Dynamic mechanical properties of polystyrene/low density polyethylene blends

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The dynamic mechanical properties of polystyrene/low density polyethylene blends and of polystyrene/polyethylene/di-block polystyrene—polyethylene copolymer blends have been investigated in the temperature range −160°C to +100°C. It is shown that anomalies in the low temperature shear modulus data of polystyrene—polyethylene blends are a consequence of non-adhesion between the components. From similar data of blends containing a partial di-block PS—PE copolymer it appears that only very small amounts of copolymer are needed to ensure adhesion between the polystyrene and polyethylene phase. Further it is shown that for modulus considerations of the blends, LDPE together with partial PS—PE copolymer can be treated as a single phase. In some cases the presence of copolymer causes formation of a continuous network throughout the polystyrene matrix, as reflected by a low value for the shear modulus of these blends. Phase reversal of polystyrene—polyethylene blends results in an increase of the loss modulus at 40°C which is ascribed to an increased friction caused by phase entanglements. This increase is more pronounced if an excess of polyethylene is present which is again a consequence of non-adhesion between the components.

INTRODUCTION

Previous papers concerning the mechanical properties of polystyrene/polyethylene blends, to which sometimes a PS–PE sequential copolymer was added, reported on the tensile elastic modulus, the tensile strength, the Poisson ratio and the impact strength of these blends[1–4]. In most cases the addition of a polystyrene–polyethylene copolymer had a profound effect on these properties, showing the importance of adhesion between the components of a non-compatible blend. In this paper the results are presented of a study concerning the dynamic mechanical properties of polystyrene/polyethylene blends and of polystyrene/polyethylene blends to which a partial di-block polystyrene–polyethylene copolymer had been added to provide for adhesion between the two phases. As it was known that the influence of adhesion on the shear modulus is rather small at room temperature it was decided to extend the temperature range to −160°C. At low temperature the shear modulus of polyethylene is much higher than at room temperature, so it is likely that the influence of adhesion on the dynamic mechanical properties will be more pronounced at low temperatures. A second advantage of measuring over a range of temperatures is that transitions can be detected, which may give more insight into the behaviour of the blends.

EXPERIMENTAL

The homopolymers used in the blends were polystyrene Styron 664, obtained from Dow Chemical Co., and low density polyethylene Stamylan 1500, from DSM, The Netherlands. The partial di-block polystyrene–polyethylene copolymer was obtained by hydrogenating a partial di-block polystyrene–polybutadiene copolymer Solprene 410 from Phillips Petroleum Co. This copolymer consists of sequences with the following molecular weights: $|PS\text{–}(PS\text{–}PB)_{random}\text{–}PB| = |22\,000\text{–}22\,000\text{–}25\,000|$. Blending was done on a Schwabenthan laboratory mill at 190°C. Bulk mixing was improved by repeatedly taking the polymer sheet out of the calendar and turning it 90°. The total mixing time was 8 minutes. The blend was then compression moulded in a Fontijne hydraulic press at 200°C to obtain a sheet out of which isotropic test specimens with dimensions of 120 × 5.7 × 2.7 mm could be machined. The test specimens were conditioned at 21°C and 65% r.h. for about 48 hours. The shear modulus and loss modulus of the blends were measured on a Nonius torsion pendulum (Nonius Instrumenten Fabriek, Delft, The Netherlands) equipped with a liquid nitrogen cooling device. The frequency was usually between 1 and 2 Hz. The thermal properties of the partial di-block copolymer were investigated using a DuPont 910 differential scanning calorimeter.

RESULTS AND DISCUSSIONS

Polystyrene, low density polyethylene and partial di-block polystyrene–polyethylene copolymer

In *Figures* 1 and 2 the shear modulus and the loss modulus of respectively polystyrene, low density polyethylene (LDPE) and the partial di-block polystyrene–polyethylene copolymer are represented. The shear modulus of polystyrene shows a steep decrease as the temperature approaches T_g, accompanied by a rise in the loss modulus. The faint shoulder in the loss modulus curve at 20°C may be associated with the β-relaxation that is attributed to the freezing-in of the phenyl groups[5]. At temperatures lower than −120°C the shear modulus of the LDPE is higher than the shear modulus of polystyrene. A steep fall of the shear modulus of

