

Non-isothermal crystallization behavior of Styrene butadiene rubber/high density polyethylene binary blends

T. K. Jayasree · P. Predeep

Received: 13 February 2011 / Accepted: 19 January 2012 / Published online: 15 February 2012
© Akadémiai Kiadó, Budapest, Hungary 2012

Abstract The thermal and crystallization behavior of the blends are studied by differential scanning calorimetry and XRD. The presence of the amorphous component in the blend is found to influence the non-isothermal crystallization of HDPE. The addition of small quantities of SBR resulted in an increase in the rate of crystallization whereas nucleation is delayed. As compared to HDPE, larger crystallite size, a narrower size distribution, were observed in low SBR (~ up to 30 wt%) content blends. The half time of crystallization also found to reduce as the SBR content in the blend increased. However, a lower degree of crystallinity was observed in these blends. The results thus show that incorporation of SBR in HDPE, while accelerating the rate of crystallization, lower the degree of crystallization. The reduction in the overall crystallization rate at high-SBR content is attributed to a decrease in the growth rate in the later stages of crystallization. It is observed that in dynamically cross-linked blends, the presence of crosslinked SBR that can acts as heterogeneous nuclei facilitated the nucleation of HDPE. However, the crystal growth may be impeded. As a result the overall crystallinity of the crosslinked blends found to decrease.

From XRD profiles it had seen that addition of SBR and dynamic crosslinking does not exert an effect on the crystalline structure of HDPE. The dynamic vulcanization of SBR/HDPE blends enhanced the process of crystallization of HDPE phase. These conclusions are supported by the thermal characterization (DSC) results also.

Keywords Polyblends · Dynamic vulcanization · Melting · Crystallization · DSC/XRD

Introduction

Polyolefin blends attract additional interest due to the possibility of recycling plastic wastes, mainly constituted by polyolefins, avoiding the complex and expensive process of separation of the different components. The practical and theoretical investigation of the properties of the polymer blends which involve a crystallizable and an amorphous component has received great attention now a days. In the case of such blends, the amorphous component may interfere with the crystallization process, inducing modifications in the phase structure of the crystalline polymer. Material characteristics such as latent heat, solvent permeability, and biodegradability all depend on the crystallinity, and thus on the crystallization procedure. Non-isothermal studies are used to elucidate structure development in the melt processing of polymers and isothermal studies are used for investigating the mechanical aspects of crystallization. In the past few years, non-isothermal crystallization studies has been gaining importance because in reality, plastics processed in industry such as fiber spinning, injection molding, and extrusion commonly experience non-isothermal treatments. In this study, the

T. K. Jayasree · P. Predeep (✉)
Laboratory for Unconventional Electronics and Photonics,
Department of Physics, National Institute of Technology,
Calicut 673603, Kerala, India
e-mail: ppredeep@gmail.com

T. K. Jayasree · P. Predeep
Centre for Advanced Scientific Research and Rural Technology,
Kollam, Kerala, India

Present Address:
T. K. Jayasree
Department of Physics, Sree Ayappa College, Thiruvananthoor,
Chengannur 689109, Kerala, India

crystallization of the binary blends was studied under non-isothermal conditions.

When a polymeric material is cooled from the liquid to rubbery state it becomes much stiffer as it goes through a certain temperature range. This stiffening is the result of one of two possible events; crystallization or glass transition. For crystallization to occur the polymer molecule must be sufficiently regular along their length to allow formation of crystalline lattices and the cooling rate must be slow enough for the crystallization process to take place before the molecular motions become too sluggish. Crystallization of polymer blends involves two consecutive processes: the formation of nuclei and their subsequent growth. When the polymer is super cooled below the polymeric melting temperature (T_m), nuclei appear throughout the mass. The nuclei may appear instantaneously at the beginning of the process (heterogeneous nucleation) or they may appear in the untransformed phase throughout the process (homogeneous nucleation). The growth of the nuclei then occurs in one, two, or three dimensions, giving rise to rods, disks, or spheres.

The morphology and melting behavior of the crystallizable component in the blends depends on the miscibility of the blends. Investigation of the crystallization behavior of incompatible polymer blends reveals the origin of changes of crystallization, whether structural, equilibrium thermodynamic, or kinetic. Detailed investigations on the fusion behavior and crystallization kinetics of polymer blends have been studied by various researchers to understand the effect of an amorphous component on the crystalline structure formed by the other component. In immiscible blends the amorphous component which finely disperses within spherulites or in interspherulitic regions in large domains has been found to have little influence on the crystallization of the crystallizable components [1–3] where as in miscible blends very fine intraspherulitic dispersion of the amorphous component is usually seen and in these blends a large decrease of crystal growth and a change of melting behavior caused by the amorphous component may be observed.

In this article, studies of the melting and crystallization behavior of HDPE in the presence of SBR will be presented. The modulus and strength of HDPE are determined by its crystalline structure. Any changes in this structure will result in a change of the properties, so it is essential to determine the effect of elastomer blending on the crystalline structure as well as on the melting and crystallization behavior of HDPE. Knowledge of the crystallization behavior of the thermoplastic elastomeric blend is also necessary for effective manipulation properties and specifies the molding conditions. The effects of crosslinking on the crystallization process are of relevance to our under-

standing of crystallization in general. Of particular interest is the effect of a crosslinked network on the crystallization process through its influence on the diffusional mobility and also on the probability of nucleation. So the effects of crosslinking of the SBR/HDPE blends on the many aspects of fusion and dynamic crystallization behavior of HDPE phase are also studied.

Experimental

Materials used

The materials used for the experiments and their specifications are given in Table 1.

Melt blended specimens of high density polyethylene (HDPE) and styrene butadiene rubber (SBR) with various compositions were prepared using in a Brabender plastimeter with a rotor speed of 60 rpm, at a temperature of 453 K. The standard procedure is reported in detail elsewhere [4].

