The Role of Styrene–Ethylene/Butylene–Styrene Triblock Copolymer as Impact Modifier in Polypropylene–Polyethylene Blends

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SYNOPSIS

The crystallization behavior of an isotactic polypropylene/linear low-density polyethylene blend (PP/LLDPE) that is modified with styrene–ethylene/butylene–styrene triblock copolymer (SEBS) has been investigated using differential thermoanalysis and polarization microscopy. SEBS, which enhances the impact resistance of the blend, has an effect on both the nucleation and crystallization kinetics of the polypropylene component. Nucleation half times, nucleation densities, and spherulite growth rates are influenced by the presence of the copolymer. It is found that SEBS, depending on its concentration in the blend, increases the adhesion between matrix and PE domains and acts simultaneously as the matrix reinforcer. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

A usual way to improve the impact properties of thermoplastics is the modification with other thermoplastics or with rubbers. It is, for example, possible to increase the impact resistance of polypropylene by blending it with polyethylene.[1-5] A further increase can be achieved by adding ethylene–propylene rubbers like EPDM or EPR.[6-11]

Recently it was found that a styrene-rubber-styrene triblock copolymer (styrene–ethylene/butylene–styrene, SEBS) also considerably enhances the impact resistance of polypropylene/polyethylene, polypropylene/polycarbonate, and polyethylene/polystyrene blends.[12-16] It was discussed that in these systems SEBS may act as an interfacial agent.[12,17]

Interfacial agents or compatibilizers are used to prevent gross segregation and to permit finer dispersion of the polyethylene component. This effect should be accompanied by morphological changes of the iPP matrix. The concept that SEBS modifies the interface between the components in PP/PE blends is certainly unusual because, due to its architecture, this copolymer should compatibilize only mixtures of styrenics with polyolefins or polyphenylene ethers and polyolefins. On the other hand, SEBS is expected to act in PP/PE blends as a matrix reinforcer by forming a thermoreversible network.[18] Some insight into this problem can be given by investigating the influence of SEBS concentration on the crystallization behavior (nucleation and crystal growth) of the iPP matrix and the dispersion of the compatibilizer in the blend. In this paper the nucleation and crystal growth of iPP in its blend with linear low-density polyethylene (LLDPE) and SEBS under isothermal and nonisothermal conditions are investigated.

EXPERIMENTAL

Sample Preparation

Blends of 80 wt % isotactic polypropylene and 20 wt % linear low-density polyethylene were prepared by dissolving both components in hot *o*-xylene at 120°C followed by precipitation into a large excess of cooled methanol. Keeping the composition of iPP/LLDPE constant (4 : 1), styrene–ethylene/butylene–styrene copolymer was added in concentrations 0, 5, 10, 15, and 20 wt %, respectively. The polymer characterization data are given in Table I.

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Samples for investigation in the calorimeter and under the optical microscope were prepared in a laboratory press.

Calorimetry

The crystallization and melting of the samples was measured in a calorimeter (Netzsch heat flux DTA) under the following conditions. Each sample ($\sim$ 8 mg) was heated up to 473 K with a rate of 5 K/min and then cooled at a cooling rate of -5 K/min to 293 K. After the crystallization was completed, the sample was heated again with the same heating rate to 473 K (second run). Three samples for each composition were measured.

From the crystallization and melting curves, the following parameters were determined[19] (cf. Fig. 1). T_p denotes the peak temperature of the crystallization, T_{onset} the onset-temperature (i.e., temperature at which the thermogram deviates from the baseline), T_c the extrapolated onset-temperature, T_p^m the temperature of the melting peak (i.e., melting temperature), T_{offset}^m the offset-temperature of the melting curve, T_c^m the extrapolated offset-temperature, and ΔT the supercooling.

