Some properties of polypropylene–butadiene/styrene radial block copolymer blends

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Experimental studies of blends containing isotactic polypropylene and radial block butadiene–styrene copolymer over the whole composition range have been carried out. Measurements of viscosity and mechanical properties as well as electron microscopic observations of the system have shown that, up to about 5% copolymer content, both components are miscible and probably only a single-phase blend exists. Above this concentration, the copolymer forms a separate phase, i.e. a two-phase blend is formed.

(Keywords: polymer blends; impact modifiers; viscoelastic properties)

INTRODUCTION

Physical modification of polymers by addition of an elastomer is one of the most important ways of producing polymeric composites with special properties. The modification of polymers having great technical importance, such a polystyrene (PS), polypropylene (PP) and polyethylene (PE), is commonly made with non-vulcanizing elastomers. The most frequently used elastomers for this purpose are: ethylene–propylene copolymer, ethylene–propylene–diene terpolymer and, for the last 15 years, thermoplastic elastomers, especially polystyrene–polydiene–polystyrene triblock copolymers. These copolymers have a two-phase structure consisting of glassy PS domains dispersed in an elastic matrix of polybutadiene (SBS copolymer), polyisoprene (SIS copolymer) or random ethylene–butylene copolymer (SEBS copolymer)[1]. Block copolymers increase the stability and impact strength when mixed with homopolymers and polymers with a chemical structure similar to one of the copolymer components[2]. In the literature some properties of PP–SBS copolymer blends[3–6] as well as of the PP–SEBS copolymer system[7–10] (obtained by hydrogenation of SBS copolymer) have been described. The addition of SBS or SEBS copolymers in amounts up to 25% to PP considerably increases the impact strength of the blends, especially at low temperatures, and simultaneously decreases the modulus of elasticity and tensile strength measured as functions of temperature by the method of dynamic modulus. The toughness of PP with thermoplastic elastomers depends strongly on temperature due to the multiphase structure of the system with separate agglomerations of each component.

The dynamic modulus spectra of PP–SBS copolymer[5] or PP–SEBS copolymer[10] blends show relaxation peaks, commonly interpreted as the main transition in polymers. They correspond to the glass transition temperature of polybutadiene or hydrogenated polybutadiene at about 213 K as well as to the glass temperature of amorphous PP at about 283 K. The glass temperature of the PS phase, however, has not been taken into consideration[5,10].

The toughening mechanism of blends at low temperature depends on the physical state of the individual blend components. According to existing opinions[10], at low temperatures the crazing mechanism dominates, while at high temperatures that of plastic shear is more frequently observed.

This paper presents some results of viscometric measurements of molten PP–$(SB)_4X$ radial block copolymer blends over the whole composition range. Mechanical properties of the system, and especially the impact strength, have also been measured as a function of temperature.

The study of the behaviour of molten polymer blends of different chemical structure is especially important for appropriate programming of their processing and properties in the solid state. Our investigations show the correlation between the behaviour of the blend in the fluid state and its morphological structure determined by the electron microscope method.

EXPERIMENTAL

Materials

The experiments have been carried out using isotactic polypropylene (iPP), Malen J-400 (*MFI* at 463 K/49 N: 4.2 g/10 min), and butadiene/styrene (B/S) radial block copolymer, Solprene 475, with 30% content of naphthene oil. This copolymer contains 40 wt% styrene, 42 wt% 1,4-butadiene and 18 wt% 1,2-butadiene as determined by ^1H n.m.r. spectroscopy. The molecular masses $M_w = 186 \times 10^3$ g mol^{-1} and $M_n = 148 \times 10^3$ g mol^{-1} were determined with a Waters model ALC/GPC 301 gel permeation chromatograph equipped with four Styragel columns ranging in pore sizes from 10^3 to 10^7 Å and using tetrahydrofuran as eluent and polystyrene as standard.

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Preparation of blends

iPP–B/S blends over the whole composition range have been obtained by double melt mixing in a single-screw extruder with an average barrel and head temperature of 463 K and screw speed of 20 rpm. Increasing the number of mixing cycles did not affect the properties of the blends, which were used in the form of granules for further operations (injection moulding, viscometric measurements).

Methods of measurements

The rheological properties of iPP–B/S blends have been measured using a capillary viscometer, which allows the shear rate to be varied continuously within the range from 1 to 10^4 s^{-1}. The measurements have been carried out at temperatures of 448, 463, 478 and 493±0.5 K. For creep and elastic recovery measurements the Höeppler consistometer and cylindrical samples with diameter and height of 10 mm were used.

