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POLYETHYLENE–POLYSTYRENE BLENDS

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Abstract—Polyethylene–polystyrene (PE–PS) blends involving three samples of PS of different molecular weight were obtained. Blending was performed on rolling mills at temperatures and shear stresses chosen so as to ensure maximum dispersion of components but to avoid chain scission. Scanning electron microscopy, differential thermal analysis and X-ray diffraction were used to examine the supermolecular structures of the blends; density, viscosity and mechanical measurements were also performed. Depending on the composition and molecular weight of PS, the morphology of the blends changed between that of spherical domains of one component dispersed in a continuous matrix of the other, to a highly nonhomogenous mixture of fibrous or cabbage-like macrodomains of both components. The presence of PS disturbed the development of PE crystallites and caused decrease of the degree of crystallinity of PE with increase in the PS content (from 0.56 to 0.41 as the PS content increased from 0 to 80 wt%). Some nonadditivity of modulus of elasticity was investigated in terms of the Takayanagi Model I.

INTRODUCTION

According to the thermodynamic criterion, polyethylene (PE) and polystyrene (PS) are immiscible [1]. From the morphological point of view, this excludes the possibility of obtaining PE–PS blends with segmental miscibility, and causes some phase separation [2]. However, there are reports on the preparation of PE–PS blends and studies of PE crystallization characteristics and the morphology of the blends [3–10].

The mode of dispersion obtained by co-extrusion of a mixture of PE and PS was studied by Van Oene [3] and by Pakuła *et al.* [4]. Two basical morphologies were observed by Van Oene viz. a ribbon-type dispersion and a droplet-type. Fibrous structures turning into droplet-type on annealing were recorded by Pakuła *et al.* The mechanism was explained in terms of Tomotika's theory [11] describing the kinetics of breaking of thin long streams of a molten polymer immersed in a melt of another polymer.

Some authors [5–9] studied the morphology of PE–PS blends obtained by mixing the two components between rolling mills. They observed spherical domains or rod-like structures close to the phase inversion. Aref-Azar *et al.* [9] investigated the effect of the morphology on crystallization characteristics of PE in the blends. They found that, with PE in excess, the kinetics of crystallization were insensitive to the morphology but, with PE present in smaller amount, they became dependent on the state of its dispersion.

The present work concerns properties and morphology of blends of PE and PS of various molecular weights, prepared in the melt under shear stress.

EXPERIMENTAL PROCEDURES

Materials

Low density PE ($\bar{M}_v = 33{,}000$) (Malen E) produced by Petrochemia Works in Płock, Poland was used. Three samples of PS (PSI–III) were obtained by solution polymerization in toluene at 343 K for 7 hr; styrene concentration was 50.0 wt%. Benzoyl peroxide was used as initiator at concentrations 0.5, 0.2 and 0.05 wt%, for PSI ($\bar{M}_v = 53{,}000$) PSII ($\bar{M}_v = 167{,}000$) and PSIII ($\bar{M}_v = 230{,}000$) respectively.

Preparation of the blends

The blends were obtained by mixing the PE on rolling mills with PS. PS content ranged from 0 to 100 wt%. The parameters of mixing, chosen so as to prevent destruction of the macromolecules of the starting polymers [12], were: $T_{mix} = 403$–413 K, mill rotation rates = 0.22 and 0.25 sec^{-1} resp., gap = 1 mm, mixing time = 900 sec, cooling time = *ca* 180 sec.

Density measurements

Densities of the samples were measured at 298 K by mercury pycnometry, and then converted into specific volumes.

Mechanical properties

Stress–elongation relationships for the samples were recorded at 298 K on Instron 1126 apparatus. Stretching rate was 2 mm/min. The linear dimensions of samples were measured microscopically. Modulus of elasticity was calculated graphically at 1% elongation.

Scanning electron microscopy (SEM)

Samples of the blends were fractured in liquid N_2 deposited with carbon and gold. The microscope was a Cambridge Stereoscan 180.

Degree of crystallinity

The degree of crystallinity of PE in the blends was estimated by the WAXS method of Hermans and Weidinger [13]. Diffractograms, taken within $2\theta = 4$–30° range, were deconvoluted into four bands: two of the crystalline PE, B3 and B4 (2θ *ca* 21 and 23°), one of the amorphous PS, B1 (2θ *ca* 9°) and a common band of the amorphous PS and PE, B2 (2θ *ca* 20°). The quantity proportional to the crystalline PE fraction was the total area of B3 and B4, and that proportional to the amorphous PE fraction was the area of B2 multiplied by the weight fraction of PE in the blend. Deconvolution was performed numerically by the method of

Marquardt [14] and Pearson VII [15] as a profile function. The average crystallite size was estimated according to Scherrer's formule [16]. The refractometer used was a HZG-4 (DDR) with CuK_α radiation and Ni filter.