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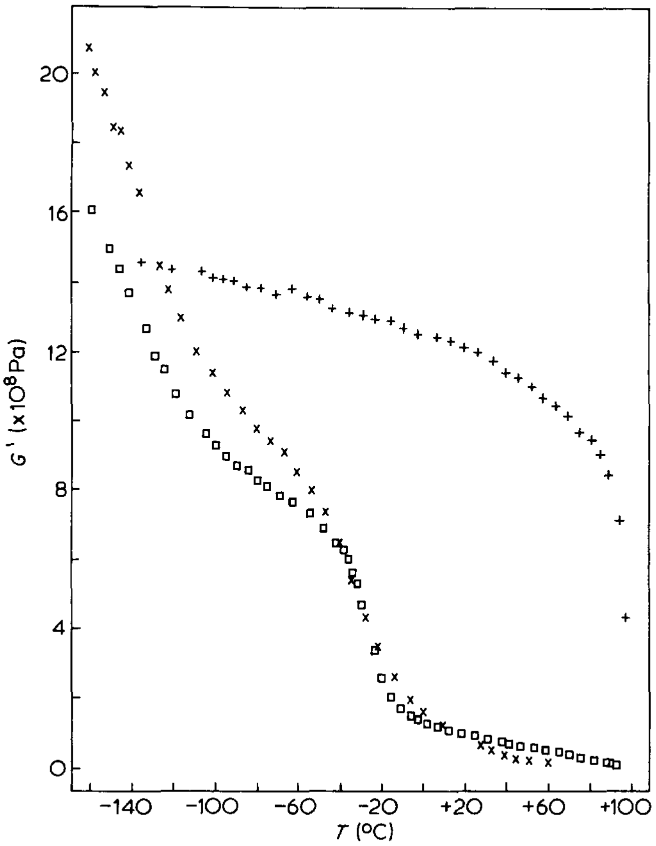

Figure 1 Shear modulus of polystyrene (+), LDPE (x) and a partial di-block polystyrene–polyethylene copolymer (□) as a function of temperature

LDPE can be observed as the temperature gets higher than −30°C. This fall is followed by a plateau region.

The loss modulus curve exhibits three relaxations: at approximately 40°C the α-relaxation caused by shear in the c-axis direction in geometric planes with crystalline regions containing the c-axis[6,7]. The β-relaxation temperature is about −30°C, and is a consequence of interlamellar shear[8], while the γ-relaxation at −130°C arises from crankshaft motions in the molecular chains[9,10].

At low temperatures the shear modulus of the *partial di-block PS–PE copolymer* is somewhat lower than the modulus of LDPE and polystyrene. This is probably caused by the presence of the random part in this copolymer. The rapid decrease of the shear modulus at temperatures higher than −40°C, as found for LDPE has been observed for this material as well. However, the plateau that follows this decrease is somewhat higher than found for LDPE due to the presence of polystyrene segments. The loss modulus curve shows the β- and γ-relaxations from the polyethylene part of the copolymer. Conspicuous is the absence of the α-relaxation. A thermogram of this material (*Figure* 3) indicates partial melting at 40°C. It may well be that, because of this partial melting, stresses are not transmitted to the crystalline regions where the α-relaxations take place.

Polystyrene/polyethylene homopolymer blends

In *Figure* 4 the moduli of the blends are plotted as a function of the polystyrene volume fraction at various temperatures. At room temperature and at higher temperatures a relatively fast drop of the modulus is observed as the polyethylene content increases[11].

As already shown above (*Figure* 1) the modulus of LDPE increases much faster than the modulus of polystyrene as the temperature gets lower. So a decrease in temperature would be expected to result in a faster rise of the modulus of blends containing an excess of polyethylene than of the modulus of blends containing an

