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Miscibility-Property Correlations in Blends of Glassy Amorphous Polymers

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Summary: Blends were prepared from seven polymers in various combinations in the entire composition range. The Flory-Huggins interaction parameter (χ_{12}) was used for the quantitative estimation of miscibility. The determination of χ_{12} was attempted by several experimental techniques including the measurement of transparency, glass transition temperature, solvent diffusion and mechanical properties. The relatively simple methods used for the estimation of miscibility work surprisingly well. Solvent absorption can be determined easily for practically all blends, thus the method offers a quantitative measure of component interaction if the solvent is selected properly. After appropriate data reduction, the composition dependence of mechanical properties also supplies a quantitative estimate of compatibility. Although the approach presented in the paper reflects well the general correlation between miscibility and properties, it must be refined and improved in order to obtain a reliable estimate of blend performance.

Introduction

Blends of both commodity and engineering plastics are used in increasing quantities in numerous fields of application1). Most of them have a heterogeneous dispersed phase structure, which usually assures high impact strength and high stiffness required in most engineering applications2). The interaction of the components must be sufficiently strong even in immiscible blends otherwise properties become extremely poor. The simple classification of blends into categories of miscible or immiscible, respectively, does not reflect the wide range of structures and properties covered. Immiscible blends usually consist of a continuous matrix in which the second polymer is dispersed in a form of well defined domains. The size of the domains and their adhesion to the matrix

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may differ significantly from one blend to the other. Large PVC domains in PP/PVC blends lead to extremely poor properties, while a finer structure in PVC/PS blends ensures a significantly better performance. The close correlation between miscibility and structure, on the one hand, and between structure and properties, on the other hand, is a widely accepted fact. In spite of this generally accepted rule, very few models exist which describe the correlation of miscibility, structure and properties quantitatively. As a consequence, the goal of this study was to prepare blends from amorphous glassy polymers of different degree of miscibility, to determine their properties, and to suggest the existence of a general correlation. Miscibility was estimated semi-quantitatively by various techniques and the obtained numbers were related to mechanical properties. The advantages and limitations of the approach are also critically evaluated in the paper.

Background

According to an approach developed a few years ago[3,4], structure is characterized by the size of the dispersed particles, miscibility by the Flory-Huggins interaction parameter and mechanical properties by a parameter (*C*) derived from tensile strength. The size of the dispersed particles can be expressed by the modified theories of Tokita[5], Fortelny[6] and Taylor[7]. Among other factors, it depends on interfacial tension, which is related to the miscibility of the components by the theory of Kammer[8]. Mechanical properties also depend on several factors including interaction and composition. Stiffness was shown to be rather insensitive to changes in miscibility and structure[6,7], but yield stress and tensile strength depend strongly on these quantities. The composition (φ_d) dependence of tensile strength can be expressed as[9]

$$\sigma_T = \sigma_{T0}\lambda^n \frac{1-\varphi_d}{1+2.5\varphi_d}\exp\left(B\varphi_d\right) \qquad \textbf{(1)}$$

where σ_T and σ_{T0} are the true tensile strength ($\sigma_T = \sigma\lambda$, $\lambda = L/L_0$) of the composite and the matrix, respectively, *n* is a parameter reflecting the strain hardening characteristics of the polymer and *B* is related to the relative load bearing capacity of the components. This latter quantity is determined by interaction, but it depends also on the inherent properties of the two polymers. Soft components carry much less load than hard ones even at the same level of interfacial adhesion. As a consequence, the parameter expressing interaction (*C*) must take into account the relative load-bearing capacity of the components, i.e.

$$B = \ln C \frac{\sigma_{Td}}{\sigma_{T0}} \qquad \textbf{(2)}$$

where σ_{Td} is the strength of the dispersed phase. To relate strength to structure and miscibility we assume that stress is transferred from the matrix to the dispersed particles through an interphase$^{9,10)}$. The strength of a blend depends on the volume of the interphase, which is defined by the interfacial area and the thickness of the interlayer. Accordingly, the correlation between mechanical properties and structure, as well as miscibility can be given as

$$C = k_1 \ell A = 3k_1 \ell \frac{\varphi_d}{r} = \frac{k_2}{\chi} \qquad \textbf{(3)}$$

where $A = 3\varphi_d/r$ is the specific surface area of the dispersed particles, ℓ the thickness of the interphase, while k_1 and k_2 are constants. The correlations presented above offer a possibility to relate miscibility, structure and mechanical properties. In the present paper we are concerned only with the relationship of miscibility and properties, we do not study the structure of the blends.

