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Mechanical and swelling properties of polystyrene–polyolefin blends

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Differential scanning calorimetry and swelling characterization have been extended to low density polyethylene–polystyrene blends. The thermal data reveal high incompatibility between the two components in the blend. Swelling measurements in the state of quasi-equilibrium show a marked anisotropy of the cylindrical extruded specimens. Mechanical measurements in the tensile mode were carried out at room temperature on blends of the same atactic polystyrene with each of four polyolefins with increasing side-chains featured in a previous work. As the composition is varied from the pure polystyrene to the pure polyolefin the stress–strain curve changes gradually from one exhibiting brittle fracture to one showing increasingly ductile yield. At a critical concentration that ranges generally from 30 up to 50% polystyrene there is clearly an inversion of phases. Below such value the blend consists of a polyolefin matrix with polystyrene fibrils oriented in the direction of extrusion, as inferred by the swelling data. Beyond this critical composition the blends consist of a glassy polystyrene matrix with polyolefin inclusions. In the latter case the anisotropy is due to the cylindrical shape of the entire specimen.

1. Introduction

The recycling of mixed scrap or waste plastics is gaining increasing attention in the world because of economic and ecological considerations [1–5]. Among the different proposed methods, mechanical blending is a very attractive technique since it could avoid any separation step, allowing for a complete recovery of the materials. Therefore, blends of low cost plastics such as polyolefins, polystyrene, poly(vinyl chloride) mostly present in polymeric waste are, of course, of particular interest.

In a previous paper, the results of a preliminary study on the thermal and swelling properties of binary polystyrene–polyolefin blends were reported [6]. The model blends were obtained by mixing atactic polystyrene with four different crystallizable polyolefins with systematically increasing side-chains. In the present paper, the same thermal and swelling characterization was extended to three low-density polyethylene–polystyrene blends. Furthermore, the mechanical behaviour in the tensile mode, was studied on all blends from both the present and the previous work.

Some rheological studies have been made by Han and co-workers [7–10] on polystyrene–polyolefin blends. They pointed out a marked incompatibility of the components even in the molten state, and underlined the influence of the viscosity difference between the components and the importance of the mixing procedures in determining the morphology of the extrudate. Natov *et al.* [11] have also contributed to the study of the rheology of a series of mixtures consisting of one crystallizing and one amorphous (glassy or rubbery) polymer. Stell *et al.* [12] have studied the mechanical properties of hot-oriented polystyrene–polyethylene blends, and the effect of suitable graft co-polymers added to such blends [13–15] in order to improve their mechanical response.

The purpose of the present work is to characterize such largely incompatible blends by a variety of techniques and particularly to determine morphological features such as can be related to the general problem of blending a glassy amorphous polymer with a crystallizable polyolefin above its glass transition temperature.

2. Experimental details

2.1. Materials

The materials used in the previous [6] and in the present study are: atactic polystyrene (PS) from BDH Chemicals, with $\bar{M}_w = 10^5$; high density polyethylene (PE) and isotactic polypropylene (PP) kindly provided by RAPRA; isotactic polybutene-1 (PB) (Petrotex-BUTUF-XB 100), and isotactic poly-4-methyl pentene-1 (P4MP) (I.C.I. TPXRT 18). In the present study three low-density polyethylenes obtained from RAPRA (LDPE 1, LDPE 3, LDPE 5 standards) were used. The polymers are characterized as high density or low density polyethylenes in Table I, together with their number average and weight average molecular weights, index of polydispersity and the melt flow index. All polymers were as-received.

TABLE I Characterization of the polyethylenes used

Polymer code	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	MFI g/10 min
PE	8	92	11.6	3.7
LDPE1	24.6	215	8.7	0.2
LDPE3	16.6	96	5.5	3.3
LDPE5	11.1	77	7.0	24.6

2.2. Preparation of blend samples

The blends were prepared using a suitable mixing mini-extruder and the cylindrical specimens obtained by extrusion were used directly in the experimental tests.