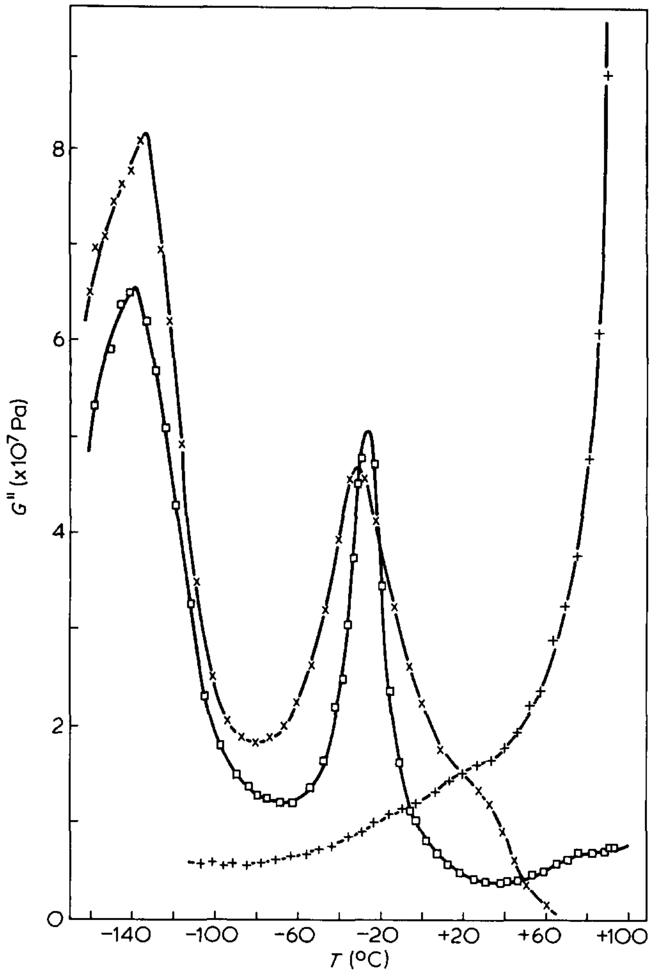

Figure 2 Loss modulus of polystyrene (+), LDPE (x) and a partial di-block polystyrene–polyethylene copolymer (□) as a function of temperature

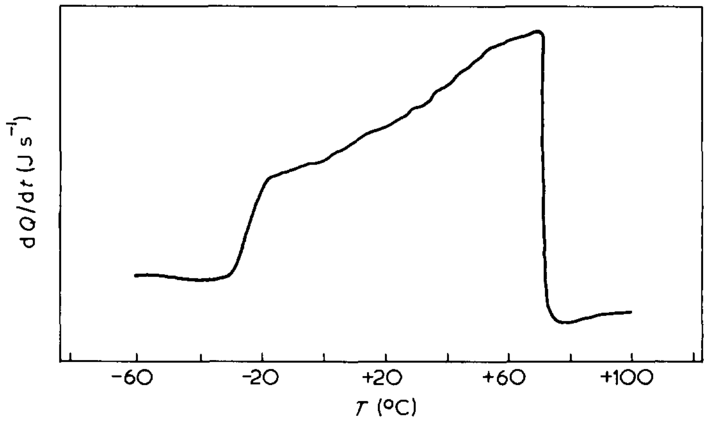

Figure 3 D.s.c. melting thermogram for a partial di-block polystyrene–polyethylene copolymer

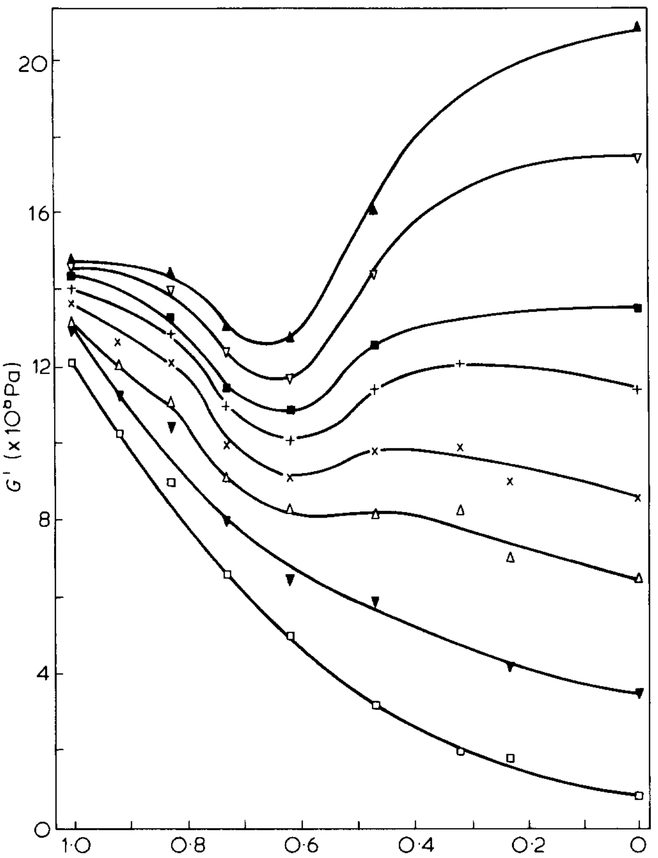

Figure 4 Shear moduli of polystyrene—polyethylene homopolymer blends as a function of the polystyrene content at various temperatures. ▲, −160°; ▽, −140°; ■, −120°; +, −100°; x, −60°; △, −40°; ▼, −20°; □, +20°C

