The Poisson ratio of polymer blends, effects of adhesion and correlation with the Kerner packed grains model

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(*Received* 16 *July* 1979; *revised* 2 *November* 1979)

The moduli and Poisson ratio of polystyrene–polyethylene blends with different compositions have been determined. In some cases a polystyrene–polyethylene copolymer was added to the blends to provide for adhesion between the components. It is shown that the Kerner packed grains model can be used to predice accurately both modulus and Poisson ratio of these blends. Deviations of both modulus and Poisson ratio from the predicted values occur in some blends containing block copolymer as a consequence of the copolymer-induced formation of a continuous low modulus phase at a relatively low concentration of the low modulus material. In the case of non-adhesion between the components only the Poisson ratio was found to deviate significantly from the predicted value. This is explained by assuming hole-like behaviour of the polyethylene particles due to non-adhesion and the misfit of the coefficients of thermal expansion of polystyrene and low density polyethylene.

INTRODUCTION

In the course of a research project on polystyrene plastics toughened with polyethylene and in some cases with a blend of polystyrene–polyethylene copolymer[1,2] an apparatus suitable for observing volume changes during tensile tests has been developed[3]. The object was primarily to study crazing phenomena. However, pre-crazing volume changes, measured by the Poisson ratio, could be determined quite accurately as well. This is of interest, since theoretically the Poisson ratio of a blend can reflect properties of the components that modulus, for example, cannot. The Kerner packed grains equations[4] for a two phase blend show that this is true, particularly for blends that consist of a stiff matrix and a ductile dispersed phase:

$$\frac{K_1-K_0}{3K_1+4G_0}f_1+\frac{K_2-K_0}{3K_2+4G_0}f_2=0$$

$$\frac{G_0-G_1}{(7-5\nu_0)G_0+(8-10\nu_0)G_1}f_1+\frac{G_0-G_2}{(7-5\nu_0)G_0+(8-10\nu_0)G_2}f_2=0$$

where K_0, K_1 and K_2 are the bulk moduli of the blend, component 1 and 2 respectively; G_0, G_1 and G_2 are the corresponding shear moduli, ν_0 is the Poisson ratio of the blend and f_1 and f_2 are the volume fractions of components 1 and 2.

For two kinds of blends, A and B, the modulus and Poisson ratio have been calculated using these Kerner equations (*Figures 1* and *2*). Blend A consists of a component 1 (modulus $G_1=10^9$ Pa, Poisson ratio $\nu_1=0.30$) and a component 2 (modulus $G_2=10^8$ Pa, Poisson ratio $\nu_2=0.45$). The components of blend B have the same elastic constants, except that the modulus of component 2 is $G_2=0.5\times10^8$ Pa. *Figure 1* shows the relative insensitivity of the modulus of a blend to a change in the modulus of the ductile dispersed phase if the volume fraction of the low modulus phase does not exceed 0.2. The Poisson ratio, however, is much more sensitive to a change in modulus in this concentration range (*Figure 2*).

The aim of this study is to explore whether the modulus and Poisson ratio of polystyrene–polyethylene blends can be described by the Kerner packed grains equations, and, secondly, whether the sensitivity attributed to the Poisson ratio as described above, can be verified experimentally.

The Kerner packed grains equations were chosen to compare the experimental data since they predict the moduli of blends as well as the Poisson ratio. These equations are based on Goodier's analysis of the elastic properties of material containing a spherical inclusion[5]. This analysis is extended to the elastic properties of a multicomponent blend by means of an averaging procedure. The packed grains equations were obtained by taking the volume fraction of the matrix material to be zero.

Application of these equations to a blend means that no *a priori* assumptions about the matrix material can be made. However, as the volume of the blend is statistically filled with the components, an excess of one of the components must result in a 'continuous' phase consisting of grains of this material. Thus it can be expected that the packed grains equations can be applied to systems that undergo phase inversion in a symmetrical fashion around the 50/50 composition. Since phase inversion of the polystyrene–polyethylene blends occurs at least approximately around this composition (*Figures 3*, *4* and *5*), it seemed profitable to compare the outcome of these equations with the experimental values for shear modulus and Poisson ratio.