Lamella thickness distribution

Thermograms of 10 mg samples encapsulated in Al were recorded in a Unipan 605 DSC apparatus. The heating rate was 10 K/min. The thermograms were then corrected for thermal lag. PE lamella thickness distributions were calculated according to Włochowicz and Eder [17].

Use was made of the assumption that, at a given temperature, the rate of heat flow is proportional to the weight fraction of lamellae with thickness determined by the Thomson equation:

$$T_m = T_0 \cdot \left(1 - \frac{2 \cdot \sigma}{l \cdot \Delta h_m}\right) \quad (1)$$

where T_m is the melting temperature of lamellae of thickness l; T_0 is the equilibrium melting temperature of an infinite crystal (4145 K [17]); σ is the surface free energy of the fold-containing plane (60.9×10^{-3} J/m^2); Δh_m is the enthalpy of fusion per unit volume (2.88×10^8 J/m^3).

By a stepwise integration of 0.2° wide strips of the corrected thermograms, it was possible to find the weight fraction of lamellae melting at the temperature corresponding to the thickness given by the Thomson equation. After normalization, the PE lamella thickness distribution curves were plotted.

RESULTS AND DISCUSSION

As a result of mixing PE and PS (I–III), blends of various appearances from transparent to milky were obtained, depending on PS molecular weight and content.

The dependence of specific volume on the blend composition (Fig. 1) revealed some nonadditivity (*ca* 2% for PE–PSII, III and *ca* 5% for PE–PSI) indicating the presence of some additional free volume (Micropores). It resulted from high PE contraction (*ca* 10 vol%) on transition from the molten to the solid state and from the differences in viscosities of the melts of the components.

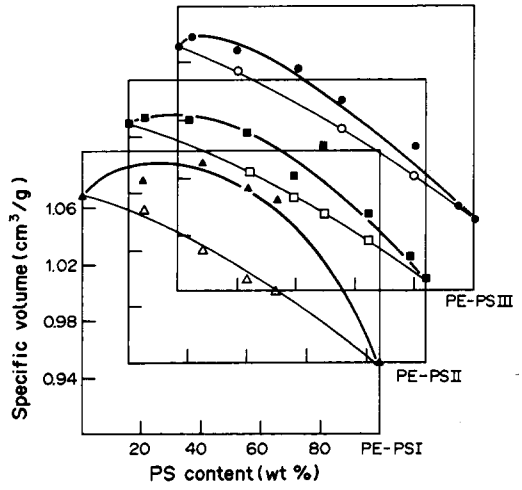

Fig. 1. Dependence of the specific volume on blend composition: PE–PSI (△, ▲) PE–PSII (□, ■) and PE–PSIII (○, ●). Filled symbols represent the measured values, open symbols represent theoretical additivity values.

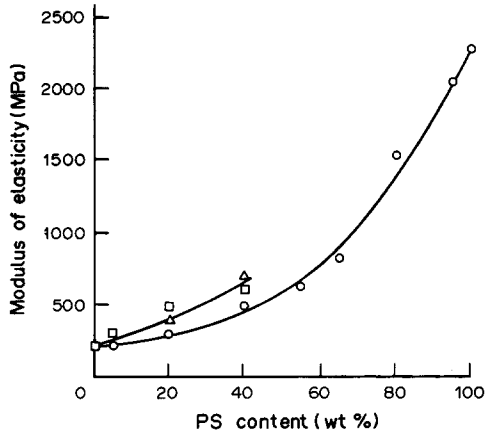

Fig. 2. Dependence of the modulus of elasticity on PS content for PE–PSI (△), PE–PSII (□) and PE–PSIII (○).

Based on the densities of the pure components, the theoretical phase inversion compositions were calculated from the equation:

$$\Phi_{PS} \cdot v_{PS} = (1 - \Phi_{PS}) \cdot v_{PE} \quad (2)$$

where Φ_{PS} is the volume fraction of PS at the phase inversion; v_{PS} and v_{PE} are the specific volumes of PS and PE respectively. Conversion of the volume fractions to weight percentages gives *ca* 56 wt% of PSI–III at the phase inversion.