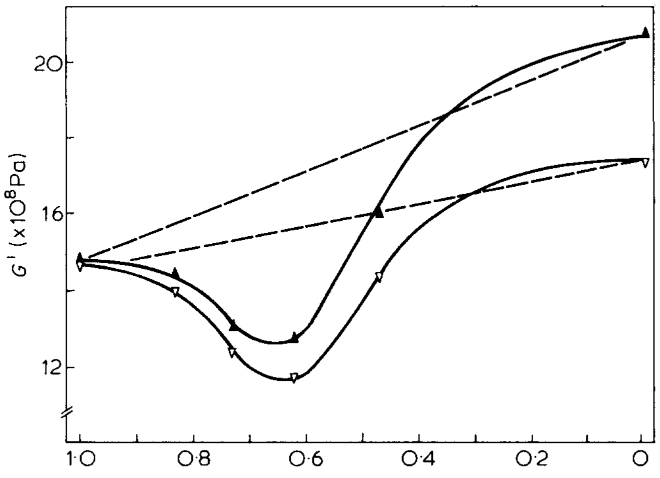

Figure 5 Shear moduli of PS—LDPE homopolymer blends as function of the polystyrene content with the Hashin—Shtrikman lower bounds on the moduli; ▲, −160°C; ▽, −140°C

excess of polystyrene. This, indeed, is what has been found experimentally, as shown in *Figure* 4. It is conspicuous, however, that at low polyethylene contents the slopes of the modulus–polyethylene content curves are always negative, even for temperatures at which the modulus of polyethylene is higher than that of polystyrene. At −140°C the moduli of blends containing less than approximately 50% polyethylene are even lower than the modulus of either component. Hashin and Shtrikman have provided rigorous bounds on the shear modulus of blends of arbitrary geometry[12]. The lower bound for a binary blend with components 1 and 2 is given by the following relation:

$$G\ (\text{lower bound}) = G_1 \frac{f_2}{\dfrac{1}{G_2 - G_1} + \dfrac{6(K_1 + 2G_1)f_1}{5G_1(3K_1 + 4G_1)}}$$

if $K_2 > K_1$ and $G_2 > G_1$. (G is the shear modulus, K is the bulk modulus and f is the volume fraction.) Assuming that the Poisson ratio of polystyrene is not very temperature dependent, the bulk modulus of polystyrene has been calculated to be 4×10^9 Pa at −160°C, and 3.8×10^9 Pa at −140°C ($\nu_{PS} = 0.33$)[11]. Using these values the lower bound on the shear modulus could be calculated for −140°C and −160°C, and is represented in *Figure* 5 by the broken curves. *Figure* 5 shows that at these temperatures the actual modulus at low polyethylene content is lower than theoretically possible.

This behaviour can be explained as follows. If the volume fraction of LDPE is less than ±30%, the blend is composed of a polystyrene matrix in which more or less spherical polyethylene particles are embedded (*Figure* 6). As a consequence of the mismatch between the coefficients of thermal expansion of the components ($\alpha_{LDPE} = 24 \times 10^{-5}$ K^{-1}, $\alpha_{PS} = 7 \times 10^{-5}$ K^{-1}) and of the lack of adhesion between the components if no copolymer is present (compare *Figure* 6 with *Figures* 7 and 8) mechanical interactions between the components will be weak. This results in a small load bearing capacity of the polyethylene particles and the material will behave more or less like a polystyrene foam with a void content that depends on the polyethylene content. At low temperatures this is reflected in the decrease of the modulus as the polyethylene content increases. At higher temperatures

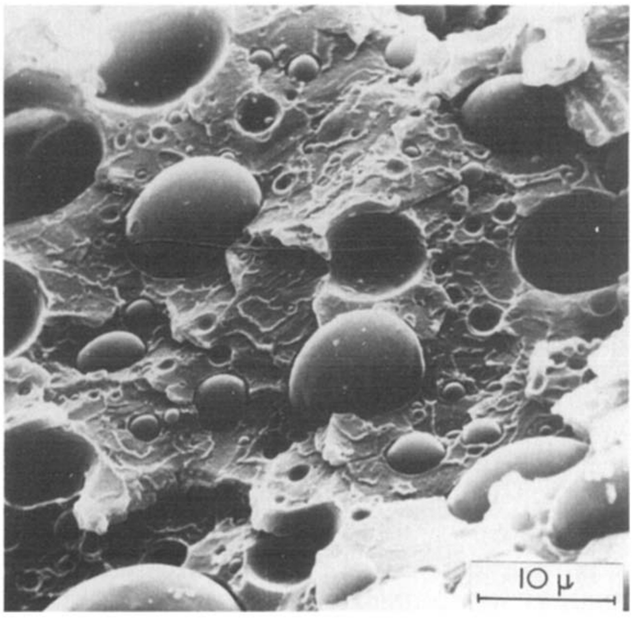

Figure 6 Scanning electron micrograph of the fracture surface of an 85/15% (v) PS/PE homopolymer blend, showing more or less spherical PE particles in a PS matrix