Microscopy

For observation in the optical microscope (Leitz Metallux II) the samples were placed between microscope slides and put in a Mettler hot stage. Here they were heated to 200°C for 5 min and then cooled to the chosen crystallization temperature T_c. Crossed polarizers were used, and the crystallization was monitored on a video screen. The images were digitized and recorded on a computer hard disk. The crystallization temperatures for the isothermal crystallization were chosen between 130 and 140°C. Each crystallization experiment was performed five to ten times, depending on the crystallization temperature, using separately prepared samples.

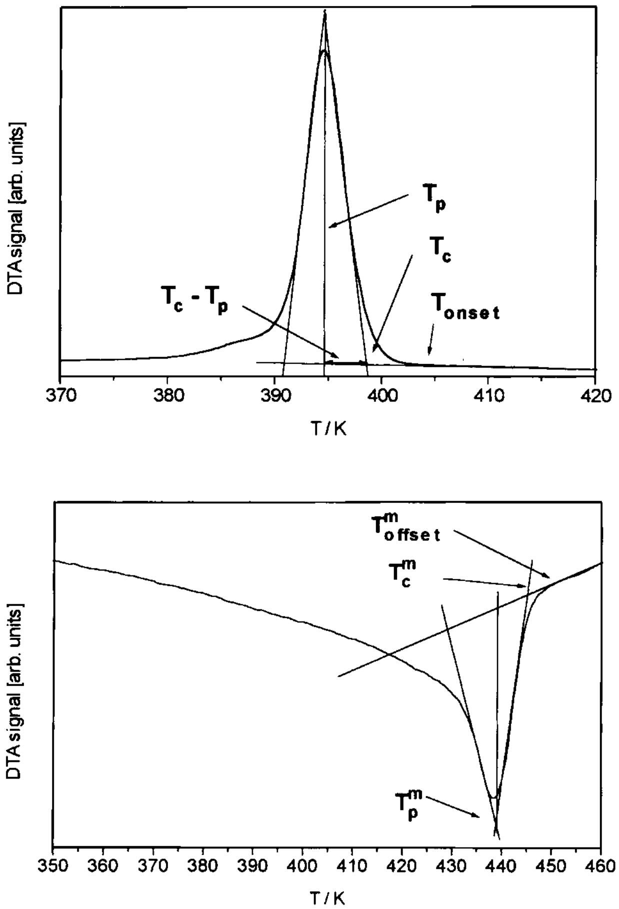

Figure 1 DTA melting and crystallization curves for iPP/LLDPE 80/20 wt % showing the determined characteristic temperatures.

RESULTS

Calorimetry

From the measured crystallization curves, some characteristics concerning the crystallization behavior can be derived.[19] The crystallization temperature, T_p, is a function of the cooling rate and is related to the supercooling of the sample. T_c, the extrapolated onset-temperature, reveals the beginning of the crystallization and is proportional to T_p.

Table I Polymer Characterization Data

Polymer	ρ/g cm^{-3}	T_m/K	M_n	M_w/M_n
iPP	0.905	166.4	57000	5.14
LLDPE	0.919	122.5	30300	3.7
SEBS	0.899		42000	1.09

Table II Results of DTA Experiments

a) Crystallization Data

SEBS Content in Wt %	T_p/K	T_c/K	T_{onset}/K	$T_c - T_p/K$
0	390.6	395.3	400.3	4.8
1	390.7	395.3	399.8	4.6
2	390.8	394.7	399.2	4.3
5	390.5	394.7	400.9	4.2
10	391.9	395.8	400.9	3.9
20	391.5	395.0	400.2	4.0

b) Melting Data

SEBS Content in Wt %	T_p^m/K	T_c^m/K	T_{offset}^m/K	$T_c^m - T_p^m/K$	$\Delta T/K$
0	440.1	448.8	451.8	8.7	49.5
1	437.7	445.6	448.9	7.7	47.2
2	437.2	445.3	449.3	8.1	46.9
5	437.1	445.0	449.9	7.9	46.6
10	437.8	445.2	450.2	7.3	45.9
20	437.2	445.1	449.8	7.5	46.0