Designation of the blends

SBR/HDPE blends with 0, 10, 20, 30, 50, and 70% of SBR were designated as S_0 , S_{10} , S_{20} , S_{30} , S_{50} , and S_{70} , respectively. S_{30} blend was crosslinked with three cure systems and the blends were designated as $S_{30}S$, $S_{30}M$, and $S_{30}D$, where the suffix S denotes the sulfur crosslinking system, M denotes the mixed system, comprising both sulfur and dicumyl peroxide and D denotes the peroxide system. The compounding recipe for dynamic vulcanization is given in Table 2.

Crosslink density

The cross-link density of the samples was determined on the basis of equilibrium solvent swelling measurements in toluene at 301 K by the application of well known Flory–Rehner equation for tetrafunctional networks. Circularly cut disc-shaped samples (dia \approx 2.00 cm) and of thickness 2 mm was immersed in toluene. After 24 h, the toluene was refreshed. After another 24 h, the swollen sample was dried, and weighed again. From the degree of swelling, the crosslink density (ν) was calculated by modified Flory–Rehner equation 1,

$$\nu = -\frac{1}{V_s} \frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_r^{1/3} - 0.5 V_r} \quad [\text{Mol ml}^{-1}] \quad (1)$$

where V_s is the molar volume of solvent, V_r is the volume fraction of rubber in the swollen network, V_r is expressed as $V_r = 1/(Ar + 1)$, where A_r is the ratio of the volume of

Table 1 Materials used


Material	Characteristics	Source
Styrene butadiene rubber (Synaprene 1502 grade) $(-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-)_n$ $(-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-)_n$ 	Density 0.938 g/cc Styrene content 21.5-25.5%	Synthetics & Chemicals, Ltd Bareilly (U. P), India
High density polyethylene Injection grade (Relene) $(-\text{CH}_2-\text{CH}_2-\text{CH}_2-)_n$	MFI 20 g/min density 0.964 g/cc	Reliance Industries Ltd Hazaria, Gujarat, India

Table 2 Compounding recipe of crosslinked blends

Ingredients	Sulfur system	Mixed system	Peroxide system
Polymer	100.0	100.0	100.0
ZnO	5.0	5.0	–
Stearic acid	2.0	2.0	–
CBS ^a	1.0	1.0	–
Sulfur	2.2	1.5	–
DCP ^b	–	2.0	4.0

Note Values are given in phr

^a *N*-Cyclohexyl-2-benzothiazyl sulfanamide

^b Dicumyl peroxide

absorbed solvent to that of rubber after swelling. χ is the polymer—swelling solvent interaction parameter or Flory–Huggins parameter.

Differential scanning calorimetry (DSC)

The influence of the second component, of the composition on quantities such as crystallinity, melting, and crystallization temperature of HDPE was studied with the help of a thermal flow type DSC 8230, Rigaku make Sapphire sample was used as a reference. The crystallization and melting behavior were investigated by the following procedure: About 10 mg of the samples were pre heated at 493 K for 1 min to destroy prehistory effects and then cooled at a rate of 10 K min⁻¹ to record the HDPE crystallization behavior; the crystallization exotherms and the crystallization temperature were registered. Thereafter they were reheated at a rate of 10 K min⁻¹ to record the HDPE melting behavior. The melting temperature and the crystallinity were determined from the DSC endotherms.

Wide angle X-ray scattering (WAXS)

Wide angle X-ray diffraction measurements on the various blend samples were performed using a Philips X-ray generator equipped with a microprocessor controlled recorder unit at a scan rate of 0.5 min⁻¹. Radial scans of intensity versus diffracting angle 2θ were recorded in the range

5–80° under identical settings using nickel-filtered Cu K α radiation of wavelength 0.154 nm. An operating voltage of 40 kV and filament current of 30 mA were used.

The X-ray diffraction patterns of the samples were separated into two parts, crystalline and amorphous. By taking SBR to be fully amorphous, the areas under the crystalline and amorphous portions were measured in arbitrary units and the degree of crystallinity (X_c) was measured using the relation,

$$X_c = \frac{I_c}{I_c + I_a} \quad (2)$$

where I_c and I_a represent the integrated intensity corresponding to the crystalline and amorphous phases, respectively, i.e., areas under the respective curves.

Result and discussions

Melting behavior

DSC thermograms of virgin HDPE and its blends with SBR in the regions of melting recorded during the heating cycle are shown in Fig. 1, were used to determine a number of parameters significant in melting behavior. These include the temperature of onset of melting (T_{mo}), the melting peak temperature (T_m), and heat of fusion (ΔH). The various parameters in the melting process are tabulated in Table 3. It can be seen from the table that, the equilibrium melting temperature of HDPE depends on the blend composition. Melting temperatures of crystalline polymers can be related to the size and perfection of their crystal units [5, 6]. HDPE shows a typical endothermic peak (T_m) at 404.7 K. The peak melting temperatures in S₁₀, S₂₀, and S₃₀ compositions are 405.6, 405.4, and 406.2 K, respectively, and the melting endotherms also start at a higher temperature (T_{mo}) in these blends (Fig. 2; Table 3). This is probably due to the larger crystallite size and narrower size distribution of HDPE in these compositions. The HDPE melting range is also considerably smaller for low SBR content blends, compared to HDPE, which also suggests a narrower crystallite distribution. This conclusion is further supported by the considerable decrease in the heat of crystallization of

