tangets at the baseline at the high-temperature side of the exotherm. The smaller the $(T_c - T_p)$, the greater the rate of crystallization.

A/m: The area under the exotherm per unit weight of the crystallizable component of the sample which is proportional to the degree of crystallinity.¹³

The data on T_p , Si, $(T_c - T_p)$, Δw , and A/m are given in Table I and their variation as a function of the blend composition is shown in Figures 4 and 5. In the unvulcanized blend system, an initial addition of 10 wt % SBS to PP results in a decrease in the degree of crystallinity of PP. The rate of nucleation becomes marginally slow with a slightly wider spherulitic size distribution as is indicated by a lower Si and marginally higher Δw and $(T_c - T_p)$ values. In the composition range of 10-30 wt % SBS content, there is a sharp increase in the rate of nucleation and degree of crystallinity. The increase in the T_p value also indicates that SBS may be acting as a nucleating agent for PP crystallization in this region. Hence, a large number of nuclei can be created with a faster rate of nucleation, producing more uniformity in the spherulite size, which is supported by the lower Δw , implying a narrower distribution of the crystallite size. As the SBS content in the blend increases from 30 to 40 wt %, there is a marginal increase in the crystallinity, although the rate of nucleation decreases. The slower rate

SBS Content (wt %)	T_p (°C)	$\begin{array}{c} (T_c - T_p) \\ (^{\circ}\mathrm{C}) \end{array}$	A/m (arbitrary units)	Si (arbitrary units)	Δw (Arbitrary Units)	$X_{c(\mathrm{app})}$
Unvulcanized ble	nds					
0	115.79	5.07	100.00	4.70	35.0	67.92
10	115.41	5.33	95.26	4.33	36.0	66.60
20	115.67	4.59	99.40	5.14	33.5	68.42
30	116.32	4.55	102.46	5.67	32.5	70.23
40	116.08	4.92	103.99	4.01	36.0	71.10
Dynamically vulc	anized blends					
10	115.07	5.33	94.21	4.33	36.0	66.60
20	112.68	7.3	99.09	2.75	37.0	67.50
30	111.31	8.78	96.84	1.73	42.0	66.25
40	111.06	8.94	95.63	1.43	45.0	65.50

Table IValues of Various Crystallization Parameters of PP Component in PP/SBS Blends from DSCThermograms and X-ray Diffraction



Figure 4 Variation of the various crystallization exotherm parameters with SBS content for unvulcanized PP/SBS blend.



Figure 5 Variation of the various crystallization exotherm parameters with SBS content for dynamically vulcanized PP/SBS blends.



Figure 6 X-ray diffractograms of unvulcanized PP/SBS blend at various SBS contents (wt %): (1) 0; (2) 10; (3) 20,;(4) 30; (5) 40.

of nucleation may cause formation of large spherulites while formation of some smaller spherulites may also take place. The morphology with the coexistence of small and large crystallites for the PP phase of the blend is supported by increase in the Δw value, indicating a wider spherulitic size distribution.

The variation in the crystallinity behavior of PP in the dynamically vulcanized blend in the composition range of 0–10 wt % SBS content is similar to that of the unvulcanized blend. However, in the region of 10–20 wt % SBS content, although there is an increase in the degree of crystallinity, the rate of nucleation decreases, resulting in a wider spherulitic size distribution which is supported by an increase in the Δw values. The rate of nucleation further decreases, accompanied by a wide variation in the spherulitic size distribution, giving rise to a decrease in the

degree of crystallinity in the range of 20-40 wt % SBS content in the blend. The gradual decrease in T_p in the dynamically vulcanized blend system with increasing SBS content, in general, indicates an increase in supercooling. The crosslinked structure formed on dynamic vulcanization may restrict the spherulitic growth and regular arrangement of the spherulites of the crystalline component in the blend and, hence, decreases its degree of crystallinity. Further, the effect of crosslinking in reducing the degree of crystallinity of PP in the dynamically vulcanized blend is significant at higher SBS loading, having a higher degree of crosslinking (refer to companion article) resulting in the opposite trend in the variation of the crystallinity with the blend composition to that in the unvulcanized blend system.



Figure 7 X-ray diffractograms of dynamically vulcanized PP/SBS blend at various SBS contents (wt %): (1) 0; (2) 10; (3) 20; (4) 30; (5) 40.



Figure 8 Variations of X-ray crystallinity with blend composition for PP/SBS blends.

X-ray Diffraction

X-ray diffractograms for PP and its blends showing the variation of intensity (I) versus the diffraction angle (2θ) are shown in Figures 6 and 7. A sharp diffraction maxima at 2θ values of 14° , 17° , 18.5° , and 21.7° , characteristic for isotactic PP,¹⁵ are present in these diffraction patterns without any additional peaks, indicating that PP is the only crystallizable component in these twophase blends.