The onset-temperature, T_{onset}, is roughly proportional to the rate of nucleation. An inspection of Table II, where these temperatures are listed, shows that values vary minimally with sample composition. A stronger dependence on the SEBS content shows the difference between crystallization and peak temperatures, $T_c - T_p$, which is a measure of the crystallization half time, $t_{c,1/2}$, and proportional to the maximum spherulite growth rate.[19]

Microscopy

From the observation of the number of nuclei as a function of time and the growth of the spherulites under the polarization microscope, a number of kinetical parameters can be derived.[20]

The nucleation rate is given by

$$\dot{N}(t) = \nu \cdot M \cdot \exp(-\nu t) \qquad (1)$$

where N is the number of nuclei per unit volume, ν the nucleation frequency, and M the nucleation density. Nucleation densities and nucleation half times, $t_{1/2}$, are obtained from the plot of the number of nuclei, N, as a function of time. In Figures 2 and 3 M and $t_{1/2}$ are plotted over the SEBS concentration.

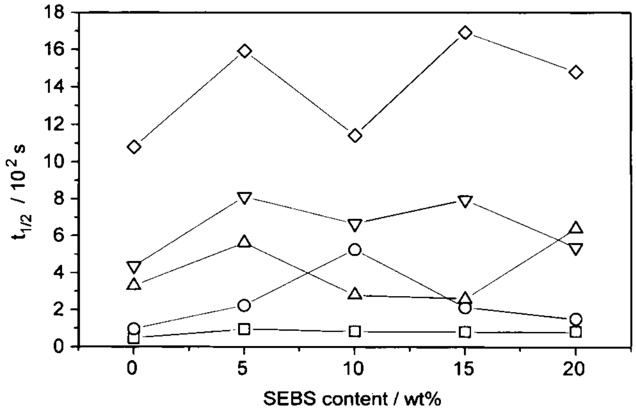

Figure 2 Nucleation half times of iPP nuclei in an iPP/LLDPE/SEBS blend as functions of SEBS weight content for the crystallization temperatures: (□) 400 K, (○) 403 K, (△) 406 K, (▽) 408 K, (◇) 411 K.

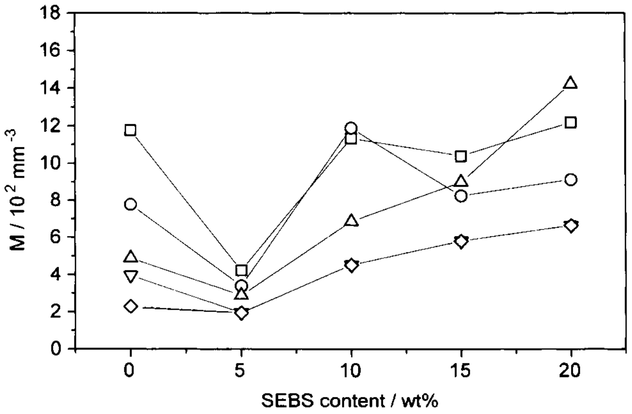

Figure 3 Nucleation densities of iPP nuclei in an iPP/LLDPE/SEBS blend as functions of SEBS weight content for the crystallization temperatures: (□) 400 K, (○) 403 K, (△) 406 K, (▽) 408 K, (◇) 411 K.

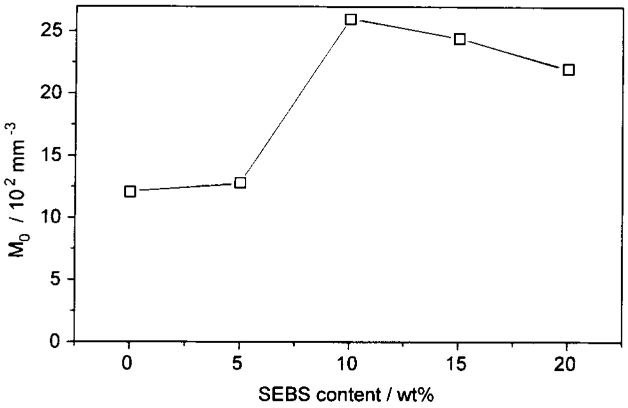

Figure 4 Total nucleation density of iPP nuclei in an iPP/LLDPE/SEBS blend as a function of SEBS weight content.