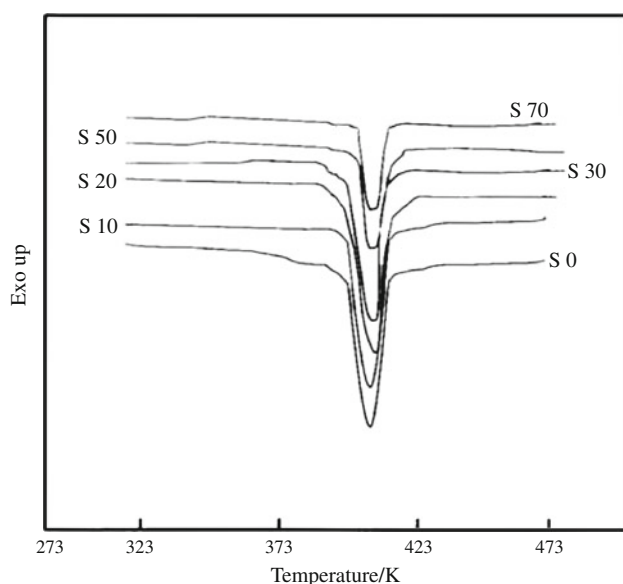


Fig. 1 DSC melting endotherms of HDPE and SBR/HDPE blends

Table 3 Melting characteristics of HDPE in SBR/HDPE blends

System	One set temp T_{mo}/K	Peak temp T_m/K	Heat of fusion $\Delta H \times 10^3/J/kg$
S ₀	384.9	404.7	216.9
S ₁₀	395.8	405.6	149.5
S ₂₀	395.0	405.4	128.3
S ₃₀	391.6	406.2	103.3
S ₅₀	380.2	404.0	53.5
S ₇₀	384.0	401.5	13.26

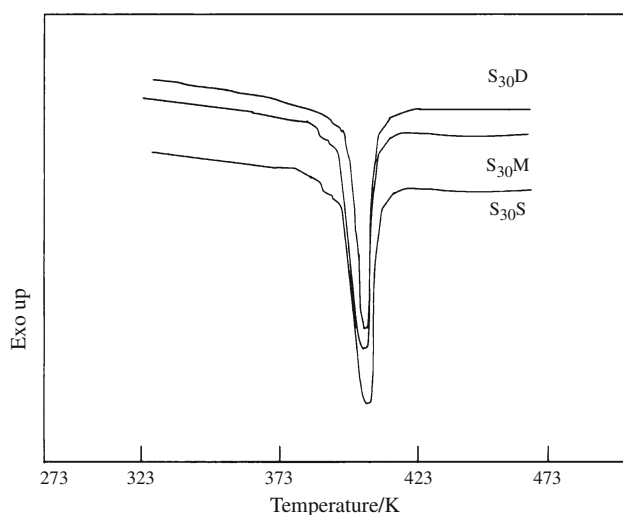


Fig. 2 DSC melting endotherms of dynamically crosslinked S₃₀ blends

HDPE (Table 4) in these blends. These features could be tentatively explained as follows. During melt-mixing in the Brabender, the amorphous content was able to selectively

Table 4 Melting characteristics of HDPE in dynamically crosslinked S₃₀ blends

System	One set temp T_{mo}/K	Peak temp T_m/K	Heat of fusion $\Delta H \times 10^3/J/kg$
S ₃₀	391.6	406.2	110.3
S ₃₀ S	380.0	405.5	105.0
S ₃₀ M	381.8	404.8	103.0
S ₃₀ D	376.2	404.2	97.2

dissolve a certain amount of the more defective HDPE molecules (i.e., of lower molecular weight). Therefore during pressure molding and the successive rapid crystallization this segregation between high molecular weight HDPE and the new SBR/HDPE phase containing defective HDPE chains was still retained. The low molecular weight fraction can crystallize faster than high molecular weight [5, 7]. Hence, more perfect crystals (high T_m and also T_c , the peak crystallization temperature) and narrower distributions of lamellae or crystallite dimension (lower width at half height of T_m and T_c peaks) for the blends than pure HDPE were obtained. Such an increase in T_m has been reported in the case of iPP/EPM copolymer blends [8] at 10 wt% of the elastomer content. A similar change in T_m is reported in the case of iPP/PIB_{LM} blends [9] and HDPE/EPR copolymer blends also [10]. In S₅₀ and S₇₀ blends T_m and the temperature of onset of melting T_{mo} of HDPE phase is lower than that of pure HDPE. This decrease in T_{mo} and T_m in the case of higher rubber content blends is due to the incorporation of SBR in the polymer chain that might bring down the average crystal size. In a crystalline/amorphous system, T_m decreases with the addition of amorphous polymer due to the kinetic effect of the amorphous phase, which may obstruct the growth of the lamellar crystallites or the spherulites of the crystalline phase and there by bringing down the average crystal size. Such a decrease in the melting temperature was observed in the case of polyamide blends with acrylonitrile–butadiene–styrene copolymer (ABS). It has been reported [11, 12] that, even with a complete incompatibility of both polymers in the melt, the observed melting point might decrease. The addition of SBR to HDPE decreases the heat of fusion (ΔH) corresponding to the melting endotherm (Table 3).

The effect of crosslinking of the SBR/HDPE blends on the many aspects of fusion behavior of HDPE phase is also studied. The melting endotherms of dynamically crosslinked S₃₀ blends are shown in Fig. 2. The characteristic melting parameters of crosslinked S₃₀ blends are given in Table 4. Dynamic vulcanization of the blends had made changes in the melting parameters. The melting endotherms of the crosslinked blends starts at a lower

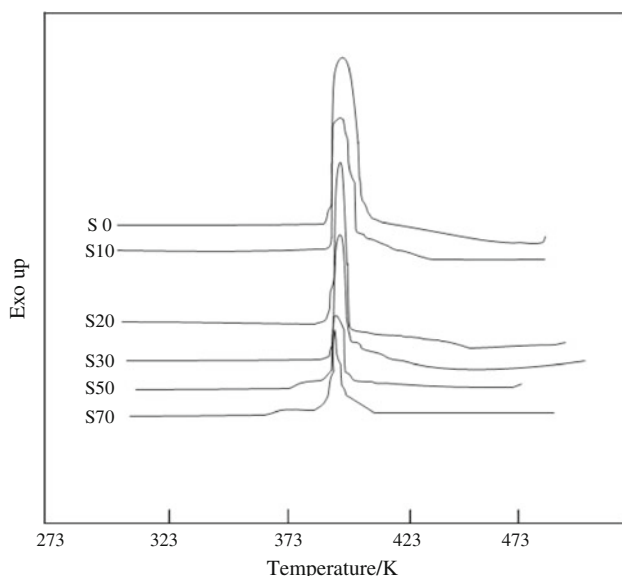
Table 5 Crosslink density of different S₃₀ blends