Changes in the diffraction pattern with the blend composition are quite systematic in terms of crystallinity, crystallite size, and relative intensities of the diffraction maxima. The degree of crystallinity of the blends was calculated from these diffraction patterns according to the method described for PP in the literature.^{16,17} The evaluated degree of crystallinity is denoted as the apparent degree of crystallinity, $(X_c)_{app}$, which may be emphasized for its comparative value alone, is given in Table I and its variation with the blend composition is shown in Figure 8. The variation of $(X_c)_{app}$ with the blend composition from the XRDE studies is in good qualitative agreement with the variation of the crystallinity parameter A/m in the DSC studies. Hence, X-ray diffraction results provide supporting evidence for the DSC studies of the effect of the SBS concentration on the crystallinity of PP in the blends.

Correlation of Tensile Properties and Crystallization

The results of the tensile testing of the PP/SBS blends are shown in Figure 9, where yield stress,

tensile modulus, and elongation at break are plotted as functions of the blend composition. Blending of PP with SBS, while decreasing the yield stress and tensile modulus, increases the elongation at break in both blend systems. Dynamically vulcanized blends have a higher yield stress and elongation at break than those of the unvulca-



Figure 9 Variations of yield stress, tensile modulus, and elongation at break with SBS content for PP/SBS blends.



Figure 10 Variation of tensile properties with DSC crystallinity parameter A/m for unvulcanized PP/SBS blend. The best-fitting straight lines and their coefficients of correlation (r) are shown for (i) all five data points (solid line) and (ii) four data points excluding the outlying one point (broken line).

nized blends at all the compositions because of the network structure and higher chain entanglements.

It is known that crystallization affects the mechanical properties of polymers. However, the effect of individual crystallization parameters such as degree of crystallinity and crystallite size distribution may have different effects on different mechanical properties. A correlation of A/m, related to the degree of crystallinity, and Δw , related to the crystallite size distribution determined from the DSC crystallization exotherms, with the tensile properties, namely, the elastic modulus, yield stress, and elongation at break, for both blend systems was examined. The coefficient of correlation (r) was determined by regression analysis. The best-fitting linear extrapolations for all five data points (solid lines) are shown in Figures 10-13 with their coefficient of correlation (*r*). The closer to unity is the value of the coefficient of correlation, the better the linearity of fit. On the basis of the extremely low values of the coefficient of correlation, linear relationships of some of the pairs of parameters may be rejected. However, the correlations obtained after excluding one of the outlying points (broken lines, Fig.10–13) are much better as indicated by their higher values of r.

The above analysis also indicates that correlations are better in the case of the parameter A/mthan of Δw in the unvulcanized blends, while in the dynamically vulcanized blends, the correlations are better in the case of Δw than of A/m. The linear correlation of the tensile properties with the crystallization parameters of PP indicates that the crystallization of the matrix plays a significant role in the tensile behavior of the PP/SBS blends.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) has been quite useful in determining the thermal stability of PP and its blends with SBS. The primary ther-



Figure 11 Variation of tensile properties with DSC crystal size distribution parameter Δw for unvulcanized PP/SBS blend. The best-fitting straight lines and their coefficients of correlation (r) are shown for (i) all five data points (solid line) and (ii) four data points excluding the outlying one point (broken line).



Figure 12 Variation of tensile properties with DSC crystallinity parameter A/m for dynamically vulcanized PP/SBS blend. The best-fitting straight lines and their coefficients of correlation (r) are shown for (i) all five data points (solid line) and (ii) four data points excluding the outlying one point (broken line).

mograms of PP and its blends show one-step decomposition. A representative primary thermogram of the PP/SBS blend at 40 wt % SBS content is shown in Figure 14. The detailed mechanism of the thermal degradations of PP, polystyrene, and polybutadiene were reported in the literature.^{18–20}

The plot of the log of the heating rate versus 1000/T at various constant conversions depicts straight lines in all the blend samples. A representative plot of the log of the heating rate versus 1000/T for the nvulcanized blends at 40 wt % SBS content is shown in Figure 15. The slope of the lines at low conversion levels are quite different from those at 10% and higher conversion levels. At 10% and higher conversion levels, the lines are parallel, having the same slope, indicating that the mechanism of degradation could be the same at these conversion levels and justifies our selection of the 10% conversion level for studying the kinetic parameters.

The data of IPDT, E_a , log z (the preexponential factor), and 60 min half-life temperature are pre-



Figure 13 Variation of tensile properties with DSC crystal size distribution parameter Δw for dynamically vulcanized PP/SBS blend. The best-fitting straight lines and their coefficients of correlation (*r*) are shown for (i) all five data points (solid line) and (ii) four data points excluding the outlying one point (broken line).

sented in Table II. The variation of the activation energy of degradation, which is indicative of thermal stability, with the blend composition is shown in Figure 16. There is a general increase in the thermal stability with increasing SBS concentration in the PP/SBS blend. The small radicals gen-



Figure 14 Primary thermogram of PP/SBS blend at 40 wt % SBS content.