2.3. Methods of characterization

The crystallinity was determined by differential scanning calorimetry (DSC), and the degree of orientation of the extrudate was estimated qualitatively from X-ray diffraction patterns in the wide-angle region, and was found to be negligible in all cases. Apparent equilibrium swelling measurements were also performed on the extruded specimens. All these techniques were described in the previous paper [6].

Mechanical measurements in the tensile mode were performed by using Instron machine (table model 1122) at room temperature with a cross-head speed of 10 mm min^{-1}. The Young's modulus, yield point, tensile strength and elongation at break were determined for the samples from the relative stress–strain curves.

3. Results and discussion

3.1. Thermal properties

The experimental melting points, T_m, and the fractional crystallinity, X_c of crystallizable component, as a function of the PS percentage for the three low-density polyethylene–polystyrene blends are reported in Fig. 1. The very slight decrease in crystallinity and in the melting point with increasing PS content can possibly be attributed to kinetic limitations of crystal growth probably due to the sudden vitrification of PS after extrusion. In addition, the same processing conditions described previously [6], imposed on all the blends can produce a distorted radial temperature distribution across the filaments. Such an effect is due to the separation of PS and polyolefin in two distinct phases, and to the fact that the morphology of the blends changes at the PS content is varied. These hypotheses were suggested in the previous work [6], dealing with PS–PE,

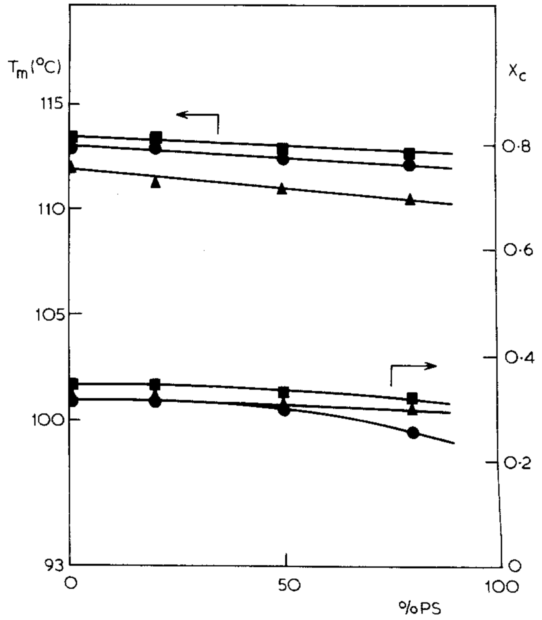

Figure 1 The effect of blend composition upon the apparent melting point, T_m, and on the fractional crystallinity X_c (right-hand vertical axis) for LDPE1–PS (●), LDPE3–PS (▲), LDPE5–PS (■) blends.

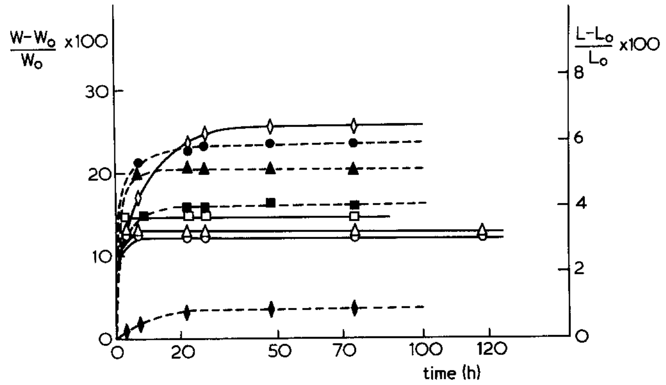

Figure 2 Kinetics of gravimetric sorption, $(W-W_0)/W_0$ (solid lines) and axial swelling $(L-L_0)/L_0$ (dashed lines) of LDPE5–PS blends at different PS percentages: ●, ○ 0%; ▲, △ 20%, ■, □ 50%, ◆, ◇ 80%.