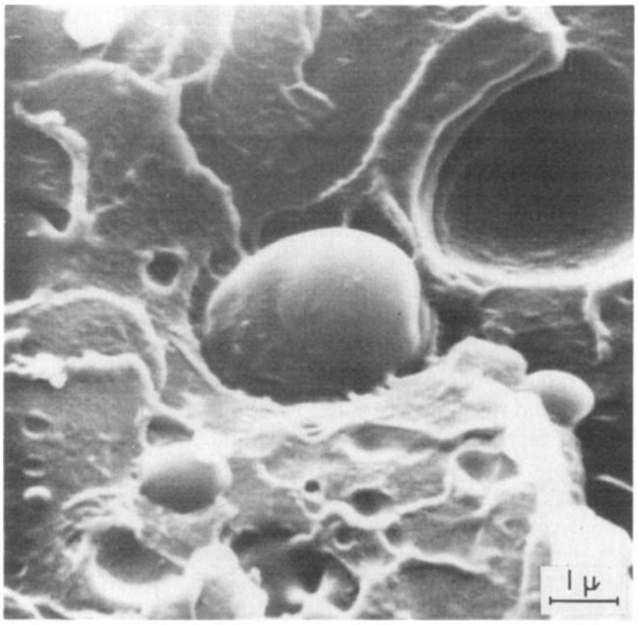

Figure 7 Scanning electron micrograph of the fracture surface of an 85/15% (v) blend to which 1% (v) copolymer has been added. Adhesion between the PE sphere and the PS matrix is readily observable

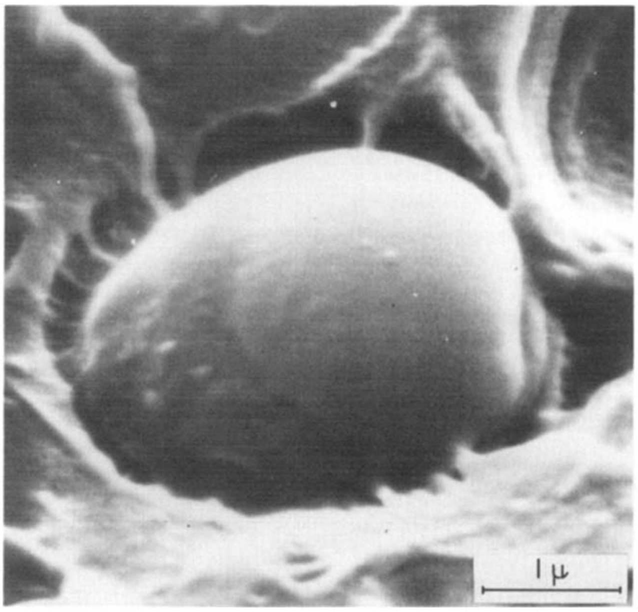

Figure 8 Detail of *Figure 7*

this effect is much smaller, as the modulus of a blend consisting of a very stiff matrix and a dispersed low modulus phase is not very sensitive to changes in the modulus of the dispersed phase. However, as demonstrated in earlier work, the Poisson ratio of such a blend still reflects the hole-like behaviour of the polyethylene particles[11].

At high polyethylene volume fractions the blends consist of a polyethylene matrix in which polystyrene particles are embedded (*Figure* 9). Now the misfit in the thermal coefficients of expansion provides strong mechanical interaction between the two phases, resulting in a normal modulus behaviour of these blends. If the modulus of the polystyrene is higher than the modulus of polyethylene, then addition of some polystyrene to polyethylene results in a higher modulus material.

In *Figure* 10 the loss modulus values for a number of polystyrene–polyethylene blends are plotted against temperature. In the curves the α-, β- and γ-relaxations of LDPE at respectively 40°C, −30°C and −130°C are readily discernible. A marked maximum in the loss modulus at 40°C (the α-relaxation) is observed if this modulus is plotted against the volume fraction of polyethylene (*Figure* 11). Since the value of the loss modulus here is higher than the loss modulus of either component, the origin of the plateau must be found in the morphology of these blends. A micrograph of a 50/50 vol.% polystyrene–polyethylene blend shows phase entanglements (*Figure* 12). Deformation of such a blend will cause slippage accompanied by friction between the stiff and the viscoelastic phases, resulting in the observed increase of the loss modulus.

As shown above mechanical interactions between the phases will be stronger if an excess of polyethylene is present. This explains why the increase of the loss modulus is more pronounced if an excess of polyethylene is present. A decrease of temperature raises the modulus of polyethylene which will reduce the friction between the entangled stiff phases. This is reflected in the relatively smooth increase of the loss modulus at −30°C (β-transition of polyethylene) as the polyethylene volume fraction increases (*Figure* 13).

