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MISCIBILITY OF CRYSTALLINE AND AMORPHOUS POLYMERS: POLYETHYLENE/POLYISOBUTYLENE BLENDS

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Abstract: Blends were prepared from a linear low density polyethylene and a polyisobutylene in the entire composition range. Flory-Huggins interaction parameters were determined from DMTA and DSC measurements. The usual technique had to be modified in the case of DSC data, since the T_g of PE cannot be determined by this technique. The two methods yielded identical results and indicated good interaction of the components, which was supported also by a SEM study and the mechanical properties of the blends.

INTRODUCTION

Polymer blends are used in large quantities in all fields of application. Beside engineering polymers also commodity thermoplastics are blended in order to prepare various products. Polypropylene is modified with EPR or EPDM elastomer to increase impact resistance, while blends of polyethylene with atactic polypropylene, polyisobutylene and other elastomers are used for the production of packaging films (Ref. 1). The study of the miscibility/structure/property correlation of such blends is of large theoretical and practical importance.

Miscibility of the components determine the structure of the blend, which, on the other hand, has a pronounced effect on properties. Numerous methods exist for the estimation of miscibility, the determination of the glass transition temperature is probably the most often

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used approach (Refs. 1,2). In amorphous polymers T_g can be determined with various techniques, including thermal analysis (DSC), dynamic mechanical (DMTA) or dielectric spectroscopy etc. The measurement of T_g and the estimation of miscibility is very difficult in polyolefin blends shown also by the limited number of miscibility data (interaction parameter, phase diagram) for these polymers. In the case of PE, the opinions differ even on the glass transition temperature, values between -120 and +70 °C are reported in the literature (Refs. 3-5). The source of these difficulties is the apolar character of PE leading to the lack of specific interactions, its crystalline structure and the ill-defined, broad transitions detected by most spectroscopic techniques.

The goal of our study was to determine the interaction parameter of a linear low density polyethylene and a polyisobutylene by two techniques and to relate the obtained values to the structure and properties of the blends prepared from the two polymers. The most important practical and theoretical aspects, as well as the difficulties of the determination are discussed in this paper.

EXPERIMENTAL

The linear low density polyethylene used in the experiments was the Stamylex 1016 LF grade of DSM, The Netherlands, while the Oppanol B50 product of BASF, Germany was applied as polyisobutylene. The most important characteristics and the parameters used in the calculations are collected in Table 1. The blends were prepared in and internal mixed at 150 °C and then compression moulded into 1 mm thick plates. The composition of the blends covered the entire composition range from 0 to 1 in 0.1 volume fraction steps.

The glass transition temperature and its changes were determined by DMTA and DSC. The dynamic mechanical spectra were recorded in the bending mode with 2 °C/min heating rate and 1 Hz frequency from -150 to 70 °C. Only the T_g of PIB could be determined by DSC, the measurements were carried out with 20 °C/min heating rate. Melting and crystallization characteristics of PE and the blends were also determined, 10 °C/min heating and cooling rates were used in this case. Two heating and cooling runs were carried out both in the relaxation and the crystallization experiments.

Table 1 *Some characteristics of the polymers studied and parameters used in the calculations*

Polymer	PE	PIB
Grade	Stamylex 1016 LF	Oppanol B 50
Producer	DSM	BASF
M_n x 10^4 (g/mol)	1.40	14.40
M_w x 10^5 (g/mol)	1.37	3.93
Density (g/cm^3)	0.86[a]	0.92
T_g (°C)	-119.2 (-120)[b]	-54.9
m	267	2564

a) Density of amorphous PE; density of the virgin polymer is 0.92 g/cm^3
b) Used in the calculation of χ from DSC results

Tensile tests were executed on a Zwick 1445 equipment with 100 mm/min cross-head speed. Yield stress and strain (σ_y, ε_y), as well as properties at failure (σ, ε) were determined. The structure of the blends was studied by scanning electron microscopy (SEM). Notched specimens were cooled to liquid N_2 temperature, they were broken and micrographs were taken from fracture surfaces.

RESULTS

PE is difficult to dissolve in most solvents due to its apolar character and crystalline structure and it form immiscible blends with basically all polymers (Refs. 1,6). Nevertheless, numerous PE blends are used in practice, various types and grades are blended to produce blown films, elastomer are added for stretch films or to decrease environmental stress cracking and even blends with PP are used occasionally (Ref. 1). As a consequence, properties of these blends must be acceptable, thus it is worth to consider the expected behaviour of the PE/PIB blends in question.