The dependence of modulus of elasticity on PS content for PSI–III is shown in Fig. 2. The observed nonadditivity was interpreted in terms of the Takayanagi Model I [18] depicted schematically in

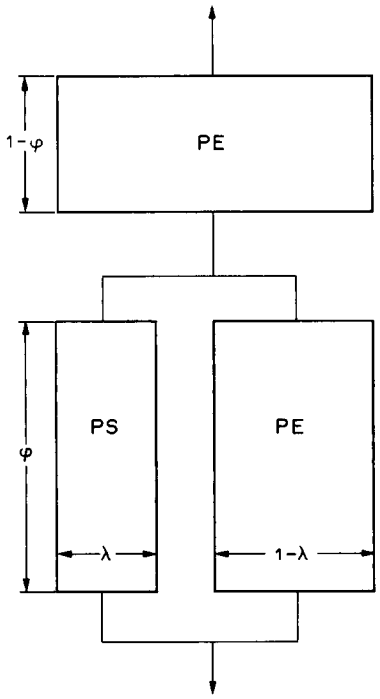

Fig. 3. Takayanagi Model I. The blocks marked PE and PS represent the mechanical properties of PE and PS phases respectively.

Table 1. Values of the parameters λ and ϕ obtained for the PE–PSIII blends from the Takayanagi Model I

PS content (wt%)	λ	ϕ
5	0.75	0.06
20	0.57	0.32
40	0.55	0.68
55	0.72	0.72
65	0.82	0.76
80	0.80	0.97
95	0.95	0.99

Fig. 3. The values of the parameters λ and ϕ for the PE–PSIII blends are shown in Table 1. The results suggest a nonuniform dispersion of PS domains at low PS contents.

SEM micrographs reveal changes in blend morphology with composition and PS molecular weight.

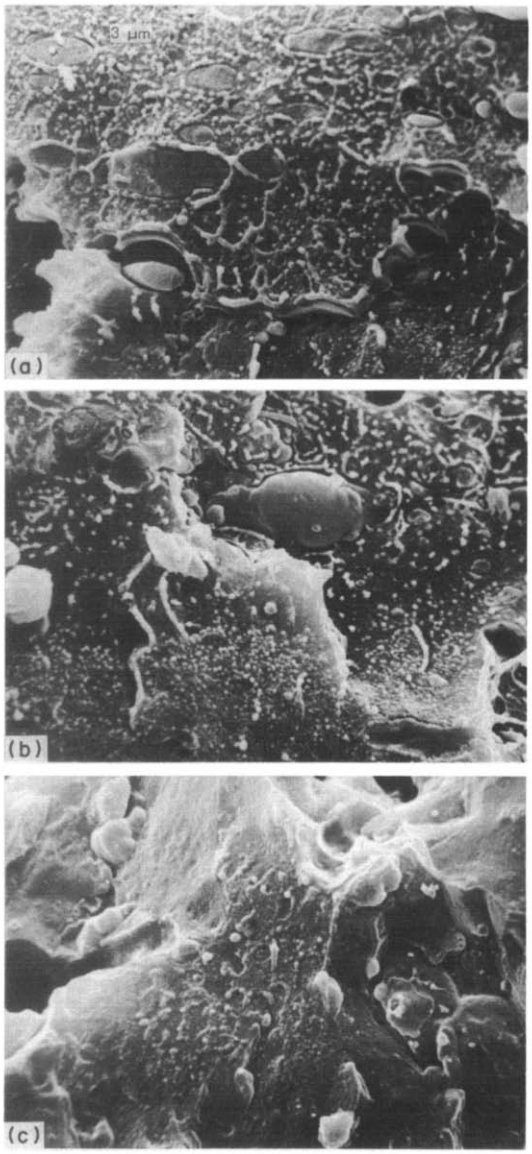

Fig. 4. Micrographs of the fracture surfaces of PE–PS blends. PS content of 20 wt%: (a) PE–PSI; (b) PE–PSII; and (c) PE–PSIII.