The impact strength of iPP–B/S blends were determined with a Dynstat apparatus. Other mechanical properties of the blends have been measured on a typical testing machine. The samples for mechanical tests have been prepared by injection moulding, compression moulding and mechanical working according to the type of measurement.

Microscope observations were carried out with a scanning electron microscope. For this purpose, samples in the form of thin rods were fractured at liquid-nitrogen temperature and then coated with gold. Other samples had been initially extracted to remove the copolymer and then coated with gold without fracturing. The material for the samples was the extrudate from viscometric measurements at low shear rates.

RESULTS AND DISCUSSION

Table 1 presents the composition and some properties of iPP–B/S blends used in the experiments.

The apparent viscosity η_{app} of iPP–B/S blends over the whole composition range has been evaluated by measuring the dependence of volumetric flow rate Q on the pressure drop Δp in a capillary with length L and diameter D.

Figure 1 shows some flow curves obtained in this manner. Because of the approximately linear form of the function $\ln \Delta p = f(\ln Q)$ the applicability of the 'power law' has been assumed.

$$\tau_w = K \exp(E/RT)\dot{\gamma}_w^n \qquad (1)$$

Table 1 Physical properties of iPP–B/S blends

Composition (wt%) iPP: B/S	Activation energy of flow (kJ mol^{-1})	Elasticity modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
100:0	22.86	1150±50	32.4±1.0	440
95:5	21.76	1050±50	29.8±0.9	310
90:10	–	1000±40	29.2±0.7	280
85:15	21.82	850±40	27.6±0.7	230
75:25	22.17	–	–	–
50:50	24.94	–	–	–
25:75	26.33	–	–	–
0:100	27.71	–	–	–

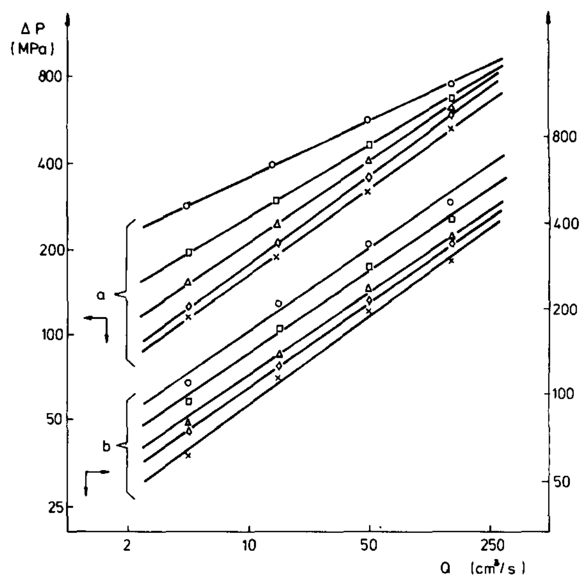

Figure 1 Flow curves of iPP–B/S copolymer blends at different temperatures (a, 448 K; b, 498 K) and copolymer concentrations: (×) 0 wt%; (◇) 25 wt%; (△) 50 wt%; (□) 75 wt%; (○) 100 wt%

$$\tau_w = (\Delta p/4L)D \qquad (2)$$

$$\dot{\gamma}_w = (32Q/\pi D^3)(3n+1)/4n \qquad (3)$$

$$\eta_{app} = \tau_w/\dot{\gamma}_w \qquad (4)$$

where K and n are material constants of the 'power law', E is the activation energy of viscous flow, R is the gas constant, T is the temperature, τ_w is the shear stress at the wall, and $\dot{\gamma}_w$ is the shear rate at the wall. The mean value of the flow exponent n determined from the slope of $\ln \Delta p$ vs. $f(\ln Q)$ was equal to 0.4. The values of n for individual blends depended weakly on their composition.

Because of the non-Newtonian behaviour of the blend melts, their properties (viscosity, energy of activation) were compared at the shear rate $\dot{\gamma} = 100\ s^{-1}$. For other shear rates within the range from 10 to 10^3 s^{-1} the relations were qualitatively similar.

Figure 2 presents the dependence of $\ln \eta$ on blend composition, from which it can be seen that the apparent viscosity of the blends containing moderately small amounts of copolymer is greater than that resulting from the rule of logarithmic additivity described by the formula:

$$\ln \eta_{blend} = \sum_i w_i \ln \eta_i \qquad (5)$$

where η_i is the apparent viscosity of an individual component i, and w_i is the weight fraction of this component.