The total nucleation density, M_0, is calculated by fitting the equation

$$M(T_c) = M_0\left[1 - \gamma \int \exp(-\pi\gamma^2(T_{1/2} - T_c)^2)\, dT\right] \tag{2}$$

with $\gamma = 1/(\sigma\sqrt{2\pi})$ and where σ = variance, M_0 = total nucleation density, and $T_{1/2}$ = temperature at $M_0/2$. Figure 4 shows M_0 over the SEBS concentration. The spherulite growth rate, which is a function of the crystallization temperature, can be written as[20]

$$G(T_c) = G_0 \exp\left(\frac{-C_1C_2}{C_2 + T_c - T_g}\right) \times \exp\left(\frac{-C_3}{T_c(T_m - T_c)}\right) \tag{3}$$

where T_g is the glass transition temperature, T_m is the melting temperature, and G_0, C_1, C_2, and C_3 are constants; G_0 and C_3 can be determined from a plot of $\ln(G + C_1/C_2 + T_c - T_g)$ versus $1/[T_c(T_m - T_c)]$, while the values of C_1 and C_2 are taken from the literature (C_1 = 25, C_2 = 30 K[20]). From the maximum of the curve, the maximum growth rate, $G_{\max}$, and the corresponding temperature, $T_{G_{\max}}$, can be obtained. $G_{\max}$ and $T_{G_{\max}}$ are plotted in Figures 5 and 6, respectively.

A measure for the mode of nucleation is the Avrami exponent, n.[21] This exponent can be determined[22] (i) by measuring the crystallinity of the sample, X_c, as a function of time and plotting $\ln(-\ln(1 - X_c))$ versus $\ln(t)$ (n is yielded from the slope of the straight line) or (ii) by using the volume half time, $t_{v,1/2}$, and calculating n from

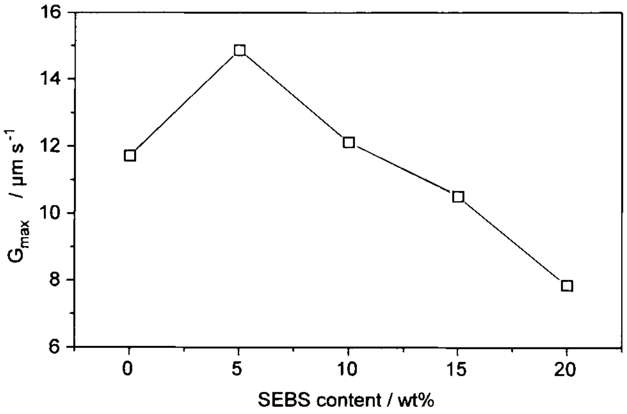

Figure 5 Maximal spherulite growth rate as a function of SEBS weight content.

$$n = \frac{\log((3 \ln 2)/4\pi G_m^3 M)}{\log t} \tag{4}$$

at $t = t_{v,1/2}$. Both methods yield different values (cf. Fig. 8).

DISCUSSION

Isotactic polypropylene and linear low-density polyethylene are considered to be strictly incompatible. However, it has been found that there is only limited segregation and that the dispersion of the PE component depends on the concentration of the minor component and on the mixing conditions. A finer dispersion obviously influences the mode of nucleation of the PP nuclei because then the dispersed particles provide a higher interface area, causing the Avrami exponent to decrease.[20,21] In our samples the value of the Avrami exponent indicates