0032–3861/81/050619–05$02.00

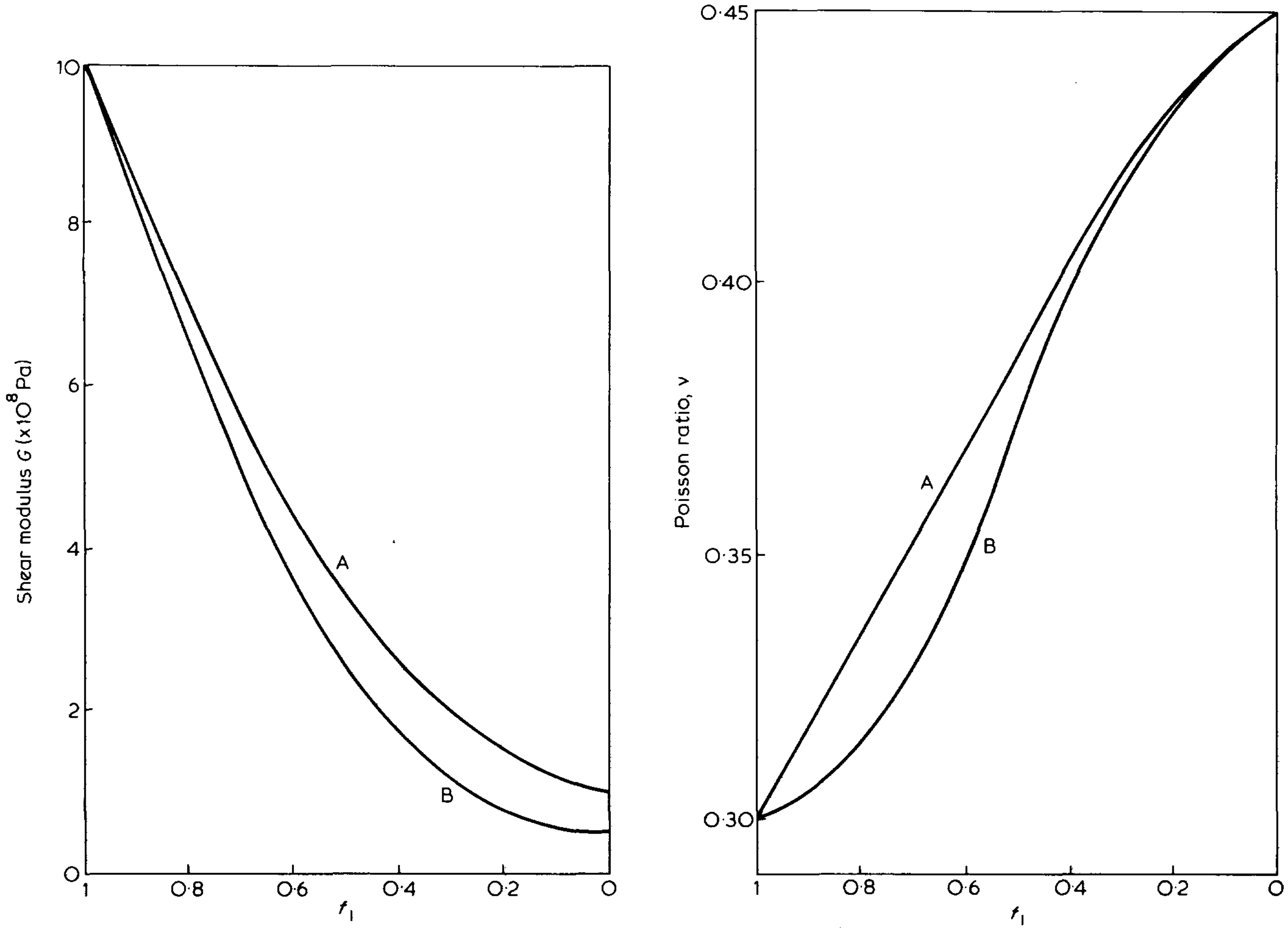
EXPERIMENTAL

The polymers used in the blends were polystyrene Styron 664 from Dow Chemical Co. ($\bar{M}_n \simeq 100\,000$, $\bar{M}_w/\bar{M}_n \simeq 2.5$), and low density polyethylene (LDPE) Stamylan 1500 from DSM, Holland ($\bar{M}_n \simeq 30\,000$–$40\,000$, $\bar{M}_w/\bar{M}_n \simeq 30$). A partial polystyrene–polyethylene diblock copolymer was obtained by hydrogenating a partial polystyrene–polybutadiene diblock copolymer (Solprene 410 from Phillips Petroleum Co.) consisting of sequences with the following molecular weights:

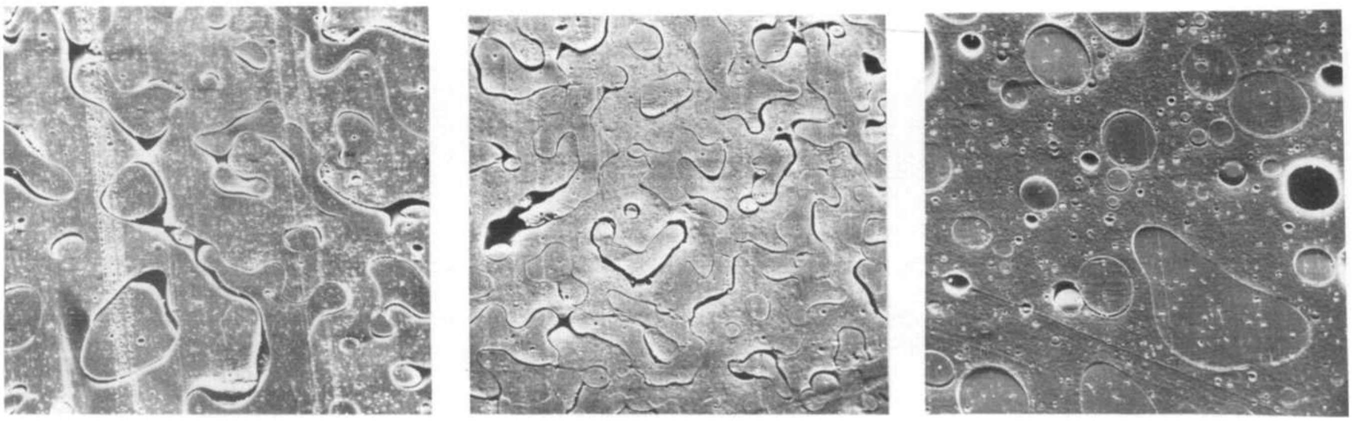
$$[\mathrm{PS}-(\mathrm{PS/PB})_{\mathrm{random}}-\mathrm{PB}] = [22\,000-22\,000-25\,000]$$

The blends were prepared on a Schwabenthan laboratory mill at 190°C. Test specimens were machined from compression moulded sheets.

The Poisson ratios of the blends were measured using a dilatometer system on a Instron tensile testing machine[3]. Volume changes of the tensile specimen during a tensile test result in a liquid displacement in the capillary attached to the dilatometer. This liquid displacement can



Figures 1 and *2* Moduli and Poisson ratio of blends predicted by the Kerner equations, showing the relative insensitivity of the modulus of the blend compared with the Poisson ratio of the blend to changes in the modulus of the ductile component, provided that the volume fraction of the ductile component is low



Figures 3, 4 and *5* Scanning electron micrographs of homopolymer blends showing phase inversion. Compositions 35/65, 50/50 and 65/35 wt % PE/PS, respectively be recorded continuously and with high accuracy using a conductivity meter. The Poisson ratio is calculated from the initial slope of the sample volume *versus* elongation curve. For samples containing less than 25% dispersed polyethylene and copolymer this initial slope corresponds to the linear elastic part of the stress–strain curve and time-dependent behaviour can be ignored. Samples containing higher concentrations of polyethylene and block copolymer will show time-dependent behaviour, but the initial slope corresponding to the Poisson ratio could be measured accurately at quite small strains ($<0.5\%$). The Poisson ratio of these samples, however, will certainly be somewhat strain rate dependent.

The tensile specimens had the dimensions as indicated by ASTM D 638 type (ii). The strain rate was 0.4 min^{-1}.

The modulus of the blends was measured on a torsion pendulum (Nonius Instrumenten Fabriek, Delft, The Netherlands). The test specimens had dimensions 120 $\times 5.7 \times 2.7$ mm.