Polystyrene–polyethylene–partial di-block polystyrene–polyethylene copolymer blends

As LDPE and the partial di-block polystyrene–polyethylene used in these blends have appromimately the same shear modulus and Poisson ratio[11] (provided that the temperature is not too low), an attempt has been made to consider combinations of both materials as a single phase in the following discussion.

The moduli of blends containing polystyrene, polyethylene and the partial di-block polystyrene–

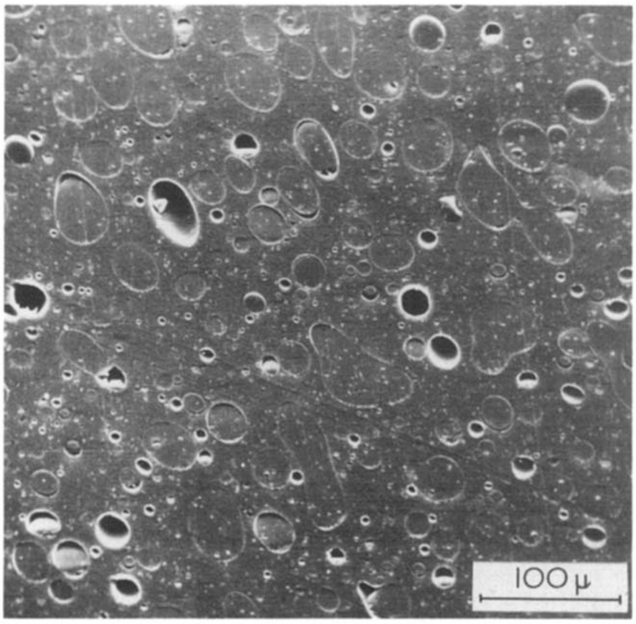

Figure 9 Scanning electron micrograph of the microtomed surface of a 65/35% (v) PE/PS homopolymer blend, showing PS particles embedded in the PE matrix

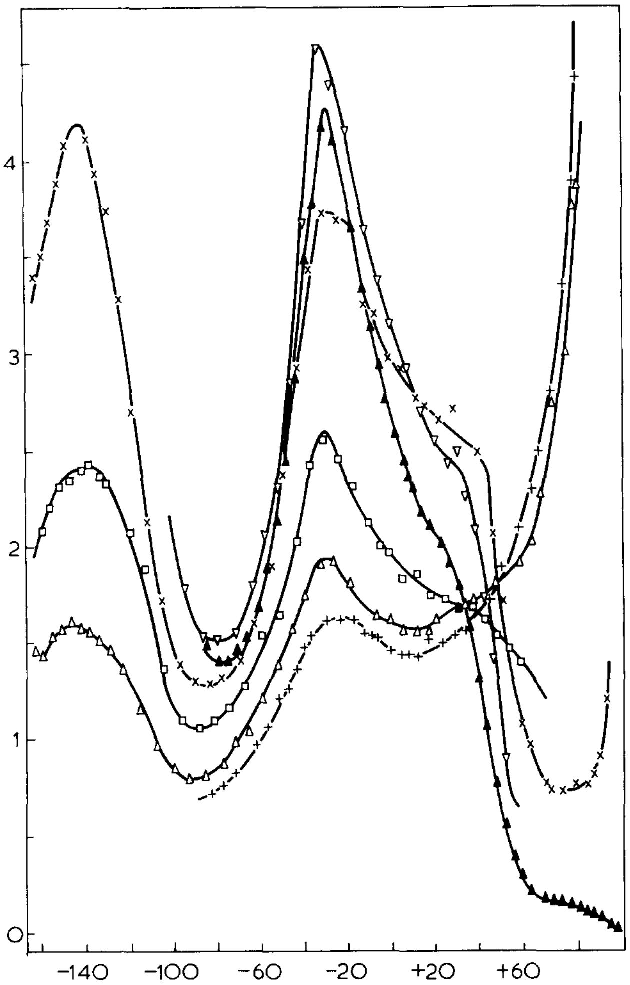

Figure 10 Loss moduli of polystyrene–polyethylene homopolymer blends as a function of the temperature. Compositions of the blends (PS/PE vol %): ▲, 23/77; ▽, 32/68; x, 47/53; □, 62/38; △, 83/17; +, 92/8

polyethylene copolymer are represented in *Figure* 14 as functions of the polystyrene content. From this Figure it can be seen that at all temperatures the different blends give more or less one curve with the exception of the blend indicated by the letter j at very low temperatures. This indicates that indeed for modulus considerations it is correct to treat combinations of polyethylene and the copolymer as one phase. In blend j the lower modulus of the copolymer at low temperatures as compared with polyethylene makes itself felt.