PS–PP, PS–PB and PS–P4MP blends where the complete immiscibility of the two components was also confirmed by density measurements for the PS–PE and PS–PP blends and by the invariance of the PS glass transition temperatures for PS–PE, PS-PP, PS–P4MP blends over the entire range of composition.

In the present work, no glass transition temperature of PS in the blends was detectable for LDPE blends since such a transition was completely obscured by the melting peak of the polyolefin, as in the previous case of PS–PB blends.

3.2. Gravimetric and axial swelling

Typical gravimetric increment data, $(W-W_0)/W_0$, and the axial elongation ratio, $(L-L_0)/L_0$, (right-hand vertical axis) are plotted versus time for LDPE5–PS blends in Fig. 2 (W_0 and L_0 are the initial weight and length of the dry specimens, respectively). All the curves corresponding to different PS concentrations, seem to approach, within the limits of experimental errors, to equilibrium values. The equilibrium gravimetric increment increases monotonically with increasing PS content, whereas the corresponding axial swelling data show, surprisingly, the opposite trend.

The apparent equilibrium swelling $[(L-L_0)/L_0]_{eq}$ as a function of total amorphous content is reported in Fig. 3. The distinct curves tend toward zero axial swelling with increasing total amorphous fraction, which in the upper limit, refers to a pure PS specimen. It should be noted that the greater the fractional crystallinity of the polyolefin, the higher must be the PS content for a given total amorphous fraction.

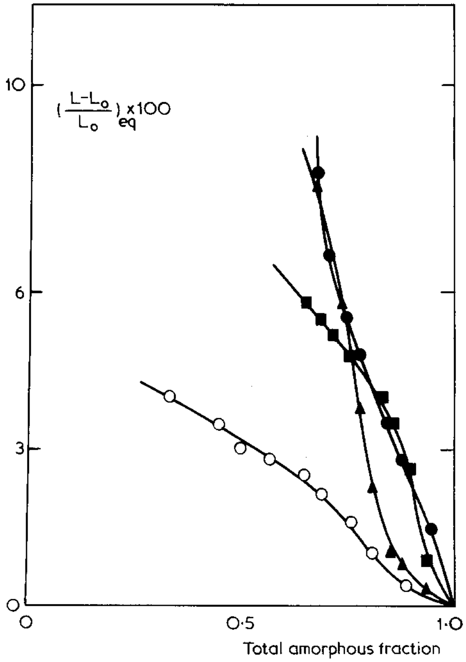

Figure 3 Curves of apparent equilibrium axial swelling $[(L-L_0)/L_0]_{eq}$ as a function of total amorphous content for the various blends: LDPE1–PS ●, PDPE3–PS ▲, LDPE5–PS ■, PE–PS ○.

The anisotropic behaviour is due presumably to the simultaneous presence in all the blends of a rubbery polyolefin and a glassy component, PS. The former swell by Fickian absorption [17] and the latter by the so called "case II" kinetics [18]. Therefore, as explained in detail elsewhere [6], due to the continuous presence of a glassy core in the PS domains, there is an increasing tendency of the cylindrical specimen to expand radially with increasing PS content up to and including the time for complete equilibrium of the entire composite. If the apparent equilibrium gravimetric swelling is plotted as a function of total amorphous fraction (Fig. 4), the data relative to the single blends combine apparently, within the limits of experimental errors, on a single master curve. This could be due to the fact that the sorption of *n*-hexane in the amorphous regions of