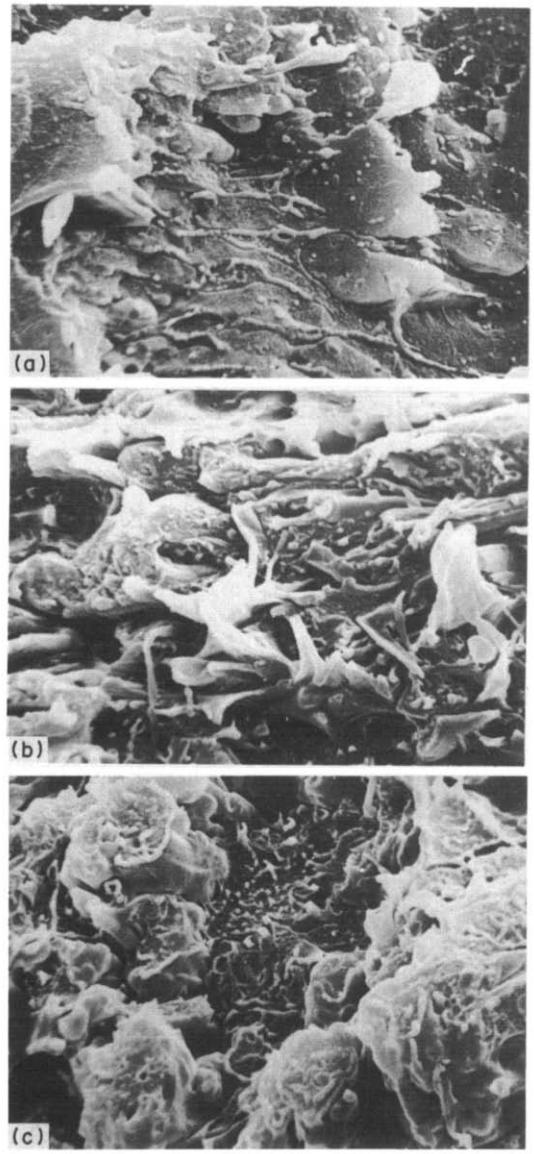

Fig. 5. Micrographs of the fracture surfaces of PE–PS blends. PS contents of 55 wt%: (a) PE–PSI; (b) PE–PSII; and (c) PE–PSIII.

A strong influence of PS molecular weight on the degree of dispersion before, as well as after the phase inversion, is evident.

Before the phase inversion and for low molecular weight PS, (PSI), relatively homogeneous blends with spherical, separated PS domains of two distinct sizes viz. 0.2–0.4 and 1–5 μm are obtained. As the molecular weight of PS increases, the small domains disappear while the other domains clearly enlarge. Highly nonhomogeneous structures are formed with PSIII (mainly *ca* 10 μm PS domains), meaning that the mixing efficiency is low. This result confirms predictions based on the Takayanagi Model.

Close to the phase inversion, the influence of molecular weight of PS is very marked. The PSI domains become flattened, interconnected at some points, with PE spherical (*ca* 0.1–0.3 μm) inclusions. With PSII, a fibrous structure is formed and a highly

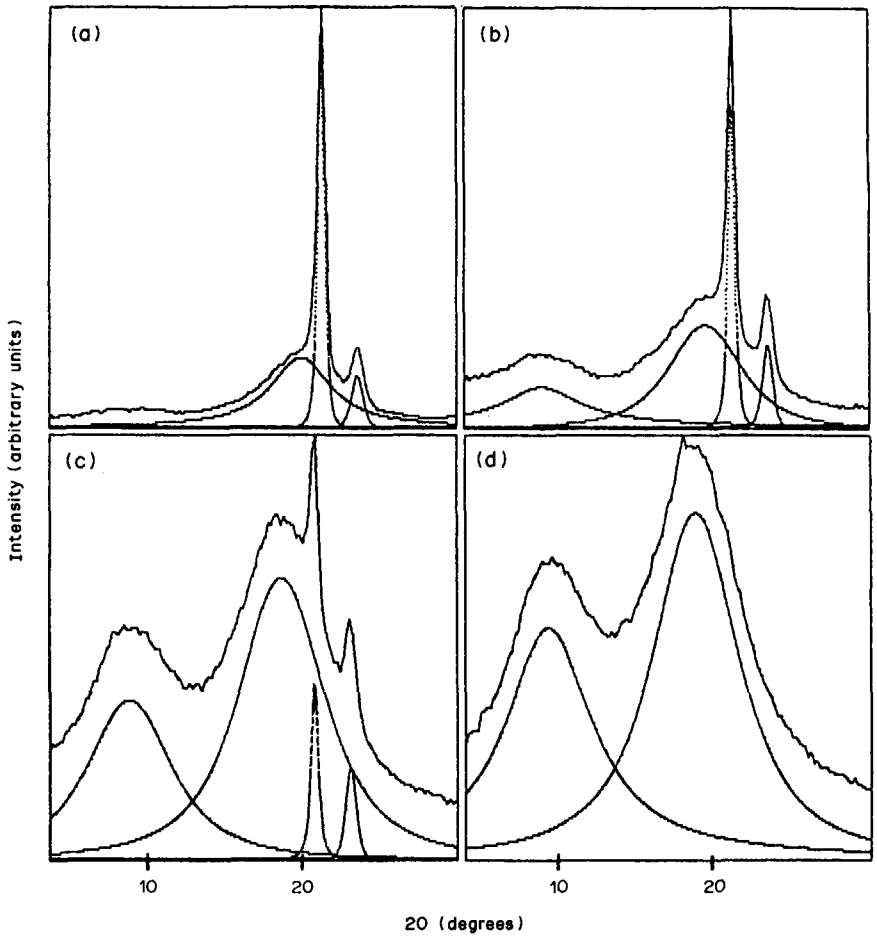

Fig. 6. Some deconvoluted diffractograms recorded for PE–PSII blends of PSII contents: (a) 0 wt%; (b) 40 wt%; (c) 80 wt%; and (d) 100 wt%.

nonhomogeneous cabbage-like structure is formed when PSIII is used.