System	Crosslink density ν /mol/ml
S ₃₀ S	0.126×10^{-3}
S ₃₀ M	0.362×10^{-3}
S ₃₀ D ₁	0.577×10^{-3}
S ₃₀ D ₂	0.981×10^{-3}
S ₃₀ D ₃	1.14×10^{-3}
S ₃₀ D	1.396×10^{-3}

temperature and has a lower peak temperature, compared with those for the uncrosslinked blend. The melting temperature of the crystallites in a crosslinked system is usually lower than that of the uncrosslinked material. In sulfur and mixed systems the melting point depression is negligible, which is ascribed to lower crosslink density values compared to peroxide system. Crosslink densities of different vulcanized SBR/HDPE blends are given in Table 5. Heat of fusion values, ΔH also decreased as a result of vulcanization. Different parameters of uncrosslinked S₃₀ composition are also included in Table 4.

Crystallization behavior

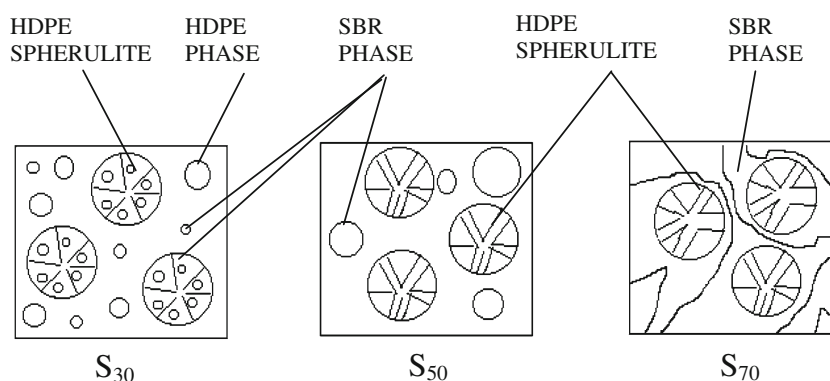
The non-isothermal DSC thermograms of virgin HDPE and its blends with SBR in the regions of crystallization, recorded during the cooling scan are depicted in Fig. 3. The parameters significant in the crystallization behavior such as the temperature of onset of crystallization (T_{co}), which is the temperature where the thermogram initially departs from the baseline on the high temperature side of

**Fig. 3** DSC crystallization exotherms of HDPE and SBR/HDPE blends**Table 6** Crystallization parameters of HDPE in the blends

System	One set temp. T_{co} /K	Peak temp. T_c /K	$\Delta C \times 10^3$ /J/kg	Width at half ht Δ_w /K
S ₀	406.7	398.8	178.3	4.93
S ₁₀	395.5	393.9	133.6	4.32
S ₂₀	395.7	394.2	113.7	3.08
S ₃₀	395.0	393.9	98.3	3.43
S ₅₀	396.6	393.8	57.4	3.5
S ₇₀	396.1	392.4	19.7	3.5

the exotherm, the peak temperature of the crystallization exotherm (T_c), the width at half height of the crystallization peak (Δ_w) and the heat of crystallization (ΔC) are shown in Table 6. Addition of increasing concentration of SBR to HDPE resulted in a decrease in T_{co} of HDPE (398.8 K). A decrease in T_{co} in the blends clearly indicates that the inclusion of a rubbery phase in HDPE results in delayed nucleation. The difference between T_{co} and T_c values of HDPE in the blends were lower than that for pure HDPE (Table 6). Such a decrease in the difference can be attributed to an increase in the rate of crystallization [13, 14]. It has been suggested that the small the difference between the onset and peak temperature ($T_{co}-T_c$), the faster the overall crystallization rate. The onset temperature indicates the beginning of the crystallization process, while the maximum of the exothermic peak indicates the occurrence of the spherulite impingement. The free expansion of spherulites occurs between the onset and peak temperatures. The increase in the peak crystallization temperature of HDPE in the lower SBR content blends relative to virgin HDPE suggested that the crystal growth of HDPE in the blend would take place at a higher temperature leading to larger crystallite size, improved crystal perfection and narrower crystallite size distribution. The addition of elastomer up to ~ 30 wt% delayed the nucleation but accelerated the rate of crystallization. But the incorporation of SBR beyond 30 wt% seems to cause a decrease in the spherulite growth rate. This behavior can be explained as follows: the HDPE spherulites grow in the presence of HDPE melt containing SBR domains as the dispersed phase. This can be schematically represented in Fig. 4. SBR was distributed both in the intra- and inter-spherulitic regions. Spherulite size of HDPE also increased on initial addition of SBR. But on addition of higher amounts of SBR ($>30\%$), the large number of nuclei created, dramatically increase the rate at which the crystallizable polymer was depleted from the amorphous phase and then occluded in interspherulitic regions, acted as physical restraints to the growth of the spherulites, thereby retarding spherulitic growth [15, 16]. In SBR/HDPE blends the presence of SBR concentration above ~ 30 wt% decreased the crystallization rate, owing to a decrease in the spherulite growth rate.

Fig. 4 Illustrative idealization of the crystalline structure of SBR/HDPE blends



These conclusions are supported by the melting characterization of the blends.

