Investigation of the structure of isotactic polypropylene–thermoplastic elastomer blends by means of X-ray scattering

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Blends of semicrystalline isotactic polypropylene (iPP) with two types of elastomer, butadiene/styrene (BS) and hydrogenated isoprene/styrene (HIS), block copolymers were investigated by means of wide-angle and small-angle X-ray scattering. Except for the sample with a low concentration of BS (5 wt%), where the copolymer macromolecules are probably dispersed in the amorphous phase of iPP, the blends can be described as two-component systems (copolymer–iPP), in which the crystalline phase of iPP is only slightly influenced by the copolymer. X-ray results in the structural investigation of the blends correlate well with the mechanical properties of the blends.

(Keywords: polymer blends; polypropylene; thermoplastic elastomer; X-ray scattering; degree of crystallinity; size of crystallites)

INTRODUCTION

The properties of semicrystalline polymers depend on the degree of crystallinity and character of the crystalline phase. Addition of modifiers can influence the crystallization process in the polymer[1–3] while, on the other hand, mixing with a polymer can lead to structural changes in a modifier. Determination of structural changes of both components in modified polymers (blends) and dependence on composition can help to explain the mechanical properties of the blends.

In this paper the structures of two series of blends of isotactic polypropylene (iPP) with thermoplastic elastomers were studied over the whole concentration range of the elastomers: butadiene/styrene (BS) and hydrogenated isoprene/styrene (HIS) block copolymers. Wide-angle (WAXS) and small-angle (SAXS) X-ray scattering were employed for characterization of the investigated samples.

EXPERIMENTAL

Samples

Blends of iPP–BS radial block copolymer and iPP–HIS block copolymer were prepared according to the method described earlier[4,5]. Samples were prepared by compression moulding at 170°C under a pressure of 1 MPa for 30 min. Samples were then cooled to room temperature under pressure over 120 min. The thickness of the samples was 1.0–1.5 mm.

WAXS

The degree of crystallinity w_{cr} and the size of the crystallites L were determined using an automatic powder diffractometer (HZG/4A). CuKα radiation was monochromatized by a Ni filter and pulse-height analyser and registered with a scintillation counter. Diffractograms were taken over the range $2\Theta = 4–60°$.

SAXS

SAXS measurements were made with a Kratky camera. CuKα radiation registered with a proportional counter was used. The scattering curves were transformed to an absolute scale by means of a standard Lupolene sample using the relation[6]:

$$\frac{d\tilde{\Sigma}}{d\Omega}(q) = \tilde{I}(q)a/(\tilde{I}_L K_L T d)$$

where $\tilde{I}(q)$ is the measured intensity of scattering, $q = (4\pi/\lambda)\sin\Theta$ is the magnitude of the scattering vector, λ is the wavelength, 2Θ is the scattering angle, a is the sample to detector distance, d and T, respectively, are the thickness and transmission of the sample, K_L is the calibration constant and $\tilde{I}_L$ is the intensity scattered by the standard at $q = (2\pi/15\ \text{nm})$.

Mechanical testing

Tensile strength at room temperature was determined using standard specimens and a conventional testing machine. Impact strength was measured on a Dynstat apparatus using specimens maintained for 1 h in a

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mixture of ethanol and solid CO_2 at strictly controlled temperatures.

RESULTS AND DISCUSSION

Wide-angle diffractograms of iPB–BS and iPP–HIS blends for the concentration range of the elastomer 0–100 wt% are given in *Figures 1* and *2*, respectively. In the given range of scattering vector, diffractograms of pure iPP exhibit four maxima corresponding to the (1 1 0), (0 4 0), (1 3 0) and overlapping (1 3 1), (0 4 1) and (1 1 1) reflections which are characteristic of the monoclinic α phase[7]. The positions of these reflections remain unchanged in blends. For the iPP–HIS blends an additional weak reflection at $2\Theta = 16.3°$, indicating the hexagonal β phase[7], appeared for samples with HIS content higher than ~ 10 wt%. This means that in both types of blend polypropylene maintains its α crystalline phase, whilst a small amount of β phase is present in iPP–HIS samples with >10 wt% HIS.