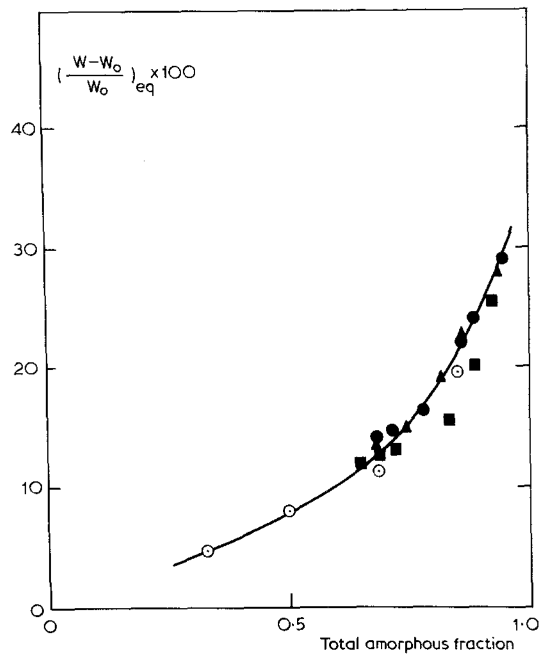

Figure 4 Master curve of apparent equilibrium gravimetric swelling $[(W-W_0)/W_0]_{eq}$ as a function of total amorphous fraction of the following blends: LDPE1–PS ●, LDPE3–PS ▲, LDPE5–PS ■, PE–PS ○.

TABLE II Equilibrium gravimetric swelling of crystallizable polyolefins as a function of their amorphous content

Polymers	Volume fraction of amorphous polymers	Gravimetric swelling based upon amorphous phase volume
PE	0.33	22
PP	0.64	18
LDEP1	0.65	19
LDPE3	0.68	20
LDPE5	0.69	21
PB	0.74	18
P4MP	0.82	22
PS*	1.00	28

*In slabs.

the polyolefins (assuming no penetration in, and no solution of, polyolefin crystals) is of the same order of magnitude, as shown in in Table II. But this is only possible if the amount of glassy PS left after absorption is small with respect to the total amorphous fraction of the blend. On the other hand, the glassy PS still present, in a such situation of quasi-equilibrium, must be able to provide the anisotropy of the specimens.

3.3. Mechanical properties

Typical stress–strain curves for most of the pure polyolefins used in the present work (namely PE, PP, PB, LDPE1, P4MP) are given in Fig. 5. The initial slope of the curves represents the Young's modulus, E, which at equal cross-head speed, is a property of the materials at vanishing elongation value. For a semicrystalline polymer, E will depend mainly upon its fractional crystallinity and upon its morphology.

The fractional crystallinity, X_c, of the examined polyolefins previously reported [6], and that of the low-density polyethylenes measured here (Fig. 1), varies according to the following sequence:

$$X_c^{\mathrm{PE}} > X_c^{\mathrm{PP}} > X_c^{\mathrm{PB}} > X_c^{\mathrm{LDPE5}} > X_c^{\mathrm{LDPE3}} \simeq X_c^{\mathrm{LDPE1}} > X_c^{\mathrm{P4MP}}.$$

Therefore, since the starting morphology of the extruded filaments is predominantly spherulitic in all cases, as shown by wide-angle X-ray diffraction analysis, E follows the same sequence of X_c, the exception being the P4MP (whose behaviour is very peculiar, see later).

It is well established, moreover, that at very high deformation values, a semicrystalline polymer can have different kinds of stress–strain curves (brittle, abruptly yielding ductile, smoothly yielding ductile). The shape of the curves will depend upon the rate of deformation, temperature of testing or on a combination of both. However, the cross-head speed and the temperatures have been kept constant in the present work for all the samples. Therefore, the brittle or the ductile behaviour will depend mainly on the starting morphology or rather on the crystallinity of the resin [19]. In fact, PE shows a marked plastic behaviour with easy necking formation. PP has a lower crystallinity content, but shows higher yield strength and elongation values. PB, however, shows a smoothly yielding ductile curve without necking dependent on its level of crystallinity and probably on its molecular weight, as discussed previously by Rakus *et al.* [20]. LDPE samples show the same mechanical behaviour as PB, again depending on their level of crystallinity, also due, in such a case, to the effect of branching. On the other hand, P4MP, in spite of its low value of fractional crystallinity, shows an abruptly yielding ductile stress–strain curve. Such behaviour can be