If the volume fraction of the combined phase is not too low, the moduli at room temperature of blends containing the di-block copolymer are somewhat lower than the

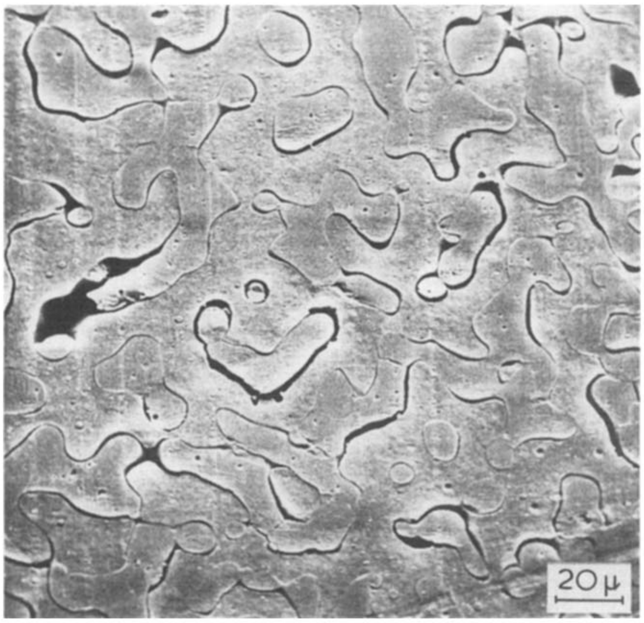

Figure 12 Micrograph of a 50/50 vol % polystyrene–polyethylene homopolymer blend, showing phase entanglements

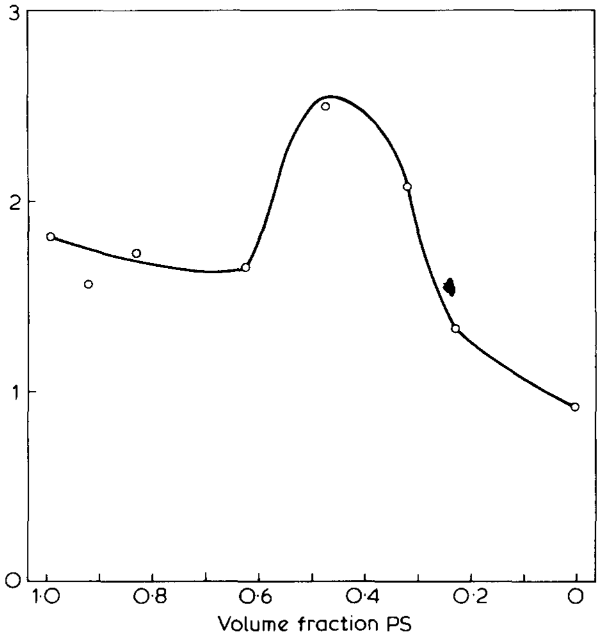

Figure 11 Loss modulus at 40°C (α-transition) as a function of the polystyrene content in polystyrene–polyethylene homopolymer blends

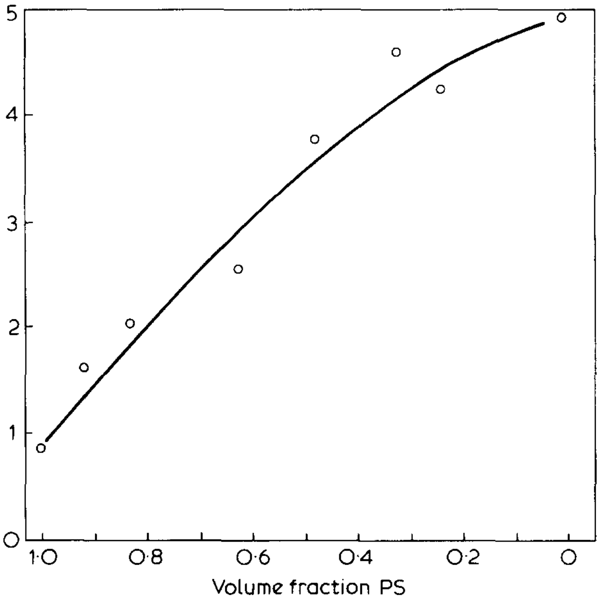

Figure 13 Loss modulus at −30°C (β-transition) as a function of the polystyrene content in polystyrene–polyethylene homopolymer blends