For lower copolymer content in the blend, the viscosity shows a positive deviation from the rule of logarithmic additivity. Moreover, with increasing temperature, an extension of the composition range corresponding to a positive deviation of the viscosity from the rule of logarithmic additivity is observed. This behaviour can be explained by assuming that in blends with small copolymer content both components clearly show mutual compatibility and limited miscibility, which increase with temperature. A consequence of this fact can be the formation of an entanglement network and hence some stiffening of the structure of the melt.

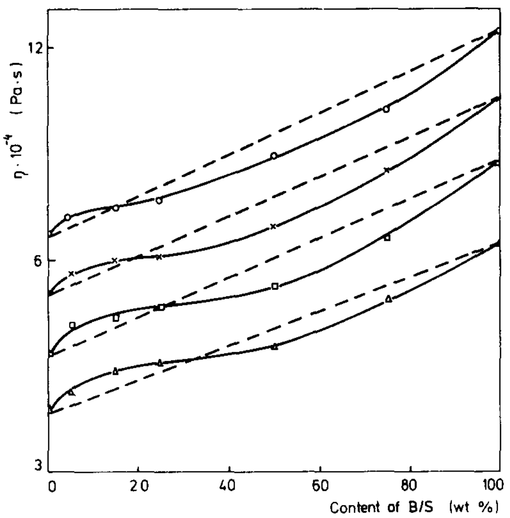

Figure 2 The effect of composition on the viscotity of iPP–B/S copolymer blends at a shear rate of 100 s^{-1} for different temperatures: (○) 448 K; (×) 463 K; (□) 478 K; (△) 493 K

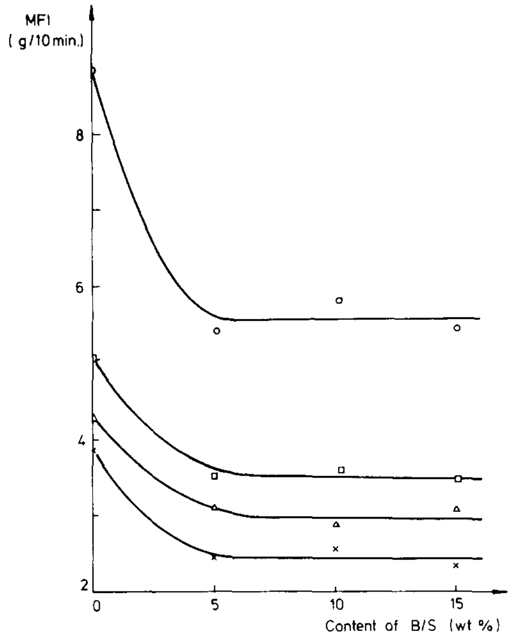

Figure 3 The influence of copolymer concentration on *MFI* values of iPP–B/S copolymer blends at different temperatures: (×) 453 K; (△) 463 K; (□) 473 K; (○) 483 K

Blends containing a greater amount of copolymer (above 15–25 wt% according to the temperature of measurement) show a lower viscosity compared with that calculated from equation (5).

According to Utracki[11] a negative deviation from the rule of logarithmic additivity testifies to the immiscibility of components, which is typical of many polymeric systems.

The changes in flow behaviour described above are confirmed by the results of measurements on the influence of blend composition (varying from 0 to 25% copolymer content) on melt flow index (*MFI*) values at various temperatures. They have been presented in *Figure 3*. In this composition range a distinct decrease of *MFI* with increasing copolymer content can be observed. This effect is especially perceptible at concentrations of 0–5 wt% copolymer.

The viscosity of iPP–B/S copolymer blends as a function of temperature can be described by the Arrhenius equation:

$$\eta = A \exp(E/RT) \qquad (6)$$

which in semilogarithmic coordinates for $\dot{\gamma} = 100\ s^{-1}$ is given in *Figure 4*.

The activation energy of viscous flow, E, of the blends depends on the composition (*Table 1*) and shows a weak minimum at small copolymer concentrations. This effect corresponds to the dependence of the viscosity on composition, discussed previously, and leads to the conclusion that the structure of the iPP–B/S copolymer blends changes from a homogeneous, single-phase one to a non-homogeneous, two-phase one.