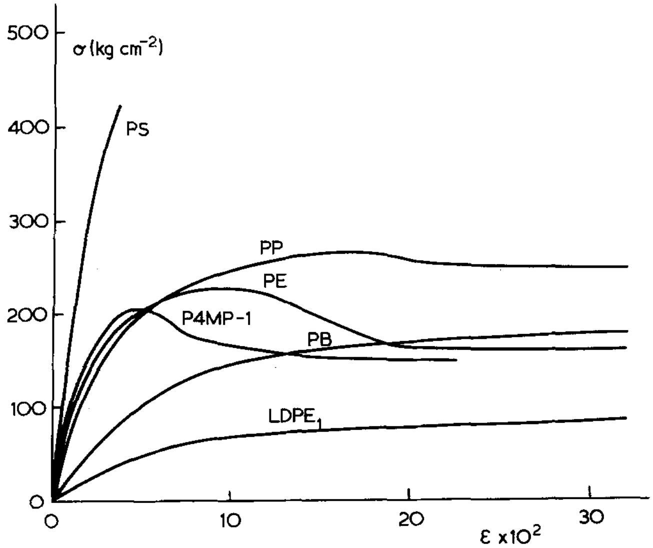

Figure 5 Stress–strain curves for the different homopolymers as indicated.

understood if one takes into account that the glass transition temperature of P4MP is very close to room temperature, ranging from 15 to 29° C depending on crystallinity [21, 22]. Therefore, P4MP can show yielding behaviour, especially if one assumes that some further relation mechanism lower than the T_g of the polymer is present at room temperature (as in the case of nylon). This can also explain why the value of E is higher than those of all the other polyolefins but lower than that of PS (whose brittle stress–strain behaviour is also reported in Fig. 5). On the basis of Fig. 5 it is possible to understand the mechanical tensile features of polyolefin–polystyrene blends.

Stress–strain curves of PE–PS blends at five different PS percentages are reported in Fig. 6. The behaviour gradually goes from brittle fracture of pure polystyrene (curve A) to a more and more plastic deformation of pure polyethylene (curve E). One can say that up to 30% PS, the blend is a two-phase system with a glassy matrix containing a PE dispersion. At a PS content less than 40%, but greater than 30%, the material undergoes an inversion of phases with a PE matrix containing a PS dispersion. Furthermore, in the latter case, as inferred by the swelling data given in the present work and also that previously reported [6], the PS dispersed phase is in the form of fibrils preferentially oriented along the direction of extrusion.

All other blends exhibit an analogous behaviour with minor different features depending on the mechanical properties of the corresponding

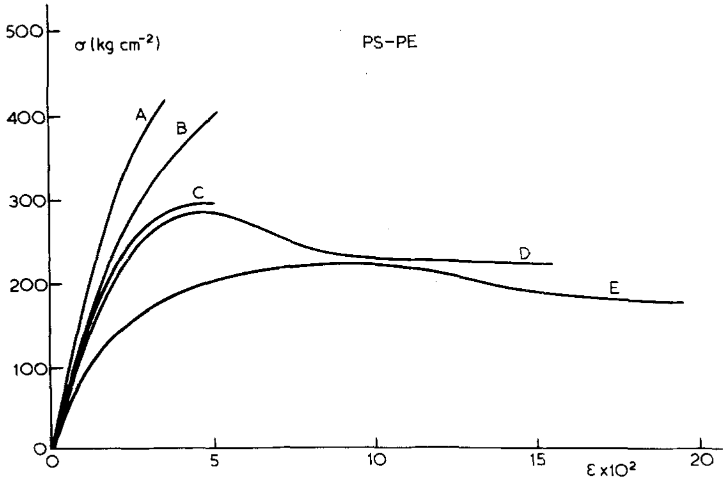

Figure 6 Typical strain curves for PE–PS blends at different PS percentages: A, 100%; B, 65%; C, 40%; D, 30%; E, 0%.