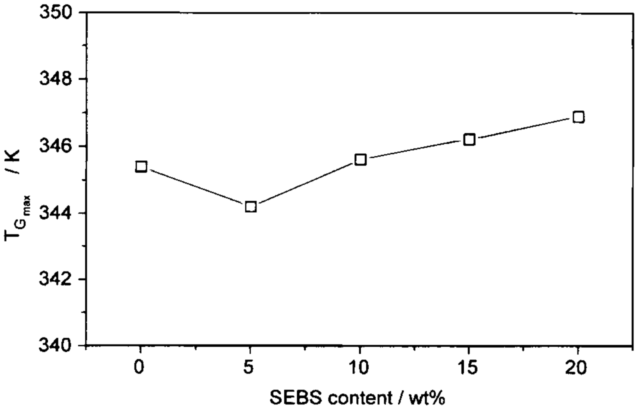

Figure 6 Crystallization temperature of $T_{G_{\max}}$ as a function of SEBS weight content.

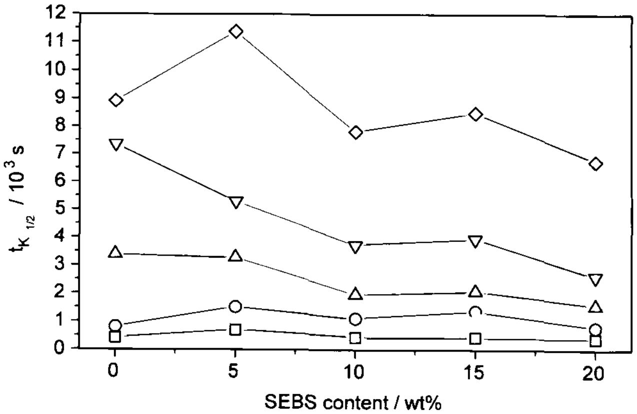

Figure 7 Crystallization half times of an iPP/LLDPE/SEBS blend as functions of SEBS weight content for the crystallization temperatures: (□) 400 K, (○) 403 K, (△) 406 K, (▽) 408 K, (◇) 411 K.

that a large interface between the two components must have been formed. The exponent n is clearly below 3, which indicates a more heterogeneous nucleation, but also above 2, which means that the nucleation is also partly homogeneous. It is rather homogeneous in the PP matrix and preferentially heterogeneous at the iPP/LLDPE interfaces.

The dispersion of the PE component in the matrix increases the impact resistance of the system, however not to its possible maximum, due to the incomplete transfer of load between matrix and PE domains. The addition of SEBS to the iPP/LLDPE blend can increase the adhesion between matrix and PE domains (i) by modifying the interface or (ii) by acting as a matrix hardener through its role as physical crosslinker and reinforcer of the matrix. The reinforcing effect of SEBS depends on the dispersion of the copolymer in the matrix and on the location of the SEBS clusters. Only when SEBS is located at the PE domains may it play a role as interfacial agent. The results of the kinetical investigations allow a discussion of these mechanisms. In principle, the following three different morphologies are possible.

1. SEBS mixes with the amorphous phase of the matrix.
2. It builds up separate domains within the iPP/LLDPE matrix.
3. It coats the surface of the LLDPE domains.

For all three cases we should find specific dependencies of the kinetical parameters on the SEBS concentration.

If SEBS mixes with the matrix, the free enthalpy of activation should increase and consequently the nucleation rate should decrease. Then, with an increasing concentration of SEBS in the blend, we should measure a higher nucleation half time and a lower nucleation density. As Figures 2 and 3 show, this is not the case, at least not for SEBS concentrations above 5%. Also the total nucleation density should decrease. Figure 4 shows that M_0 increases for SEBS concentrations > 5%. We further expect that the maximum spherulite growth rate, $G_{\max}$, decreases with increasing SEBS content because the spherulitic growth is hindered by the presence of the SEBS chains. We see (Fig. 5) that $G_{\max}$ indeed decreases, however only for higher SEBS concentrations. Concurrently the corresponding temperature $T_{G_{\max}}$ (Fig. 6) increases for SEBS concentrations above 5%. The crystallization half times, $t_{1/2}$ (Fig. 7), decrease slightly with the SEBS content, but this decrease does not *correlate with a possible increase in the amorphous* phase of the matrix. Therefore, we conclude that for concentrations above 5% SEBS does not dissolve in the matrix.