This conclusion can be confirmed from the scanning electron microscope (SEM) observations of the surfaces of rod-like samples, which have been extruded from a capillary viscometer and then extracted to remove the copolymer phase. The photographs (*Figure 5*) show the changes in the surface structure of the samples with different copolymer concentrations. The isolated cavities originating from the dispersed phase of extracted copolymer can be seen in blends that contain a relatively small amount of copolymer. With increasing copolymer concentration, the non-homogeneity of the system increases and at 50% copolymer content two continuous, interpenetrating phases can be observed.

Figure 6 shows the effect of copolymer concentration on the impact strength of iPP–B/S copolymer blends within the temperature range from 253 to 293 K and varying copolymer concentration in the range 0–25 wt%. The shape of the resulting curves depends essentially on the temperature, which is due to the fact that the glass temperature of polypropylene lies between 273 and 283 K according to the method of measurement. At about 293 K, i.e. above the glass temperature of PP, a minimum of the impact strength at 5% copolymer content can be observed. At low temperatures (below the glass temperature of PP) the minimum vanishes.

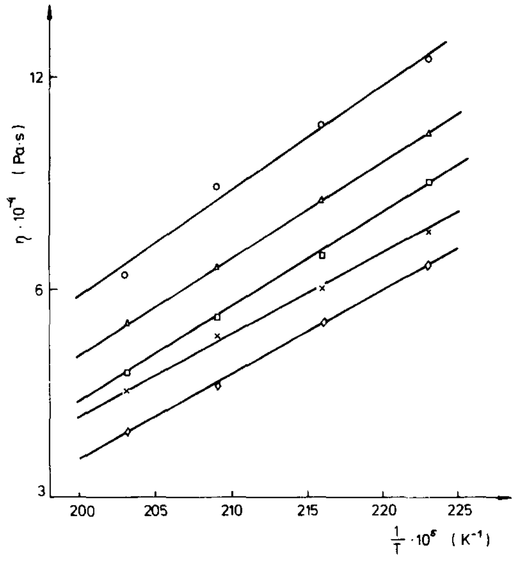

Figure 4 The effect of temperature on the viscosity of iPP–B/S copolymer blends for different copolymer contents: (◇) 0 wt%; (×) 25 wt%; (□) 50 wt%; (△) 75 wt%; (○) 100 wt%