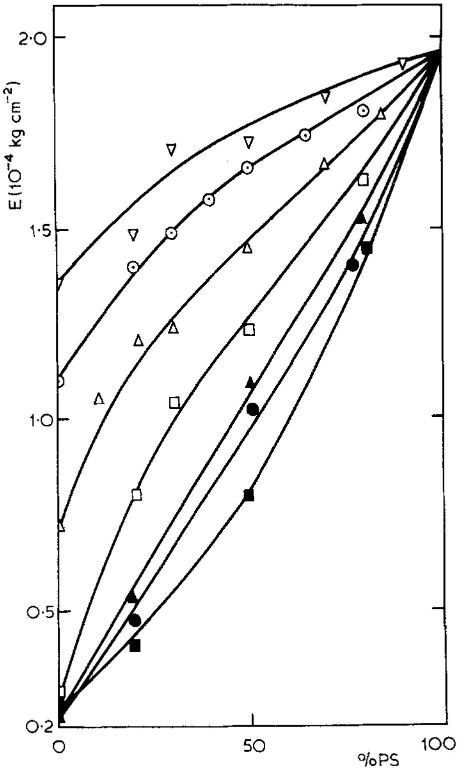

Figure 7 Young's modulus, E, as a function of PS percentage for the blends P4MP–PS ▽, PE–PS ○, PP–PS △, PB–PS □, LDPE1–PS ●, LDPE3–PS ▲, LDPE5–PS ■.

polyolefins. The Young's modulus, E, as a function of PS percentage, reported in Fig. 7, shows a monotonic increase with increasing PS, i.e. as increase in rigidity, for all the blends examined. It should be noted that no anisotropy was revealed by the mechanical behaviour since all tensile measurements were made only in the direction of extrusion and not transverse to it.

4. Conclusions

Polyolefins and polystyrene are very incompatible materials in the molten state but, various overall morphologies can according to their different viscosities be obtained, and to their relative amounts. Even at the very low strain rates used in their preparation [6], where no orientation in the crystalline regions was detected by X-ray diffraction technique, the overall morphology of the two distinct domains can give rise to a marked anisotropy in the specimen, as revealed by swelling measurements.

At low PS contents, the anisotropy can be attributed to the presence of microfibrils preferentially oriented along the direction of extrusion. Such microfibrils are presumably obtained by the squeezing of the PS particles throughout the die and by the subsequent rapid cooling of the filaments below the PS glass transition temperature. Therefore, up to a given PS concentration, the blend will consist of a polyolefin matrix with PS dispersed as oriented microfibrils. Beyond such a value, an inversion of matrix with an interconnected PS phase and a polyolefin dispersion is obtained. In this case, the anisotropy is due to the cylindrical shape of the whole specimen, which can only expand radially up to the equilibrium time of the entire composite. Taking in account the master curve of Fig. 4, one can say that the swelling data refer to a quasi-equilibrium state in which the small amount of remaining glassy PS are still effective to give the observed anisotropy. With repect to the mechanical properties of such blends, it should be noticed that their behaviour is substantially dependent upon the macroscopic properties of PS, i.e. upon its brittleness, irrespective of its microstructure. In fact, analogous mechanical behaviour was also observed in blends of poly(ethylene-oxide) of two different molecular weights [16]. In such a case, the lower molecular weight samples was very brittle because of its very high crystallinity, whereas the higher molecular weight sample had a classical semicrystalline mechanical behaviour.

The present work underlines that swelling measurements are a very interesting technique for obtaining morphological information on this type of blend. Nevertheless, in order to make this investigation more conclusive, work in progress to correlate the rheological properties of the pure components and blends in the molten state and the methods of mixing, to the morphology of the extrudate specimens. Such a morphological study will be accomplished by optical, transmission and scanning electron microscopy.

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