Figure 5 shows the plot of wt fraction crystallized with time for SBR/HDPE blends. From the figure, it emerges out that, the HDPE phase in all the blends crystallized much faster than pure HDPE. Another important parameter in describing crystallization kinetics is the crystallization half time ($T_{1/2}$). It is defined as the time spent from the onset of the crystallization to the point at which the crystallization is 50% complete. It should be noted that the reciprocal of the crystallization half time is often used to characterize the overall rate of the crystallization process. The crystallization half time is inversely related to the crystallization rate, i.e., a large crystallization half time corresponds to a slow rate of crystallization. Figure 6 illustrates the dependence of the amorphous content on the crystallization half times of the corresponding binary blends. Addition of SBR in the blend tremendously decreases the crystallization half time of the HDPE phase and a leveling-off of the parameter can be seen after 50 wt% SBR. This indicates that SBR is accelerating the crystallization of the HDPE and is possibly acting as a nucleating agent.

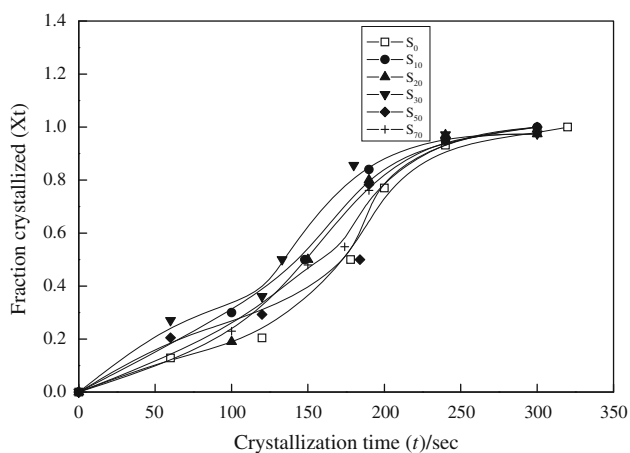


Fig. 5 The fraction transformed with time of SBR/HDPE blends

The width at half height of the crystallization peak Δ_w related to the distribution of crystallite size; the narrower the crystallite size distribution, the smaller will be the Δ_w . On initial addition of 30 wt% SBR a drop can be seen in Δ_w , which then level off to constant values with higher rubber content. Decrease in Δ_w reveals that faster nucleation results in almost simultaneous creation of most crystallites that subsequently grow to form a more uniform crystallite size distribution, where as slow nucleation does not.

The effects of crosslinking on the crystallization process are of relevance to our understanding of crystallization in general. Figure 7 shows the DSC thermograms of the vulcanized S_{30} blends and the thermal data are given in Table 7.

The vulcanized blends register higher onset crystallization temperature (T_{co}) values. A crosslinked network in the blend affects the crystallization process through its influence on the diffusional mobility and also on the probability of nucleation [3, 17, 18]. Among the crosslinked blends, T_{co} is the highest for $S_{30}D$ blend and minimum for $S_{30}S$. $S_{30}M$ takes the medium position. This increase in crystallization temperatures of the blends was ascribed to the crosslinked SBR, which may acts as the nucleating agent.

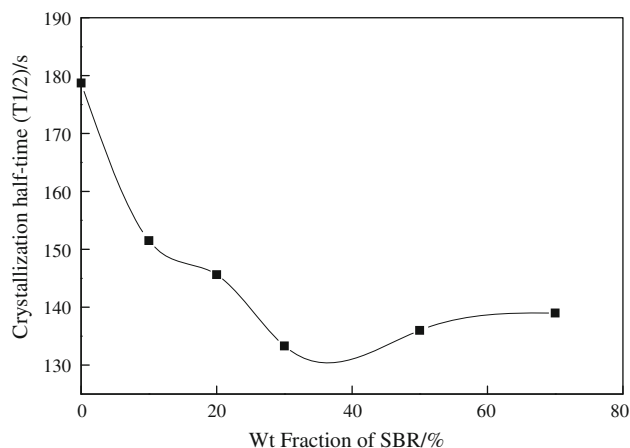


Fig. 6 Half-time of crystallization as a function of SBR content in the blend

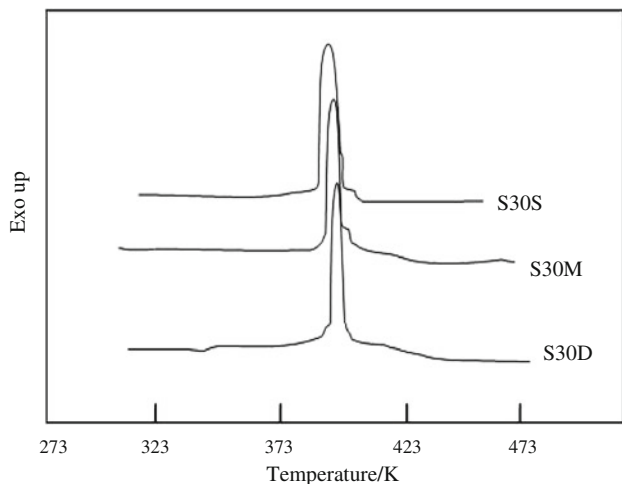


Fig. 7 DSC crystallization exotherms of dynamically crosslinked S₃₀ blends

Table 7 Crystallization parameters of HDPE in dynamically cross-linked S₃₀ blends

System	One set T _{co} /K	Peak T _c /K	ΔC × 10 ³ /J/kg	Width at half ht Δ _w /K	Crystallization half-time/T ^{1/2} /S
S ₃₀	395.0	393.9	98.3	3.43	133.3
S ₃₀ S	397.3	394.6	102.7	3.38	91.8
S ₃₀ M	399.2	395.8	101.2	3.32	86.3
S ₃₀ D	402.8	397.3	108.9	3.32	49.9

The crosslinking of the blend seems to decrease the peak crystallization temperature slightly. However, the difference between the onset and peak temperature of crystallization (T_{co}–T_c) is higher for all vulcanized blends compared with that of unvulcanized one, indicating the retarding influence of crosslinked SBR on HDPE spherulite growth [3, 18]. The over all crystallization rate is the combined effect of two mechanisms; namely nucleation rate and growth rate. It is seen that the presence of small dynamically crosslinked rubber particles, accelerates the crystallization of the semi crystalline polymer HDPE, which is attributed to the formation of a higher number of nuclei during the process, due to better dispersion of the elastomeric phase. The increase in the nucleation density increased the crystallization rate, but due to the increase of viscosity that the system undergoes with crosslinking decreases the spherulite growth rate [19, 20]. Crystallization of polymers proceeds via two process: diffusion and absorption of the crystallizable polymer on the crystal growth surface. The rigid crosslinked amorphous component was unable to diffuse to the spherulitic growth sites [13, 16]. The width of the crystallization exotherm (Δ_w) measured at half height (Table 7) was also found to decreased upon crosslinking, indicating faster nucleation.