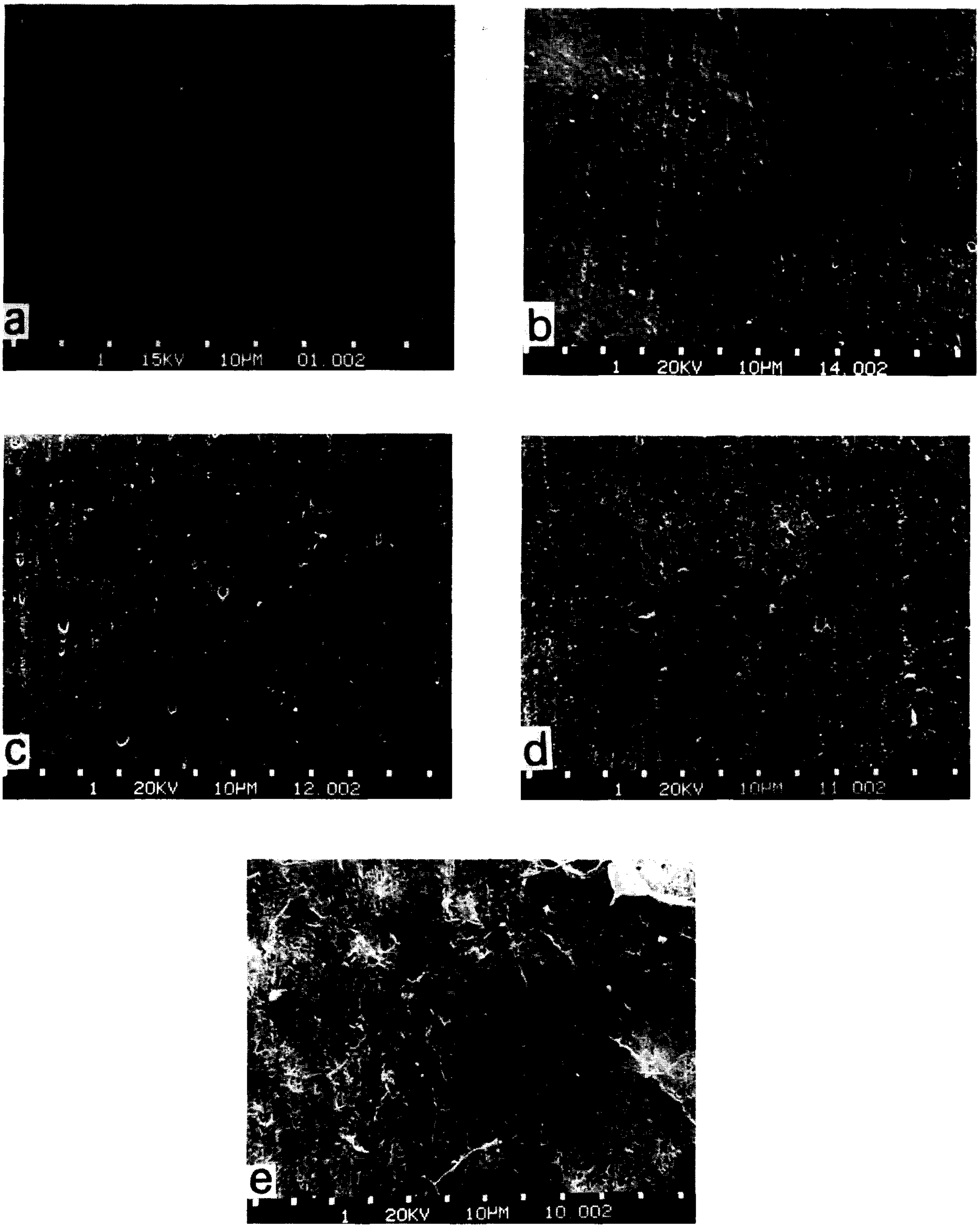

Figure 5 Electron micrographs of the surface structure of samples of iPP–B/S copolymer blends with different copolymer concentration: (a) 0 wt%; (b) 5 wt%; (c) 15 wt%; (d) 25 wt%; (e) 50 wt%

It seems that the variations of the impact strength with varying temperature can be explained by assuming a mechanism that is analogous to the case of blends in the fluid state: up to 5% copolymer content the blend essentially consists of isolated B/S copolymer molecules or their agglomerates with mean radius $<0.5\,\mu$m, assembled in the amorphous region of PP. In isolated form these molecules are characterized by much lower capacity for energy absorption. Simultaneously, they can be treated as a factor that disturbs the PP structure, especially due to the existence of PS domains. Because of the increased mobility of PP chains above the glass temperature, this behaviour can lead to a decrease of the impact strength. This effect gradually vanishes owing to the increase in the number of energy absorption centres at higher concentrations of copolymer, which begins to form a separate phase.

Below the glass temperature of PP, the effect related

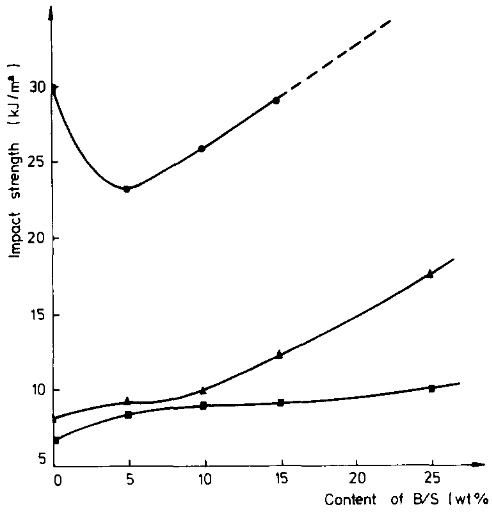

Figure 6 The influence of copolymer content on impact strength of iPP–B/S copolymer blends at different temperatures: (●) 293 K; (▲) 273 K; (■) 253 K

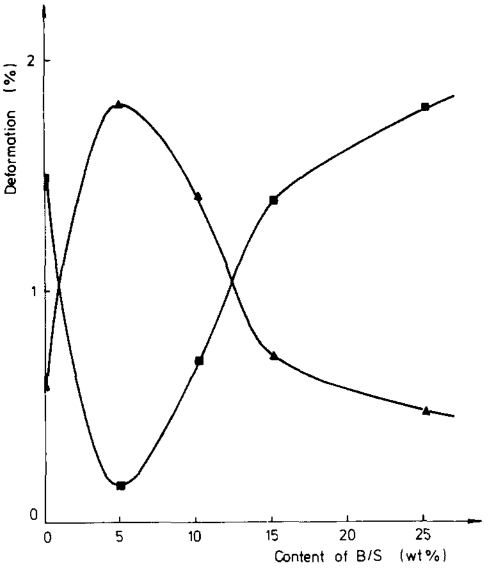

Figure 7 The effect of composition of iPP–B/S copolymer blends on different deformation types in the solid state: (■) reversible (elastic) deformation; (▲) irreversible (viscous) deformation

to the capacity for energy absorption of isolated molecules becomes stronger compared with that resulting from the disturbance of PP structure by these molecules. As a consequence of this behaviour, the minimum vanishes and an increase of impact strength can even be observed.