Figure 3 shows the dependence of w_{cr} on blend composition. The value of w_{cr}, i.e. the mass fraction of the crystalline phase, was determined by WAXS according to the formula[8]:

$$w_{cr} = \int_0^\infty I_{cr}(q) q^2 \, dq \Big/ \int_0^\infty I(q) q^2 \, dq$$

where I_{cr} is the intensity of radiation scattered by crystalline domains and I is the overall scattering intensity. Separation of the crystalline peaks from the amorphous halo was made according to Weindinger and Hermans[9].

The value of w_{cr} decreases linearly with copolymer content in both types of blend whilst its value with respect to the polypropylene content is constant (*Figure 3*).

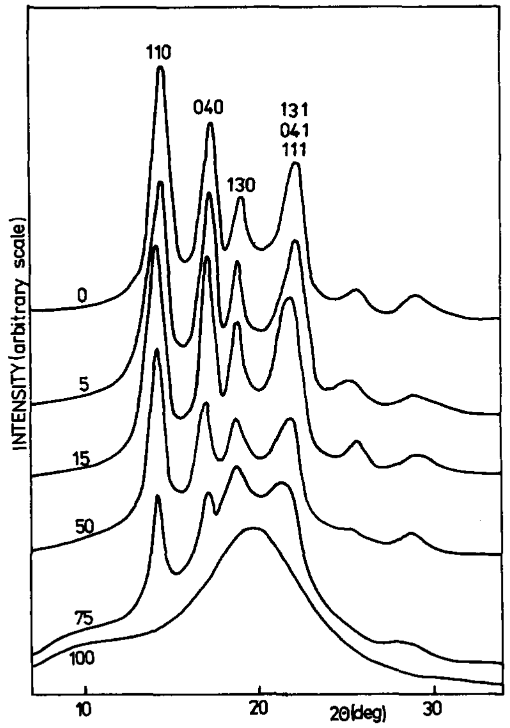

Figure 1 Wide angle diffractograms of iPP–BS blends. Numbers on the curves denote the BS content (wt%)

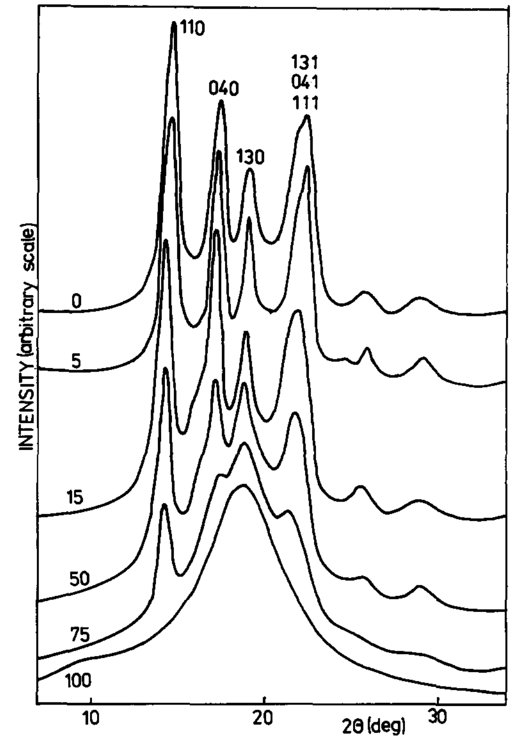

Figure 2 Wide angle diffractograms of iPP–HIS blends. Numbers on the curves denote the HIS content (wt%)