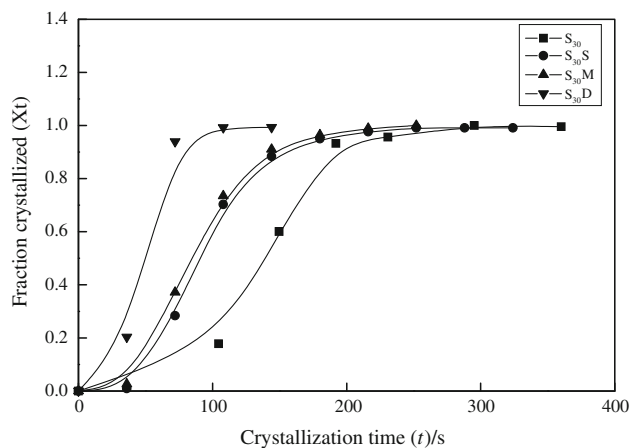


Fig. 8 The fraction transformed versus time of dynamically cross-linked S₃₀ blends

The fraction transformed with time of the crosslinked S₃₀ blends is given in Fig. 8. It can be seen that the rate of crystallization of the dynamically cured samples is higher than those of uncrosslinked blends, which is reflected in the notable decrease of the half time of crystallization. The crystallization half times of S₃₀ blend with different crosslinking systems are tabulated in Table 7. This reduction in crystallization half time (T_{1/2}) occurs as a result of dynamic crosslinking. The decrease is more evident in the case of S₃₀D system. The reduction observed for the half time indicates that the crosslinked SBR bond to HDPE molecule chain may increase the nucleation rate.

Crystallinity of SBR/HDPE blends

Crystallinity measurements offer a useful way to ascertain the influence of SBR on the crystallization behavior of SBR/HDPE blends. The percentage crystallinity X_c of the blend was calculated from the diffraction patterns as explained in the experimental section.

Crystallinity of the material can also be estimated if the latent heat of fusion of a perfect crystal is known. For HDPE it is generally accepted that a value for the latent heat of fusion in the neighborhood of 289.8 × 10³ J/Kg is appropriate. The heat of fusion value depends on the crystallinity of the material and was calculated using the relation ship:

$$X_c = \frac{\Delta H}{\Delta H_0} \times 100 \tag{3}$$

where ΔH₀ is the heat of fusion of 100% crystalline HDPE. The values of the crystallinity degrees of HDPE in the blends presented in Table 8. Addition of the amorphous component SBR causes a serious drop in overall crystallinity of HDPE in the blends, which is due to the migration of SBR into the crystalline phase of pure HDPE, reducing

Table 8 Degree of crystallization (X_c)/% of HDPE in SBR/HDPE blends

System	Degree of crystallization X_c /%	
	DSC	XRD
S ₀	74.8	79.4
S ₁₀	51.5	56.2
S ₂₀	44.2	50.1
S ₃₀	38.0	42.5
S ₅₀	18.4	23.4
S ₇₀	4.6	6.4
S ₃₀ S	36.2	41.5
S ₃₀ M	35.5	40.2
S ₃₀ D	33.5	38.3

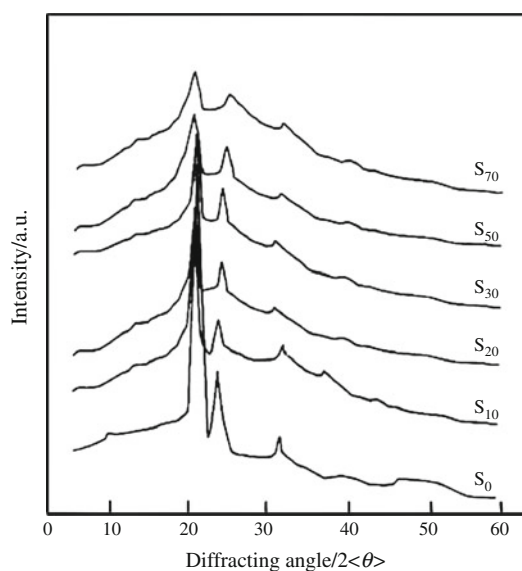
the crystalline domains of the HDPE sample. The crystallization of HDPE segments is controlled by the segmental diffusion rate of other polymeric chains. The separation is enhanced as rubber content is increased. Incomplete crystallization thus leads to decrease in ΔH and hence crystallinity. Thus, the progressive addition of SBR results in continuous decrease of crystallinity.

Crosslinking also produced a reduction in the crystallinities of the blends. The degree crystallinity of HDPE phase in sulfur-cured SBR/HDPE system is 41.5%, which is less than the corresponding uncrosslinked SBR/HDPE system. Sulfur crosslinks the SBR phase in SBR/HDPE system. It retards the crystallite growth rate and hinders the crystallization of HDPE from the melt. In the mixed and peroxide cured systems crystallinity got reduced still further because dicumyl peroxide can react with polyethylene in the melt unlike sulfur system. Crystallinity measurements from DSC are also provided in the same table. As can be seen, the degree of crystallinity of HDPE in different blends measured by XRD is higher than that determined by DSC. This is in tune with the observation that the value of X_c depends very much on the method of preparation of the sample and the technique of measurement. The lower value of crystallinity from DSC as compared to XRD has also been reported earlier [16, 17].