Expected behaviour

The complete absence of reactive or any functional groups characterize both components, thus specific interactions cannot form between them. On the other hand, dispersive forces are active in the case of all materials, also in the PE/PIB blends studied. These are not material specific, thus the interaction between all molecules must be very similar, but dispersive forces are expected to give unfavourable interactions (Ref. 7). Similarly unfavourable is the effect of free volume on miscibility, but this is small for PIB (Ref. 7). Although combinatorial enthropy is small in polymer blends, it favours miscibility. Since two of the these three effects are unfavourable for mixing immiscibility is expected, which is strongly supported by experience. However, the strength of interaction is difficult to predict, but preliminary experiments indicated some interaction and limited miscibility between PIB and the amorphous phase of PE.

The crystalline structure of PE resists even strong solvents, PE can be dissolved only at high temperatures. Strong solvents usually exert their influence through specific interactions (H-bond, charge transfer), which are ineffective in the case of PE. At high temperatures the crystalline structure melts, thus solubility improves. Since PE/PIB blends are prepared above the melting point of PE, some interaction and limited miscibility might be expected. The relative magnitude of the heat of crystallization and solution determines the final structure of the blend and the extent of miscibility. According to Fig. 1 the two polymers interact with each other, the heat of melting continuously decreases with increasing PIB content and above 0.8 volume fraction of PIB it becomes very low.

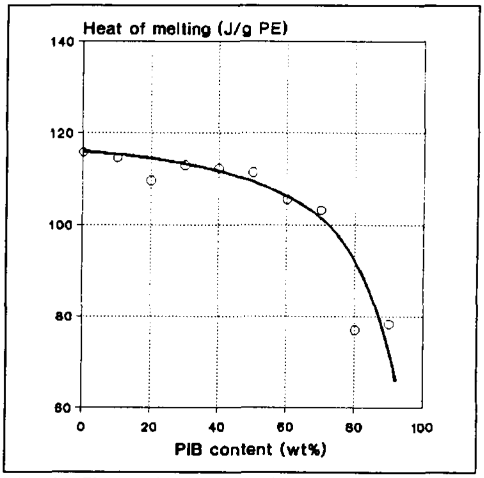

Fig. 1 *Change in the crystallinity of the PE phase with increasing PIB content of the blends*

Nevertheless, the structure of PE plays a decisive role in the determination of miscibility and influences its measurement. Amorphous molecules attached to the crystalline phase have decreased mobility leading to some of the relaxation transitions at higher temperatures. Practically all relaxation peaks in PE have low intensity and the transitions are broad, determination of the exact temperature of the transition is difficult. Moreover, the determination of the amount of the interacting phases is almost impossible as well. These factors all must be kept in mind during the evaluation of the experimental results and the calculation of miscibility.

Determination of interaction

In amorphous polymers the glass transition temperature can be determined easily, usually a very intense relaxation peak is observed in the temperature dependence of tgδ and loss modulus, with the corresponding step in storage modulus. In crystalline polymers the glass transition of the amorphous phase is less pronounced because its smaller amount and the decreased mobility due to the presence of the crystalline phase. The opinions are widely divided about the number of transitions in PE and their assignment to the actual physical process, or more exactly, to the related structural units. The T_g values reported in the literature can be found in three temperature ranges, at around -140 - -120 °C (γ), -40 - -20 °C (β) and 60 - 70 °C (α). The α transition can be related to the relaxation of the chains attached to the crystalline phase (Refs. 8,9), the β to branches (Refs. 5,10-13) - it is absent in linear PE - while the γ transition to the movement of methylene units (Refs. 9-11, 13,14). It is obvious that this latter must be considered in interactions, the possible changes in the position of this transition may give information about the extent of miscibility in blends.

Unfortunately this transition is very broad and of low intensity. This is demonstrated well by Fig. 2, where tgδ of a blend is plotted against temperature. The glass transition of PIB is well discernible, while that of PE is very badly defined. Nevertheless, as it is shown by the insert, the position of the maximum seems to change with composition indicating some interaction of the components. The position of the maximum was taken as T_g and it was determined by curve fitting techniques. It must be emphasized tough, that in spite of all efforts the determination is difficult and the values are inaccurate, which must be kept in mind during the evaluation of the results.