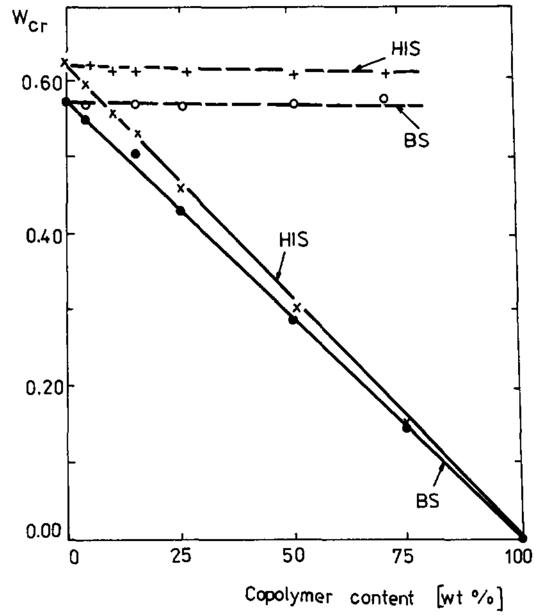

Figure 3 Dependence of the degree of crystallinity w_{cr} on the elastomer content. The broken lines refer to the crystallinity of the iPP matrix

Small changes in the structure of the crystalline phase in blends with varying elastomer content are indicated by the sizes of crystallites. Apparent dimensions of crystallites L_i along the direction perpendicular to the crystal plane i can be determined using the Scherrer equation[8]:

$$L_i = \frac{K\lambda}{\beta_i \cos(\Theta_i/2)}$$

where β_i is the half-width of the reflection corrected for the instrumental broadening, Θ_i is the position of the reflection maximum, and K is a constant usually assigned

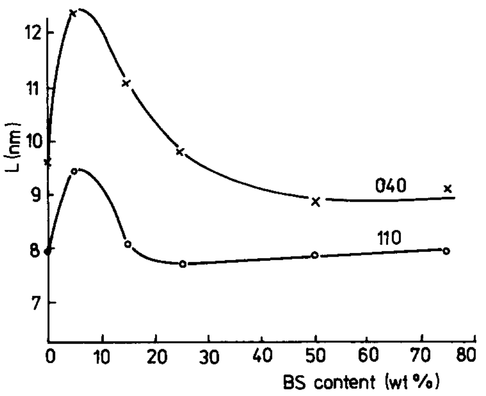

Figure 4 Size of crystallites L along the direction perpendicular to the (1 1 0) and (0 4 0) planes in iPP–BS blends

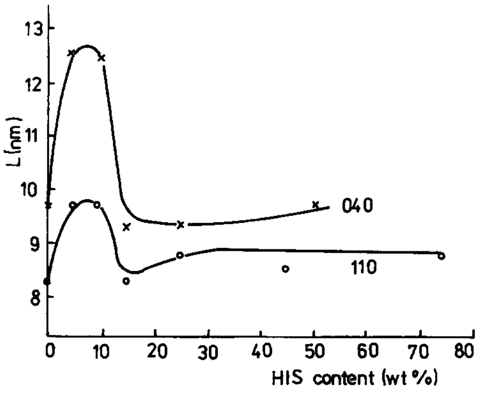

Figure 5 Size of crystallites L along the direction perpendicular to the (1 1 0) and (0 4 0) planes in iPP–HIS blends

a value of unity. Care must be taken in using this equation for calculating the crystallite sizes in polymers, because broadening of reflections may also be influenced by lattice distortions. Nevertheless, narrow crystalline peaks indicate better development of the crystalline phase.

The apparent dimensions of crystallites along the direction perpendicular to the (1 1 0) and (0 4 0) planes are given for both systems in *Figures 4* and *5*. Values of these parameters for iPP–HIS blends with copolymer content of >10 wt% were determined with great uncertainty due to the overlap of reflections belonging to the β phase. Enlargement of the crystallites in the samples containing up to 10 wt% elastomer can be explained by partial miscibility of the components in the melt and a subsequent entanglement of the polymer chains of both components. Disentanglement of such a network can slow down the crystallization process, resulting in better developed crystallites. This assumption is supported by viscosity measurements of the iPP–BS blend melts[4]. It has been shown that the viscosity of blends containing moderate amounts of the copolymer exhibit a positive deviation from the rule of logarithmic additivity, indicating some stiffening of the structure of the melt.

Small-angle scattering curves of both systems are shown in *Figures 6* and *7*. The characteristic scattering curves of pure semicrystalline polypropylene are modified by the addition of an elastomer. SAXS curves of the blends exhibit an additional maximum which can be ascribed to the two-phase structure of the elastomer.