X-ray diffraction profiles (XRD)

The X-ray diffractograms of SBR/HDPE blends were taken and examined in order to ascertain if changes in the fine structure were induced while blending and vulcanization.

Figure 9 shows the XRD peak profiles of the virgin HDPE and its blends. XRD of HDPE reveals high intensity peaks, which correspond to the crystalline regions and low intensity bands, correspond to the amorphous regions. The distribution of the scattering intensity for a blend is a superposition of contribution from each component. The

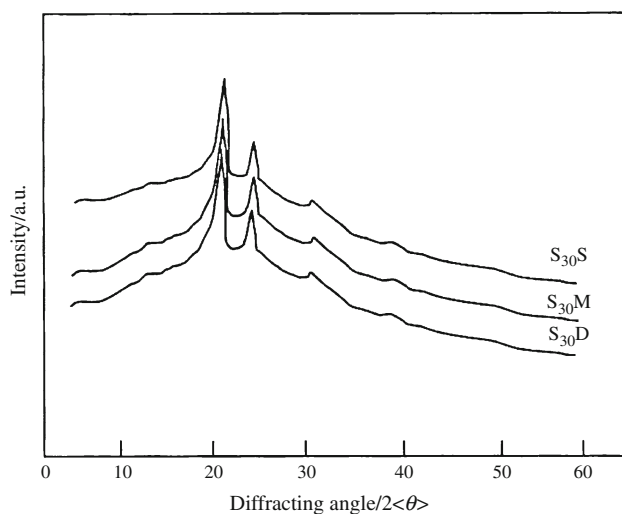
**Fig. 9** X-ray diffraction profiles of HDPE and SBR/HDPE blends

crystalline structure of HDPE is orthorhombic, with lattice constant $a = 0.742$ nm, $b = 0.495$ nm, and $c = 0.255$ nm, corresponding to 21.8° (110 plane), 24.3° (200 plane), and 36.5° (020 plane), respectively. For the blends the positions of the Bragg diffraction peaks do not shift significantly with respect to those of pure HDPE. This clearly indicates that the crystal structure of HDPE remains unchanged upon addition of different weight percentages of SBR, i.e., addition of SBR did not exert an effect on the crystalline structure of the PE through out the composition range, indicating the occurrence of no molecular level interaction. As the SBR content in the blend increases, the intensity of the crystalline diffraction peaks decreases and there is an enhancement of the diffuse amorphous scattering. These variations in the peak heights could be due to the variation of the mean spherulite size or their distribution, deformation at the spherulite boundaries or any long-range order induced in the structure by the dispersion of SBR domains in the HDPE matrix [21, 22]. The width at half height of the XRD peaks also increased upon the addition of SBR. This also indicates the increase in amorphous nature of the blends as compared to the virgin HDPE. Further more, the d -values corresponding to different planes obtained from XRD studies also increase with the initial addition of SBR (Table 9). This is due to the migration of rubber particles in the intra-spherulitic structure of HDPE [18, 20]. However, when the SBR content increased to 50 wt% and above, the d -values decreased than that of pure PE. This indicates that the rubber particles have been occluded in the interspherulitic regions due to the increased size of the rubber particles at higher concentrations [13, 16].

The XRD patterns of dynamically vulcanized S₃₀ compositions are shown in Fig. 10. The XRD data of the

Table 9 XRD parameters of SBR/HDPE blends

System	Reflections					
	100		200		020	
	$2\theta/^\circ$	d/nm	$2\theta/^\circ$	d/nm	$2\theta/^\circ$	d/nm
S ₀	21.0	0.418	23.76	0.374	35.95	0.249
S ₁₀	21.0	0.424	23.53	0.377	35.84	0.250
S ₂₀	20.82	0.426	23.87	0.375	36.14	0.252
S ₃₀	21.41	0.421	23.83	0.375	36.1	0.250
S ₅₀	21.42	0.418	23.65	0.374	35.89	0.248
S ₇₀	21.84	0.412	22.91	0.372	35.52	0.247

**Fig. 10** X-ray diffraction profiles of dynamically crosslinked S₃₀ blends**Table 10** XRD parameters of dynamically crosslinked SBR/HDPE blends

System	Reflections					
	100		200		020	
	$2\theta/^\circ$	d/nm	$2\theta/^\circ$	d/nm	$2\theta/^\circ$	d/nm
S ₃₀	21.41	0.421	23.83	0.375	36.1	0.250
S ₃₀ S	21.84	0.422	24.24	0.382	36.49	0.253
S ₃₀ M	21.84	0.426	24.22	0.386	36.48	0.256
S ₃₀ D	21.65	0.426	24.13	0.386	36.39	0.256

crosslinked blends are given in Table 10. As can be seen, crosslinking did not make any appreciable change in the 2θ values corresponding to the position of the main XRD peaks, i.e., dynamic curing did not alter the crystal structure of HDPE in the blends. The d -values are also reported in the same table, corresponding to different planes. There is an increase in d -values corresponding to different planes as compared with the unvulcanized blend. The increase in interplanar distance shows the appreciable migration of

rubber into the interchain space of HDPE. The width at half height of the diffraction maxima was also found to increase upon vulcanization, which revealed the presence of intraspherulitic dispersion of the crosslinked SBR. The increase in the nucleation density in the polymer increases the crystallization rate. These results thus provide support for the DSC observation that dynamic vulcanization of SBR/HDPE blends results in a better crystallization of HDPE phase.