Typical micrographs of PE–PS blends of PSI-III contents of 20 and 55 wt%, are presented in Figs 4 and 5.

As a result of mixing of PE and PS, a three-phase system i.e. crystalline PE, amorphous PE and amorphous PS is obtained. For such a system, some influence of PS on the crystallinity of PE could be expected.

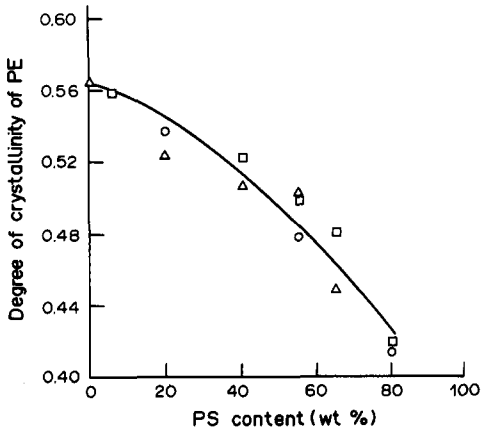

Fig. 7. Dependence of the degree of crystallinity of PE on PS content for PE–PSI (△), PE–PSII (□) and PE–PSIII (○).

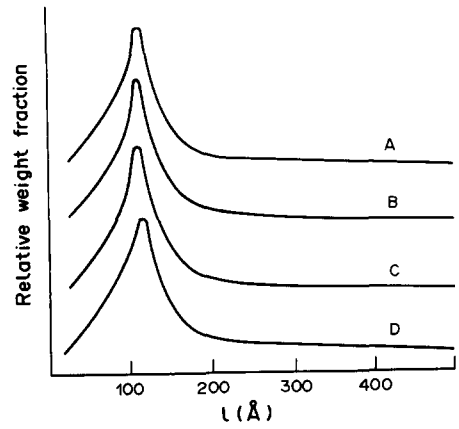

Fig. 8. Distribution of PE lamella thicknesses in the PE–PSI blends having PSI contents: (A) 0 wt%; (B) 20 wt%; (C) 40 wt%; and (D) 65 wt%.

Figure 6 shows deconvoluted diffractograms recorded for PE–PSII blends of various compositions. The dependence of the degree of crystallinity of PE on PS content for PSI–III is presented in Fig. 7. The dependence is nonlinear and, to a first approximation is identical for all samples of PS. The degree of crystallinity of PE in the blends decreases as the PS content increases, meaning that PS disturbs the development of the crystallites in agreement with the results of Aref-Azar *et al.* [9]. When the PS content increases from 0 to 80 wt%, the degree of crystallinity of PE decreases from 0.56 to 0.41. Based on this dependence, specific volumes of the blends were calculated assuming additivity, from the formula:

$$v = w_{PE} \cdot X \cdot v_{PEc} + w_{PE} \cdot (1 - X) \cdot v_{PEa} + (1 - w_{PE}) \cdot v_{PS} \quad (3)$$

where: v, v_{PEc}, v_{PEa}, v_{PS} are the specific volumes of the blend, crystalline PE, amorphous PE and PS respectively; w_{PE} is the weight fraction of PE in the blend; and X is the degree of crystallinity of PE. The resulting curves are plotted in Fig. 1.

The average dimensions of the PE crystallites do not depend on the PS content in the blends, and are equal to those of the starting PE [154 Å and 111 Å, in the directions perpendicular to (110) and (200) planes respectively]; This result was confirmed by DSC measurements. The PE lamella thickness distribution curves for some PE–PSI samples are shown in Fig. 8.

CONCLUSIONS

PE–PS blends using three samples of PS of different molecular weights were obtained. Depending on the composition and the molecular weight of PS, the morphology of the blends changed between spherical domains of one component dispersed in a continuous matrix of the other, to highly nonhomogeneous fibrous or cabbage-like structures formed close to the phase inversion.

The presence of PS disturbed the formation of the crystallites, causing decrease of the degree of crystallinity of PE with increasing PS content.

Some nonadditivity of the modulus of elasticity was investigated in terms of the Takayanagi Model I.

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