Interaction of the components was characterized by the Flory-Huggins interaction parameter (Ref. 15). This can be easily calculated by the technique introduced by Kim and Burns (Ref. 16), which was successfully applied for several systems since then (Refs. 17, 18). In the case

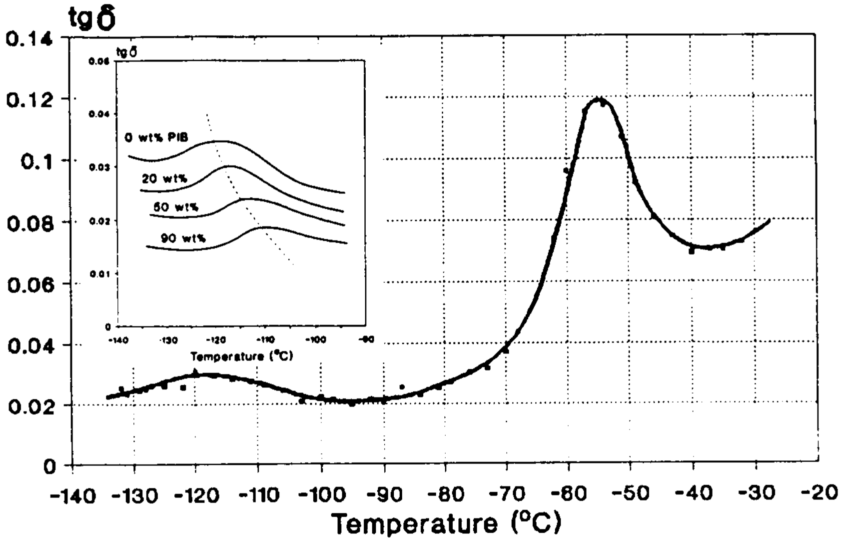

Fig. 2 *DMTA spectra of a PE/PIB blend (20 wt% PIB). Insert: shift in the T_g of PE with increasing PIB content*

of limited miscibility we have two phases, which consist of a major an a minor component, the second being present in relatively low amounts. The composition of the conjugate phases can be calculated from the Fox equation (Ref. 1) if the T_g of both components is known, i.e.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (1)$$

where T_g is the glass transition temperature of the blend, while T_{g1} and T_{g2} are the values of the matrix polymers. Introducing the T_g value of the PIB phase of one of the blends into Eq. 1, for example, leads to the weight fraction of PIB in the PIB rich phase (w_2'') and the correlation $w_1'' + w_2'' = 1$ gives the PE content of the same phase. The composition of the PE rich phase can be calculated in a similar way. In the above equation and in further calculations subscript 1 stands for PE and subscript 2 for PIB; accordingly single prime designates the PE rich, while double prime the PIB rich phase. The composition of the conjugate phases can be calculated from the Wood (Ref. 19) or Couchman (Refs. 20,21) equations, as well.

From the composition, the Flory-Huggins interaction parameter can be calculated by

$$\chi_{12} = \frac{\ln\frac{\phi_1''}{\phi_1'} + \left(1 - \frac{m_1}{m_2}\right)(\phi_2' - \phi_2'')}{m_1(\phi_2'^2 - \phi_2''^2)} \tag{2}$$

where ϕ_1', ϕ_2', ϕ_1'', ϕ_2'' are the volume fractions of the components in the two phases, while m_1 and m_2 are related to the molecular weight of the polymers. They can be calculated from the average molecular weight of the polymer, its density and the lattice site volume. As usual, we chose the larger repeat unit of PIB as lattice site volume in our calculations. The volume fractions in Eq. 2 can be derived from the weight fraction of the phases and the density of the components. It must be emphasized here that interaction takes place only in the amorphous phases, thus the density of amorphous PE was used in the calculations. Accordingly, the w and ϕ values relate to the amorphous polymers and completely neglect the crystalline part of PE. This, however, does not influence the calculations and the determined χ values, especially since the γ transition of PE used for the calculation of composition is claimed to by independent of the crystalline phase (Ref. 9). An equation similar to Eq. 2 lead to χ_{21}; the two interaction values χ_{12} and χ_{21} should be identical within the experimental error of the determination (Refs. 16,18).