Since the polypropylene structure in blends remains practically unchanged, we can determine the scattered intensity related to unit volume of the elastomer

$$(\mathrm{d}\tilde{\Sigma}/\mathrm{d}\Omega)_{\mathrm{E}} = \frac{1}{v_{\mathrm{E}}}(\mathrm{d}\tilde{\Sigma}/\mathrm{d}\Omega) - \frac{v_{\mathrm{iPP}}}{v_{\mathrm{E}}}(\mathrm{d}\tilde{\Sigma}/\mathrm{d}\Omega)_{\mathrm{iPP}}$$

where v is the volume fraction and the subscripts E and iPP refer to elastomer and polypropylene, respectively. These curves (*Figures 8* and *9*) indicate that the maximum typical of a two-phase structure of block copolymers nearly vanishes in the iPP–BS sample with 5 wt% BS, while in the iPP–HIS blends the maximum

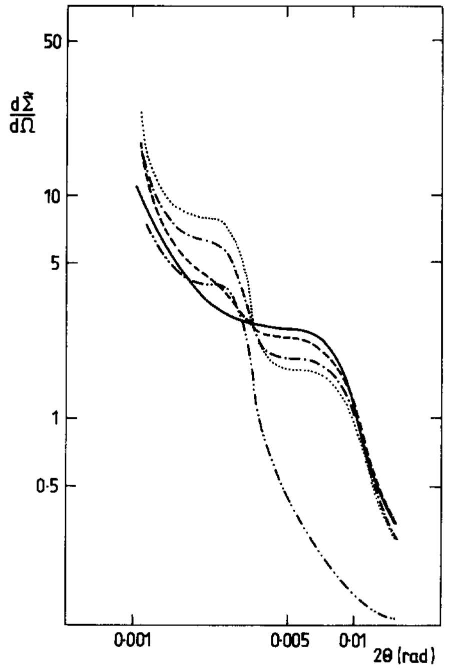

Figure 6 Variation of SAXS curves of iPP blends with BS content (wt%): ———, 0; – – –, 5; –·–, 15; ···, 25; –···–, 100

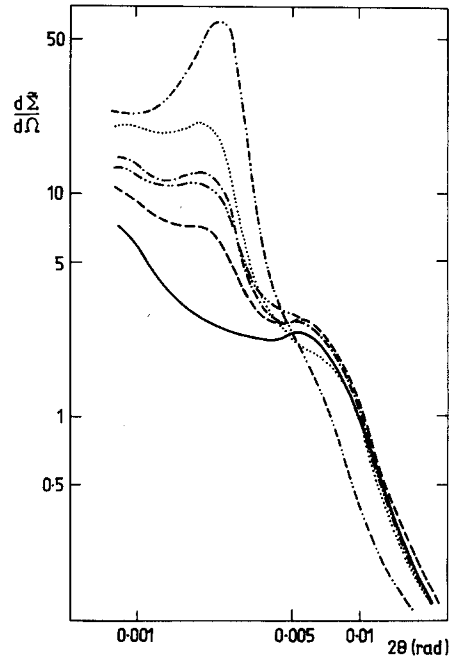

Figure 7 Variation of SAXS curves of iPP–HIS blends with HIS content (wt%): ———, 0; – – –, 5; ·–·–·, 10; –·–, 15; ···, 25; ·–––·, 100