Table 1 Mechanical properties of the blend components

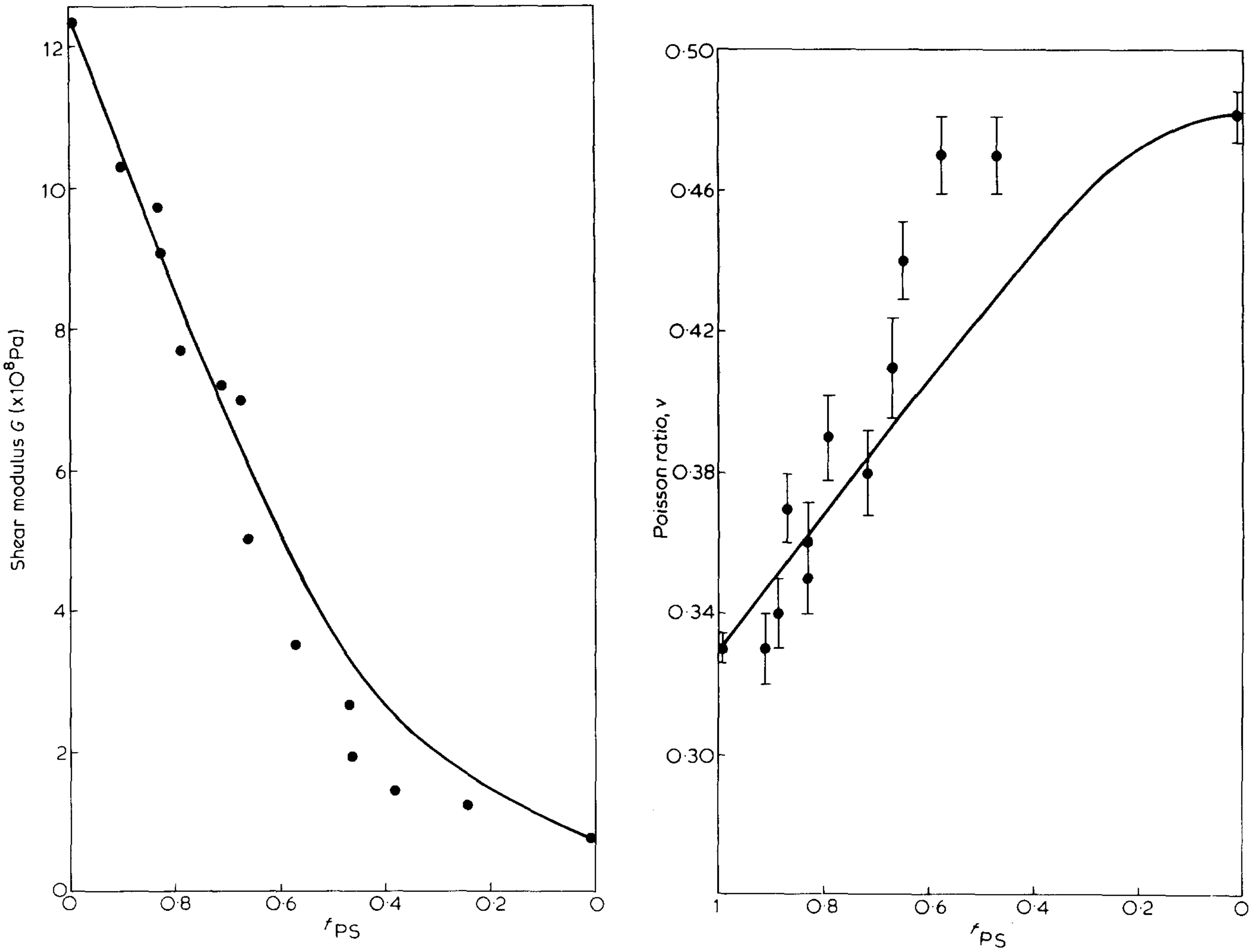
	Shear modulus ($\times 10^8$ Pa)	Poisson ratio
Polystyrene	12.2	0.33
Low density polyethylene	0.87	0.48
Polystyrene–polyethylene Diblock copolymer	0.95	0.47