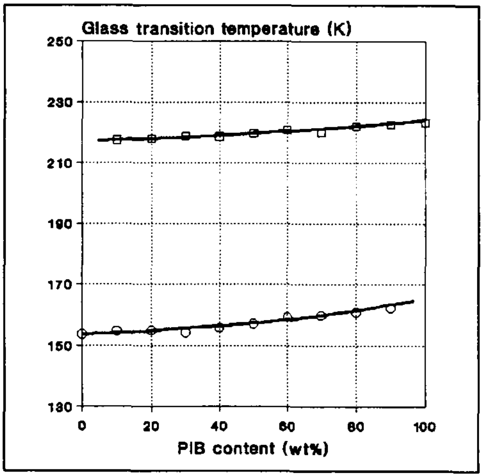

Fig. 3 *Dependence of the T_g of the two phases on composition; (○) PE, (□) PIB*

The T_g of the PIB and PE rich phases are plotted against the total PIB content of the blends in Fig. 3. Both values change continuously in the entire composition range. The shift in the maximum of tgδ is 8.6 °C for the PE and 5.9 °C for the PIB phase at 90 % of the other component. These changes indicate that PE dissolves more in PIB than vice versa. The calculations showed, indeed, that about 17 wt% PIB dissolves in the PE phase at a PE/PIB composition of 10/90, while the PIB phase contains only about 6 wt% PE in 90/10 blend.

The Flory-Huggins parameters were calculated according to the principles presented above (see Eqs. 1 and 2) and the results are plotted against composition in Fig. 4. The calculated values are rather low, significantly lower than the values determined by the same technique for other polymer pairs. An average value of 0.035 ± 0.010 was reported by Kolařík et al (Ref. 18) for PC/PMMA blends, for example. The low value indicates that in spite of the lack of specific interactions the components show some miscibility, indeed, in spite of the two unfavourable factors influencing interaction. As Fig. 4 shows, the χ_{12} and χ_{21} values are not identical; the differences exceed the standard deviation of the determination. Similar differences were observed by Kolařík (Ref. 18), who listed the improper choice of m_1 and m_2, non-equilibrium conditions and the effect of interphase as possible reasons. Also the systematic increase of χ_{12} is unexpected, an unambiguous explanation cannot be given for it at the moment.

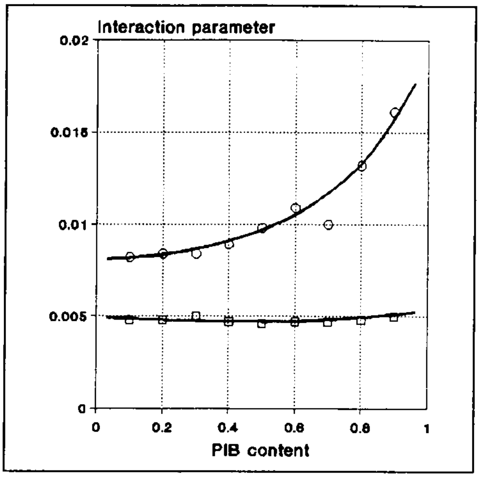

Fig. 4 *Composition dependence of χ determined form DMTA measurements; (○) χ_{12}, (□) χ_{21}*

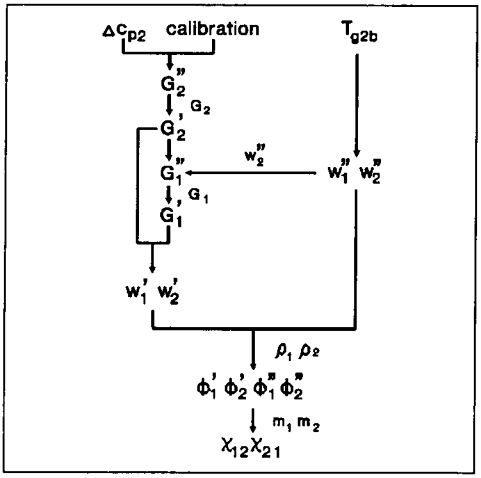

Fig. 5 *Calculation of χ from DSC data*

It is impossible to use the procedure described above for the determination of χ from DSC measurements, since the T_g of PE cannot be determined by this technique. The information which can be obtained from a DSC trace is the glass transition of the PIB phase and the change in the specific heat at this transition. This latter, however, is proportional to the amount of relaxing material and can be used for the determination of the composition of the phases. A modified scheme of the calculations is presented in Fig. 5 and includes the following steps:

1) w_1'' and w_2'' is calculated from the T_g of the PIB phase as before, i.e.

$$w_2'' = \frac{T_{g2}(T_{g1} - T_{g2b})}{T_{g2b}(T_{g1} - T_{g2})} \tag{3}$$

and

$$w_1'' = 1 - w_2'' \tag{4}$$

2) The amount of relaxing material in the PIB phase is determined from the specific heat change

$$G_2'' = a\,\Delta c_{p2} \tag{5}$$

where a is a constant determined by separate measurements (calibration).