Figure 7 presents the effect of blend composition on the irreversible (viscous) and reversible (elastic) deformations obtained in consistometric measurements at 293 K. At 5% copolymer content the extreme values of irreversible deformation (maximum) and of reversible deformation (minimum) are observed. Under these conditions the concentration of copolymer in polypropylene probably reaches its maximum, equilibrium, value, whereupon the separate copolymer phase appears.

The next argument, which indirectly confirms the change of the phase structure of iPP–B/S copolymer system at small copolymer content, is the electron microscope photographs of sample fractures at 0, 5, 15

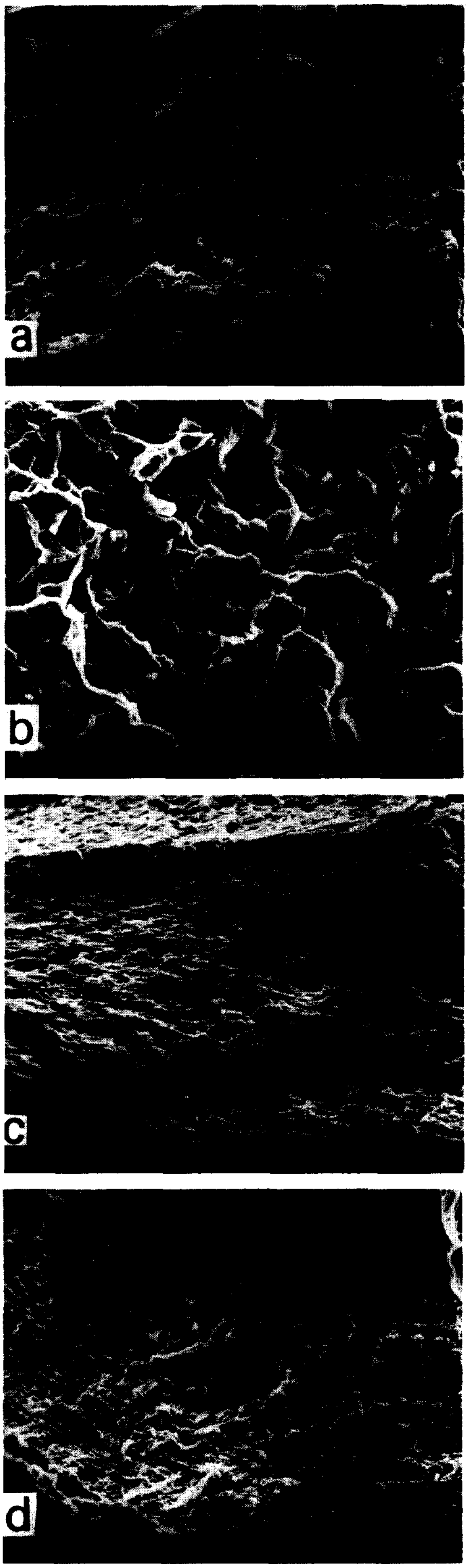

Figure 8 Electron micrographs of sample fractures of iPP–B/S copolymer blends at different copolymer concentrations: (a) 0 wt%; (b) 5 wt%; (c) 15 wt%; (d) 25 wt%

and 25% copolymer concentrations. They are shown in *Figure 8*. A distinct morphological similarity of the fractures at 0 and 5% copolymer contents suggests that both samples represent the same type of phase structure, which differs essentially from that related to the samples with 15 and 25% copolymer. The last two samples are also similar to one another, especially in the shape and dimensions of the microcracks, which may be a result of the same structure type.

CONCLUSIONS

The analysis of the variations of viscosity, activation energy, impact strength and other physical and mechanical properties as well as of the surface structure according to the variation of the composition of polypropylene–radial block copolymer blends presented above, shows that at about 5% copolymer content a gradual change of the phase structure of the system takes place. In the concentration range up to about 5 wt% B/S, the copolymer probably does not exist in the form of a separate phase, which appears when this limiting equilibrium concentration (5%) has been exceeded.

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