Figure 15 Plot of log of heating rate versus 1000/T for unvulcanized PP/SBS blend at 40 wt % SBS content.

erated during the chain scisson of PP in the first stage of degradation may get diffused into the polystyrene phase, resulting in hydrogen abstraction, and the radicals which would normally contribute to the degradation of PP are thus stabilized.¹⁸ The dynamically vulcanized blends are thermally more stable than are the unvulcanized blends, especially at higher SBS loading. As one adds more SBS, increasing amounts of the resol curative are also added. The resol, after reaction with the diene polymer, can give rise to hindered phenolic structures, which could act as antioxidants.

CONCLUSIONS

The crystallization behavior of PP was affected by the presence of SBS in both the unvulcanized and dynamically vulcanized blends. In the unvulca-

SBS				60-Min Half-Life	
Content	IPDT	E_a	$\log(z)$	Temperature	
(wt %)	(°C)	(kJ/mol)	(\min^{-1})	(°C)	
Unvulcanized bl	lends				
0	478.42	241.4	16.83	398.6	
10	475.0	214.4	14.91	391.6	
20	476.5	252.8	17.90	392.4	
30	478.46	322.4	23.28	394.7	
40	477.00	263.1	18.84	388.2	
100	_	217.8	15.75	370.0	
Dynamically vu	lcanized blends				
10	474.92	212.0	14.64	395.0	
20	477.0	253.0	17.81	396.2	
30	478.90	374.7	27.31	397.2	
40	479.10	386.0	27.93	397.9	
100	—	338.0	25.46	372.2	

Table II Data on IPDT and Various Kinetic Parameters for PP/SBS Blends



Figure 16 Variation of activation energy (E_a) of degradation with blend composition for PP/SBS blends.

nized blend system, there is a decrease in the degree of crystallinity and the rate of nucleation in the composition range of 0-10 wt % SBS content. As the SBS concentration in the blend increases from 10 to 30 wt %, there is a sharp increase in the rate of nucleation and degree of crystallinity with a wider spherulitic size distribution. In the composition range of 30-40 wt % SBS content, the degree of crystallinity increases marginally with a slower rate of nucleation and a wider spherulitic size distribution.

In the dynamically vulcanized blends, there is a general decrease of the rate of nucleation and degree of crystallinity accompanied by increase in the spherulitic size distribution with increasing SBS content from 0 to 40 wt %, although there is an increase in the degree of crystallinity in the composition range of 10-20wt % SBS content.

There is a nonlinear increase in the thermal stability with increasing SBS concentration in the

blend. Blending of PP with SBS results in decrease in the yield and tensile modulus and increase in the elongation at break. A distinct role of the crystallinity and crystallite size distribution on the various tensile properties is revealed. The tensile properties are predominantly dependent on the crystallinity in the unvulcanized blends and the crystallite size distribution in the dynamically vulcanized blends.

REFERENCES

- Plochocki, A. P. in Polymer Blends, Vol. 2, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978, p. 319.
- Bianchi, L.; Cimino, S.; Forte, A.; Greco, R.; Martuscelli, E.; Riva, F.; Silvstre, C. J Mater Sci 1985, 20, 895.
- Jang, B. Z.; Uhlmann, D. R.; Vandersande, J. B. J Appl Polym Sci 1984, 29, 4377.
- Varghese, H.; Bhagwan, S. S.; Rao, S. S.; Thomas, S. Eur Polym J 1995, 31, 957.
- Coran A. Y.; Patel, R. Rubb Chem Technol 1983, 56, 210.
- Goettler, L. A.; Richwine, J. R.; Wille, F. J Rubb Chem Technol 1982, 55, 1448.
- 7. Dao, K. C Polymer 1984, 25, 1527.
- Karger-Kocsis J.; Kiss, L. Polym Eng Sci 1987, 27, 254.
- Gupta A. K.; Purwar, S. N. J Appl Polym Sci 1984, 29, 1595.
- 10. Gupta A. K.; Ratnam, B. K. J Appl Polym Sci 1991, 42, 297.
- Choudhary, V.; Varma, H. S.; Varma, I. K Polymer 1991, 32, 2534.
- 12. Doyle, C. J Anal Chem 1961, 33, 77.
- Gupta, A. K.; Gupta, V. B.; Peters, R. H.; Harland, W. G.; Berry, J. P. J Appl Polym Sci 1982, 27, 4669.
- 14. Rybnikar, F. J Appl Polym Sci 1982, 27, 1479.
- 15. Natta G.; Corradini, P. Nuovo Cimento Suppl 1960, 15, 40.
- 16. Ruland, W. Acta Crystallogr 1961, 14, 1180.
- Sotton, M.; Arniaud, A. M.; Rabourdin, C. Bull Sci Inst Text Fr 1978, 7, 265.
- Hawkins, W. L. Polymer Degradation and Stabilisation; Springer-Verlag: Berlin, Heidelberg, New York, 1984; p. 9.
- Kiang, J. K. Y.; Vclen, P. C.; Chien, J. C. W Polym Degrad Stab 1980, 2(2), 13.
- Bevilacqua, E. M. in Thermal Stability of Polymers, Vol.1, R. T. Conley, Ed., Marcel Dekker: New York, 1970; Chapter 7.