3) The amount of PIB in the PE phase is obtained from

$$G_2' = G_2 - G_2'' \tag{6}$$

4) while the PE dissolved in the PIB from

$$G_1'' = \frac{w_2''}{G_2''} - G_2'' \tag{7}$$

5) The knowledge of the amount of PE in the PIB rich phase leads to its amount in the PE phase

$$G_1' = G_1 - G_1'' \tag{8}$$

6) From G_1' and G_2' the composition of the PE phase can be easily calculated

$$w_1' = \frac{G_1'}{G_1' + G_2'} \tag{9}$$

In Equations 5-9 G_1 and G_2 are the total amount of PE and PIB in the blend, respectively, which are given by the composition and the weight of the sample used for the measurement, while G_1', G_2', G_1'' and G_2'' are the absolute amounts of the polymers in the two phases. The scheme has two critical points. The first is the proportionality of the relaxing material in the blend to Δc_p. This was proven by calibration, but even more by the linear correlation between this quantity and the concentration of the relaxing component in a given phase for the most diverse blends, as the measurements of Kim and Burns (Refs. 16,17,22) show. The second question is the determination of G_l' in Step 5. G_l is the total amount of PE including the crystalline phase, which was claimed to be excluded from interactions. Although we did not do the correction, it can be easily done by the measurement of the crystallinity of PE in the blend, thus the above presented scheme can be used for the calculation of χ.

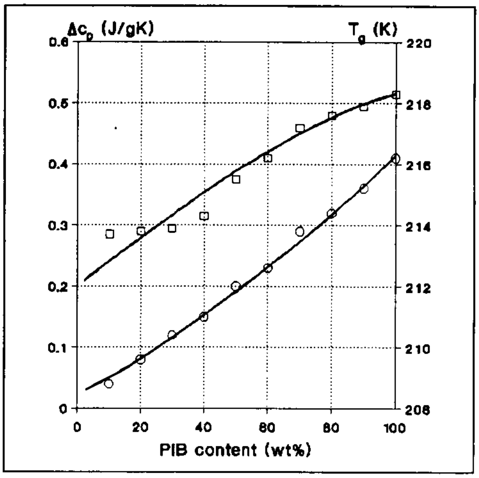

Fig. 6 *T_g (□) and Δc_p (○) of the PIB phase determined by DSC*

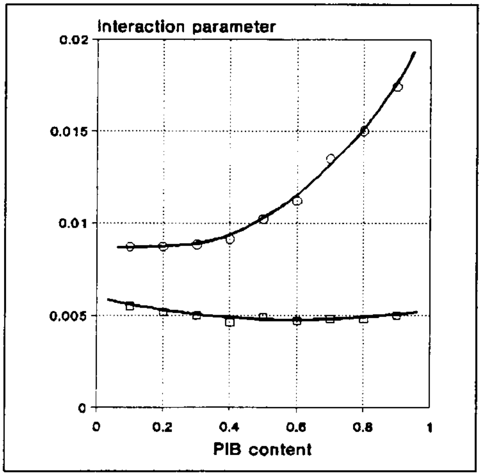

Fig. 7 *Effect of composition on χ values deduced from DSC measurements; (○) χ_{12}, (□) χ_{21}*

The T_g and Δc_p values used in the calculations are presented in Fig. 6. The total change of T_g is 4.6 °C, which compares well with the 5.9 °C measured by DMTA. The correlation of Δc_{p2} and the total PIB content of the blend is not completely linear, but it should be linear as a function of the PIB content of the PIB phase and not the total PIB content of the blend. The composition of the conjugate phases was calculated according to the above presented scheme and the χ values were determined by Eq. 2. The results are presented in Fig. 7. The correlation is very similar to that of Fig. 4, although slight differences can be found in the absolute values. The similarity, or more exactly, the identity of the interaction parameters determined by DMTA and DSC is clearly demonstrated by Fig. 8, where the two set of parameters are plotted against each other. The deviations are in the range of the standard deviation of the measurement, indeed. In spite of the inaccuracy of some of the measured quantities - T_g of the PE phase in DMTA and Δc_p of PIB in DSC - the two methods give identical information. A few questions remain open though, like the systematic difference of χ_{12} and χ_{21}, the increase of χ_{12} as a function of the PIB content of the blend and the effect of crystallinity on the χ values calculated from the DSC measurements.