Conclusions

As expected, the effects of the amorphous polymer on the nucleation, crystallization and crystallinity of the crystalline polymer HDPE are by no means negligible. The addition of SBR up to ~ 30 wt% delayed the nucleation, but accelerates the rate of crystallization of HDPE. However, a large amount of SBR content (>30 wt%) in the blends retards and hinders the crystallization of the matrix polymer. The presence of small rubber particles-dynamically crosslinked, accelerates the crystallization of the matrix, which can be attributed to the formation of a higher number of nuclei. The nucleation effect causes an increase of the overall crystallization rate. But due to the increased rigidity of the crosslinked amorphous component, it was unable to diffuse into the spherulitic growth sites, thereby obstructing the spherulite growth rate. This results in reducing the overall rate of crystallization. For the uncrosslinked and crosslinked SBR/HDPE blends, the positions of the Bragg diffraction peaks do not shift significantly with respect to those of neat HDPE, so no change in unit cell dimensions and hence in crystal structure is apparent. From these results, it was concluded that the processing conditions or preparation method of dynamic curing did not alter the crystal structure of HDPE. Blending of HDPE with small quantities of SBR may accelerate the crystallization of HDPE. Crosslinking of the blends also found to be effective in creating nucleation sites for crystallization and also effective in enhancing crystallization from the melt. To be a useful engineering plastic material for injection molding applications, HDPE must have the ability to crystallize rapidly, as it is cooled from the melt. The rapid crystallization of HDPE from the melt in the presence of SBR would be helpful in lowering the mold temperature and shortening the mold cycle.

References

- Sreeja R, Predeep P. Electro-optic materials from co-polymeric elastomer-acrylonitrile butadiene rubber (NBR). *Polymer*. 2006; 47:617–22.
- Yang J, McCoy BJ, Madras G. Kinetics of nonisothermal polymer crystallization. *J Phys Chem B*. 2002;109(39):18550–7.

3. Liu YJ, Guo W, Su Z, Li B, Wu C. Non-isothermal crystallization of recycled poly(ethyleneterephthalate)/poly (ethylene octene) blends. *J Macro Mol Sci Part B*. 2009;48(2):414–29.
4. Jayasree TK, Predeep P. Thermal conductivity and Thermal diffusivity of Thermoplastic elastomeric blends of SBR/HDPE; Effect of blend ratio and dynamic crosslinking. *Trends Appl Sci Res*. 2006;1(3):278–91.
5. Choudhury NR, Chaki TK, Bhowmick AK. Thermal characterization of thermoplastic elastomeric natural rubber-polypropylene blends. *Thermochim Acta*. 1991;176(25):149–61.
6. Sreeja R, Quamara JK, Predeep P. Development of transparent flexibleconducting thin films by in- situ dispersion, polymerization of pyrrole in prevulcanized NR latex. *Mater Manufact Proc*. 2007;22(1):561–7.
7. Ou C-F, Chao M-S, Huang S-L. The crystallization behaviors of PBT blended with co[poly(butylene terephthalate-*p*-oxybenzoate)] copolyesters. *Eur Polym J*. 2000;36(12):2665–70.
8. Seki M, Yamauchi S, Matsushita Y. Miscibility and crystallisation kinetics for the blend of iPP/ethylene-propylene random copolymer. *J Phys Chem Sol*. 1999;60(8/9):1333–6.
9. Ma G-Q, Sun H, Li J-Q, Zhao Y-H, Sheng J, Yu M (2008) Confined crystallization in polymer blends: DSC studies of the behavior and kinetics of isothermal crystallization of PP in poly(cis-butadiene) rubber blends. *J Macro Mol Sci Part B*. 2008; 47(5): 874–90.
10. Yang J, McCoy BJ, Madras G. A distribution kinetics approach for crystallization of polymer blends. *J Phys Chem B*. 2006; 110(31):15198–204.
11. George S, Varughese KT, Thomas S. Thermal and crystallization behavior of isotactic polypropylene/nitrile rubber blends. *Polymer*. 2000;41(14):5485–503.
12. Pratap A, Sharma K. Applications of some thermo-analytical techniques to glasses and polymers. *J Thermal Anal Calorim*. 2011;106(1):47–52.
13. Kishore K, Vasanthakumari R. Crystallization behaviour of polyethylene and i-polybutene-1 blends. *Polymer*. 1986;27(3): 337–43.
14. Huang H, Gu L, Ozaki Y. Non-isothermal crystallization and thermal transitions of a biodegradable, partially hydrolyzed poly(vinyl alcohol). *Polymer*. 2006; 47: 3935–45.
15. Maria LauraDiLorenzo, Cimmino S, Silvestre C. Nonisothermal crystallization of isotactic polypropylene blended with poly(α -pinene). 2. Growth rates. *J Macro Mol*. 2000;3(10):3828–32.
16. Suri S, Bamzai KK, Singh V. Growth and thermal kinetics of pure and cadmium doped barium phosphate single crystal. *J Thermal Anal Calorim*. 2011; 105(1): 229–38.
17. Ziabicki A, Sakjiewitz A. Crystallisation of polymers in variable external conditions.III: experimental determination of kinetic characteristics. *Colloid Polym Sci*. 1998;276(8):680–9.
18. Wang Y, Shen H, Li G, Mai K. Crystallization and melting behavior of PP/CaCO₃ nanocomposites during thermo-oxidative degradation. *J Thermal Anal Calorim*. 2010;100(3):999–1008.
19. Li G, Wang K, Li S, Shi Y. Isothermal melt crystallization kinetics for poly(trimethylene terephthalate)/poly(butylene terephthalate) blends. *J Macro Mol Sci Part B*. 2007; 46: 569–80.
20. Majhi K, Varma KBR. Crystallization kinetics of SrBi₂B₂O₇ glasses by non-isothermal methods. *J Thermal Anal Calorim*. 2009;98(3):731–6.
21. Li Z, Wang Y-Z, Yang K-K, Wang X-L, Chen S-C, Li J. Effect of PEG on the crystallization of PPDO/PEG blends. *Euro Polym J*. 2005;41(6):1243–50.
22. Cimmino S, Di E, Martuscelli E, Silvestre C. Syndiotactic polystyrene-based blends: crystallization and phase structure. *Polymer*. 1993;34(13):2799–803.