RESULTS AND DISCUSSION

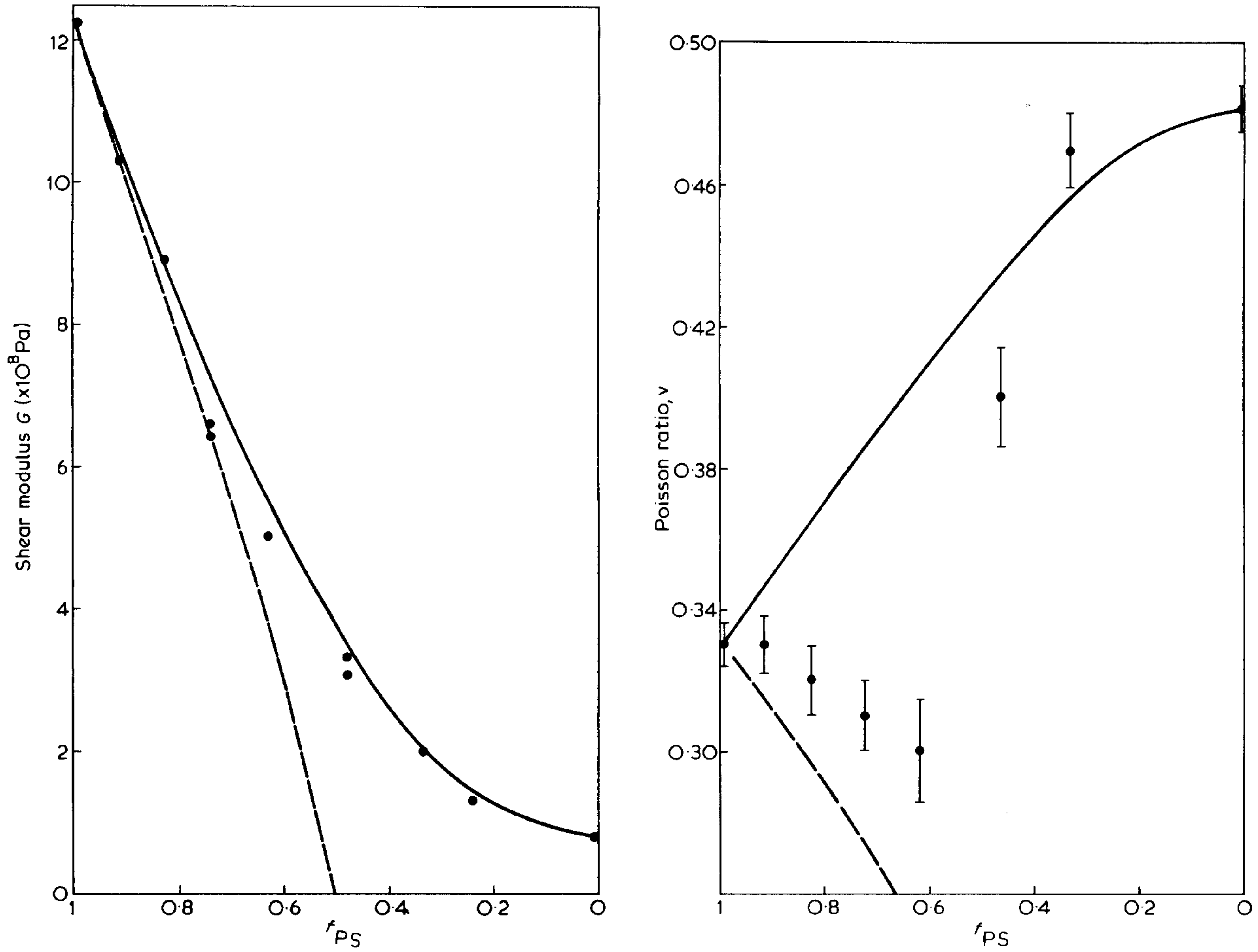
The experimentally found values for the shear modulus and the Poisson ratio of the homopolymers and polystyrene–polyethylene diblock copolymer are listed in

Table 2 Mechanical properties of PS–PE blends containing partial PS–PE diblock copolymer

PS (g)	PE (g)	Diblock PS–PE (g)	Vol. fraction PS	Shear modulus ($\times 10^8$ Pa)	Poisson ratio
92.13	7.12	0.75	0.91		0.33
90.25	5.25	4.50	0.89	10.3	0.34
88.00	3.00	9.00	0.87		0.37
85.00	0	15.00	0.83	9.8	0.36
84.25	14.25	1.50	0.83	9.1	0.35
80.50	10.50	9.00	0.79	7.6	0.39
73.75	23.75	2.50	0.71	7.2	0.38
70.00	0	30.00	0.67	7.0	0.41
67.50	17.50	15.00	0.65	4.9	0.44
60.10	36.10	3.80	0.57	3.5	
60.00	10.00	30.00	0.57	3.4	0.47
50.00	0	50.00	0.47	2.7	0.47
49.60	45.60	4.80	0.47	1.9	
41.20	53.20	5.60	0.38	1.4	
26.50	66.50	7.00	0.24	1.2	



Figures 6 and *7* Moduli and Poisson ratio of blends containing partial diblock PS–PE copolymer (*Table 2*). The full curves represent the values predicted by the Kerner packed grains equations



Figures 8 and *9* Moduli and Poisson ratio of PS–PE homopolymer blends (*Table 3*). Full curves represent the values predicted by the Kerner packed grains equations. The broken curves give the predicted values if the shear modulus and the compression modulus of the ductile component are taken to be zero, representing a situation in which no adhesion between the stiff matrix and the ductile dispersed phase exists