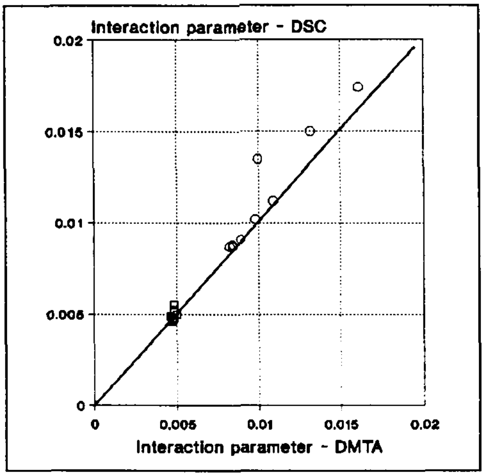

Fig. 8 *Correlation of χ values determined by the two techniques; (○) χ_{12}, (□) χ_{21}*

Structure and properties

In accordance with the positive χ value, the blends exhibit heterogeneous, two phase structure. At low PIB content PE is the continuous phase, PIB particles of about 0.5 2.0 μm size are evenly dispersed in the matrix. At the other end of the composition range PE is dispersed in the continuous PIB phase. At intermediate compositions the blends have co-continuous structure. The transition can be found approximately between 25 and 70 wt% PIB content. The relatively wide transitional range is also and indication of the comparatively good compatibility of the components. SEM micrographs are omitted due to the lack of space here.

In blends containing a dispersed phase with comparable strength to the matrix, the composition dependence of mechanical properties, especially yield stress and strength, gives a clear indication of interaction (Refs. 23,24). Strong interaction or eventual miscibility leads to a composition dependence close to additivity, while weak interaction to a strong decrease of the above mentioned characteristics. However, in PE/PIB blends, it is rather difficult to estimate the strength of the interaction between the components from the composition dependence of mechanical properties. The modulus, yield stress and strength of PIB is very low resulting in a small load bearing capacity. As a consequence, yield stress and tensile strength of the blends decrease continuously with increasing PIB content. Tensile strength and elongation-at-break values of the blends are plotted against their composition in Fig. 9. The broken line indicates zero interaction (Refs. 25,26), i.e. zero load carried by the dispersed PIB phase. The difference between the calculated and the measured values indicates relatively good interaction of the components. A further proof is given for this interaction by the high elongation-at-break values and the maximum observed at around 0.8 % PIB content. Further study is needed though, to find a clear explanation for this latter phenomenon. SEM micrographs do not indicate the formation of a special structure in the range which could explain the appearance of the maximum.

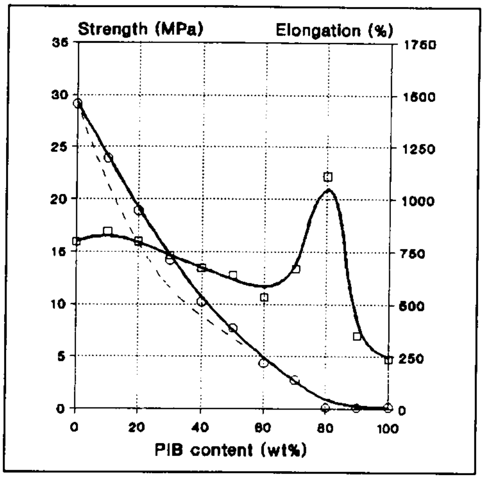

Fig. 9 *Composition dependence of the ultimate properties of the blends; (○) tensile strength, (Δ) elongation-at-break, - - - - strength at zero interaction (Ref. 23)*

CONCLUSIONS

In accordance with the expectations the PE and PIB used in this study formed a heterogeneous, two phase blend. The Flory-Huggins interaction parameters deduced from the results of DMTA and DSC measurements indicated relatively strong interaction of the components, which was further supported by the composition dependence of mechanical properties. The small interaction parameter obtained indicates that in spite of expectation dispersive forces are sufficient to create interaction and limited miscibility. Although the results are consistent, the determined parameters must be treated with care. The determination of some quantities is difficult (T_g of PE, Δc_p of PIB), the standard deviation of the measurements is large. Some unexplained phenomena need further study, the significant difference between the χ_{12} and χ_{21} values and the increase of χ_{12} with composition could not be explained on the basis of available information. Nevertheless, the techniques can be used to estimate the interaction in polymer blends. The modified technique proposed by us further extends the possibilities of the approach for systems in which the T_g of only one component can be determined by DSC.

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