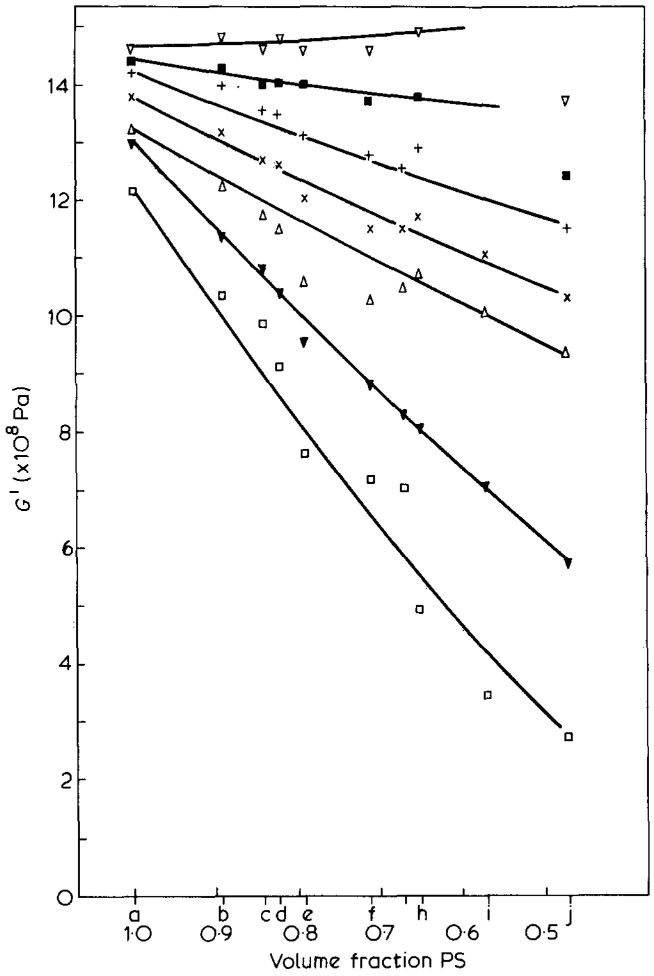

Figure 14 Shear moduli of blends containing the partial di-block polystyrene–polyethylene copolymer as a function of the PS content. Temperatures: ▽, –140°; ■, –120°; +, –100°; x, –60°; △, –40°; ▼, –20°; □, +20°C. Composition (PS/PE/copolymer vol %): (a) 100/0/0; (b) 89/5.1/5.9; (c) 82.5/15.8/1.7; (d) 83.4/0/16.6; (e) 78.2/11.7/10.1; (f) 71.2/26.0/2.8; (g) 67.4/0/32.6; (h) 64.1/19.3/16.6; (i) 56.2/11.2/32.6; (j) 46.9/0/53.1

moduli of blends without copolymer of equal PS content. This can be ascribed to the weakening of the polystyrene matrix due to the formation of a low modulus continuous phase throughout the matrix[2,11].

Treating combinations of polyethylene and the copolymer as one phase makes it possible to compare copolymer containing blends with homopolymer blends. It is interesting to note that contrary to the homopolymer blends no dip can be observed in the modulus–volume fraction curve at low temperatures (*Figure* 14), even if only a very small amount of copolymer is present. This supports our view, based on *Figures* 6, 7 and 8, that the dip in the modulus–polyethylene volume fraction curves of blends that do not contain copolymer is caused by non-adhesion between the two phases. Secondly, it shows that only very small amounts of copolymer are needed to ensure good adhesion between the polystyrene and polyethylene phase.

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REFERENCES

1 Heikens, D., Hoen, N., Barentsen, W., Piet, P. and Ladan, H. *J. Polym. Sci.* (*Polym. Symp.*) 1978, **62**, 309
2 Coumans, W. J., Heikens, D. and Sjoerdsma, S. D. *Polymer* 1980, **21**, 103
3 Barentsen, W. and Heikens, D. *Polymer* 1973, **14**, 579
4 Barentsen, W., Heikens, D. and Piet, P. *Polymer* 1974, **15**, 119
5 Yano, O. and Wada, Y. *J. Polym. Sci.* (*A*-2) 1971, **9**, 669
6 Stachurski, Z. H. and Ward, I. M. *J. Macromol. Sci.* 1969, **B3**, 427
7 Stachurski, Z. H. and Ward, I. M. *J. Macromol. Sci.* 1969, **B3**, 445
8 Stachurski, Z. H. and Ward, I. M. *J. Polym. Sci.* (*A*-2) 1968, **6**, 1817
9 Shatzki, T. F. *J. Polym. Sci.* 1962 **57**, 496
10 Boyer, R. F. *Rubber Rev.* 1963, **34**, 1303
11 Sjoerdsma, S. D., Bleijenberg, A. C. A. M. and Heikens, D. *Polymer* in press
12 Hashin, Z. and Shtrikman, S. *J. Mech. Phys. Solids* 1963, **11**, 127