Table 3 Mechanical properties of PS–PE homopolymer blends

PS (g)	PE (g)	Vol fraction PS	Shear modulus (x 10^8 Pa)	Poisson ratio
92.5	7.5	0.92	10.3	0.33
85.0	15.0	0.87	9.0	0.32
75.0	25.0	0.73	6.4	0.31
75.0	25.0	0.73	6.6	
65.0	35.0	0.62	5.1	0.30
50.0	50.0	0.47	3.2	0.40
50.0	50.0	0.47	3.0	
35.0	65.0	0.32	2.0	0.47
25.0	75.0	0.23	1.4	

Table 1, the values for the polystyrene–polyethylene diblock copolymer-containing blends are listed in *Table 2*. As the shear modulus and the Poisson ratio of LDPE and the partial diblock polystyrene–polyethylene copolymer are approximately the same, it is possible to apply the Kerner model to a combination of both materials dispersed in polystyrene as a single phase that will adhere to polystyrene due to the presence of the copolymer[2]. Doing this, the experimentally obtained values for the modulus and the Poisson ratio of the blends have been plotted in *Figures 6* and *7*.

By inserting the experimentally obtained values for the modulus and Poisson ratio of the components in the Kerner equations, *Table 1*, the curves drawn in *Figures 6* and *7* were obtained. Up to a volume fraction of 0.3 of the ductile components, the Kerner equations describe both modulus and Poisson ratio accurately. However, if the volume fraction of the ductile components exceeds 0.3, the experimental values of the modulus are too low and the experimental values of the Poisson ratio are too high, as compared with the predictions of the Kerner model. Micrographs of these blends containing considerable amounts of copolymer no longer show the more ductile components as a particulate phase[6]. Apparently the emulsifying effect of the copolymer used is very strong. This gives rise to the formation of a semicontinuous network consisting of polyethylene and copolymer throughout the polystyrene matrix. In this way the rigidity of the matrix is strongly reduced. Deformation will for the greatest part take place in the semicontinuous low modulus phase, resulting in a reduced modulus and an increased Poisson ratio[7].

In *Figures 8* and *9*, data taken from *Table 3* are represented for the modulus and Poisson ratio behaviour, again as a function of the volume fraction of ductile material. Here the ductile material consists only of low density polyethylene. This implies that there will be less adhesion between the two components. At low volume fractions of the ductile material the moduli do not differ much from the moduli of the composites in which adhesion between the components does exist, although there is a general tendency to lower values.

The Kerner equations describe the modulus of the composites quite accurately. However, while Kerner predicts an increase in the Poisson ratio, an initial decrease is found.

The cause of this discrepancy must be sought in the lack of mechanical interaction between the components. Since no copolymer has been added to these blends there will be no adhesion between the phases. Secondly, the thermal coefficient of expansion of polystyrene is smaller than that of low density polyethylene ($\alpha_{\mathrm{LDPE}} = 24 \times 10^{-5}\ \mathrm{K}^{-1}$, $\alpha_{\mathrm{PS}} = 7 \times 10^{-5}\ \mathrm{K}^{-1}$). This will cause the polyethylene particles to loosen themselves from the polystyrene matrix during cooling after the compression moulding of the samples.

To verify this, the Kerner model was used to calculate moduli and Poisson ratios of polystyrene filled with holes. This can be assumed to represent a situation in which no adhesion whatsoever exists between the components. The results are represented in *Figures 8* and *9* by the broken curves. Indeed the moduli of the composites are initially even better described by this hole model. Contrary to the increase in Poisson ratio calculated and experimentally found for composites in which adhesion does exist between the components, a decrease of the Poisson ratio is now predicted. The actual decrease in Poisson ratio is somewhat less than predicted by the Kerner equations for a matrix filled with holes. Clearly in absence of copolymer, some interaction still exists between the components.

CONCLUSION

The modulus and Poisson ratio of polystyrene–polyethylene blends are accurately predicted by the Kerner packed grains model. In blends containing copolymer, deviations arise due to the copolymer-induced formation of a low modulus continuous network at relatively low volume fractions of the low modulus phase. This results in low values for the modulus, and high values for the Poisson ratio as compared with the Kerner equations.

Another kind of deviation occurs if there is non-perfect adhesion between the components. While this does not influence the modulus much, it lowers the Poisson ratio, showing the sensitivity of the Poisson ratio to the extent of mechanical interactions between the dispersed phase and the matrix.

ACKNOWLEDGEMENT

W. J. Coumans and J. Dalmolen are gratefully acknowledged for their experimental work.

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