Thus, a phase separation of the matrix and SEBS seems to be possible. SEBS would form separate domains that should, through its interfaces, influence the mode of nucleation of the matrix. Because the nucleation should then become even more heterogeneous, the Avrami exponent should further decrease with rising SEBS content. The measured Avrami exponent (Fig. 8) varies only slightly with the SEBS concentration in the blend. However, it is known that primary nucleation in isotactic polypropylene is preferentially heterogeneous.[23,24] This may be an effect of catalyst residues, but it seems

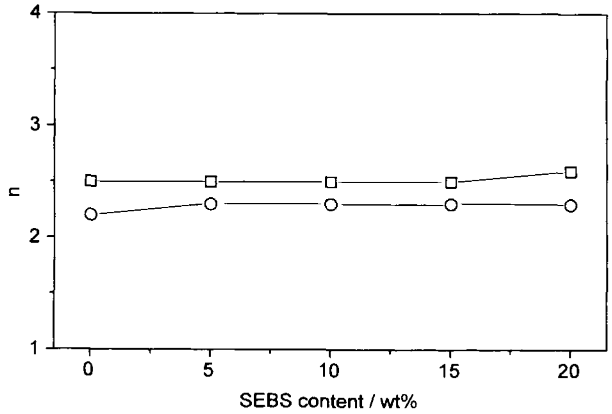

Figure 8 Avrami exponents as functions of SEBS weight content, determined by (□) plotting ln(−ln(1 − X_c)) versus ln(t) (Avrami plot), (○) using eq. (4).

that already natural impurities are responsible for this behavior.[25] Therefore, in unseeded PP one observes a mixture of homogeneous and heterogeneous nucleation[26] and the Avrami exponent should be between 2 and 3. Here, the interface volume may be too small to contr2ibute considerably to the overall Avrami exponent. On the other hand, we see the spherulitic growth rate decreasing and the total nucleation density increasing for SEBS concentrations $> 5\%$. We therefore conclude that for low SEBS concentrations SEBS does not form separate domains, while for higher SEBS concentrations this seems likely. On the other hand, the assumption that at least part of the SEBS coats the LLDPE particles cannot be totally excluded. In this case, part of the SEBS component increases the interface volume by migrating into the existing interface, but it does not further increase the interface area that is responsible for the heterogeneous nucleation. Consequently, the Avrami exponent does not change. Nucleation half times and spherulite growth rates should equally not change. However, we find a dependency of both parameters on the SEBS concentration in a way that suggests there might exist an "optimal" SEBS concentration. It is known that the mass of the compatibilizer that is necessary to cover the interface is connected with the original blend volume (without compatibilizer):[27] Mass of compatibilizer/original blend volume = $(3\Phi_A M/aRN)$, where Φ_A is the volume fraction of LLDPE dissolved in iPP, M the molecular weight, a the interface area covered by the compatibilizer, R the radius of the LLDPE domains, and N the Avogadros number. Does the SEBS exceed the concentration given by this equation? It forms a separate phase in the iPP/LLDPE matrix. Because we could not measure the sizes of the LLDPE domains (or the interface area), we were not able to determine the maximal compatibilizer concentration. On the other hand, the results of the kinetical measurements yield this value in good approximation. Above 5% SEBS content, some parameters (M_0, $G_{\max}$, $T_{G_{\max}}$) reveal interactions between SEBS and the matrix. We conclude that part of the SEBS indeed may act as a compatibilizer in the system iPP/LLDPE in so far as it collects in the interface between iPP and LLDPE, thus modifying the compatibility between both components. This effect has its maximum at a SEBS concentration around 5%. Above this concentration, SEBS partly forms domains and influences both the nucleation and spherulite growth.

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