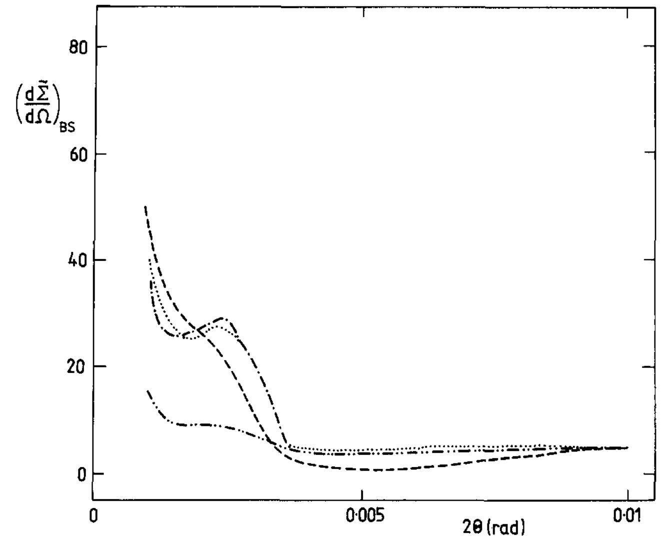

Figure 8 Variation of the BS contribution to the iPP-BS SAXS curves, related to the unit volume of BS, with BS content (wt%): ——, 5; —·—, 15; ···, 25; —··—, 100

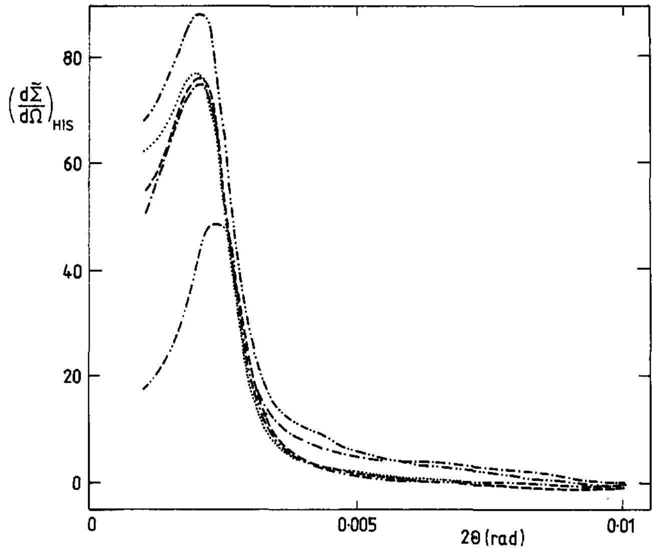

Figure 9 Variation of the HIS contribution to the iPP-HIS SAXS curves, related to the unit volume of HIS, with HIS content (wt%): ——, 5; ·—··, 10; —·—, 15; ···, 25; ·——·, 100

Table 1 Mechanical properties of iPP-BS and iPP-HIS blends

Copolymer content	Relative impact strength at 293 K		Tensile strength (MPA) at room temperature	
(wt%)	BS	HIS	BS	HIS
0	1.0	1.0	32.4	33.7
5	0.83	2.3	29.4	30.1
10	0.92	4.0	29.2	25.8
15	1.05	–	27.6	23.7
25	–	–	–	18.5

is clearly developed over the whole copolymer concentration range. This finding supports the hypothesis presented in our earlier paper[4] that in the iPP–BS blends with copolymer content up to ~5 wt% the copolymer molecules are incorporated in the amorphous phase of iPP instead of being assembled in the separate phase.

The results of X-ray scattering measurements for iPP–BS and iPP–HIS blends help to explain the mechanical properties of these systems (*Table 1*). In the case of iPP–BS blends a minimum of relative impact strength and an 'inflection point' in the tensile strength curve corresponding to 5 wt% copolymer content are observed. In the iPP–HIS system both properties change monotonously with copolymer concentration.

CONCLUSIONS

On the basis of the WAXS and SAXS investigation, iPP–BS and iPP–HIS blends can be described as two-component systems of a copolymer and a semicrystalline iPP. Blends with BS content up to ~5 wt% are an exception, as the SAXS maximum typical of a two-phase copolymer system vanishes. The structure of polypropylene in blends is only slightly influenced by the elastomer. The degree of crystallinity of iPP does not vary with elastomer content and iPP maintains its monoclinic α phase, but a small amount of hexagonal β phase is also present in iPP–HIS blends with HIS content of >10 wt%. Both systems exhibit a better developed crystalline phase for elastomer concentrations ranging from ~5 to 10 wt% which is probably due to the slower crystallization rate of these samples from the melt. The observed structural differences between the two systems studied are in agreement with the variation in their mechanical properties with elastomer content.

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