Experimental

Seven different glassy amorphous polymers were used for the preparation of the blends. Their most important properties are listed in Table 1. PMMA and PS were commercial products; PVC contained a tin stabilizer, an epoxydized soya bean oil and an external lubricant. The P(MMA-co-St) random copolymers contain the monomers in the amount indicated in the first column of the table. The Hildebrand solubility parameter of the polymers was calculated from the group contributions of Hoy$^{11)}$. The solubility parameters are very similar with the exception of the δ value of PVC, which is considerably larger than that of the other polymers. As a consequence PVC blends are expected to be immiscible, while in the others a better interaction should prevail. The investigated blends and some of their characteristics (the number of phases, the difference in component T_g's, estimated miscibility) are listed in Table 2.

Table 1 Characteristics of the studied polymers

Polymer	Density (g/cm^3)	M_n x 10^{-4} (g/mol)	T_g (°C)	δ (J/cm^3)
PMMA	1.182	28.90	119.0	18.99
P(MMA-co-St) - 70/30	1.136	4.95	110.1	18.77
P(MMA-co-St) - 60/40	1.112	4.00	106.0	18.76
P(MMA-co-St) - 50/50	1.108	4.53	104.4	18.75
P(MMA-co-St) - 20/80	1.074	6.91	103.5	18.68
PS	1.050	8.75	98.5	18.62
PVC	1.410	4.86	75.8	**19.51**

The blends were prepared in the entire composition range in 0.1 volume fraction steps. The components were homogenized in an internal mixer at 50 rpm for approximately 10 minutes at various temperatures. PVC was processed at 185 °C, while all other blends at 190 °C. The homogenized samples were compression molded into 1 mm thick plates, which were used in all further experiments. The glass transition temperature of the blends was determined by a Mettler DSC 30 cell on 10 mg samples in two runs. Heating and cooling rates were 20 °C/min in both runs and the results of the second run were used for evaluation. The methanol uptake of the samples was measured at 50 °C on 10 x 5 x 1 mm large compression molded samples. Light transmittance through the plates was measured by a Spekol MK 6/6 UV-visible photometer at 650 nm wavelength. Mechanical properties were characterized by tensile measurements carried out on a Zwick 1445 tensile testing machine at 5 mm/min cross-head speed and 50 mm gauge length. Young's modulus (E), yield stress (σ_y) and yield strain (ε_y) as well as ultimate properties, i.e. tensile strength (σ) and elongation-at-break (ε), were calculated from the recorded force vs. elongation traces.

Table 2 Predicted miscibility of the investigated blends

Blend	No of phases	ΔT_g (°C)	χ_{Hoy}[11,12]	χ_c
PS/P(MMA-co-St) - 20/80	**1**	**5.0**	**0.0002**	**0.0027**
PS/P(MMA-co-St) - 70/30	**2**	**11.6**	**0.0009**	**0.0032**
PMMA/P(MMA-co-St) - 70/30	1	8.9	0.0019	0.0011
PMMA/P(MMA-co-St) - 60/40	**2**	**13.0**	**0.0020**	**0.0024**
PMMA/P(MMA-co-St) - 50/50	2	14.6	0.0023	0.0022
PMMA/P(MMA-co-St) - 20/80	2	15.5	0.0037	0.0016
PMMA/PS	2	20.5	0.0054	0.0014
PVC/PMMA	2	43.2	0.0108	0.0015
PVC/PS	2	22.7	0.0314	0.0025

Miscibility

The simplest way to predict interactions from the structure of the components is the calculation of solubility parameters from group contributions[11)] and then the determination of the Flory-Huggins interaction parameter[12)]. If the obtained number is smaller than the critical χ_c value, i.e.

$$\chi_c = 0.5\left(\frac{1}{x_1^{1/2}}+\frac{1}{x_2^{1/2}}\right)^2 \tag{4}$$

where x_1 and x_2 are the degree of polymerization of the two polymers, the components should be miscible and a homogeneous blend obtained[13,14)]. Interaction parameters estimated in this way and the critical values are collected in Table 2. Although this approach is extremely rough, it might indicate the performance of the blends. According to Table 2 large differences exist among the interaction parameters of the studied blends, the largest χ_{12} value was obtained for the PVC/PS blend. On the other hand, three of the polymer pairs are expected to be miscible (they are printed in bold in Table 2), to yield homogeneous blends. The solubility parameter offers a first estimate of miscibility, but it is not able to give accurate numbers or distinguish fine differences.

Transparency reflects the miscibility of the components and, to a degree, the structure of a blend. Fig. 1 shows the composition dependence of transparency for some of the studied blends. Transparency covers the complete range from 90 to practically 0 % and it depends also on composition. Composition dependence is related to changing the size of the dispersed particles and indicates the limited miscibility of the components. Fig. 1 clearly demonstrates the imperfection of the solubility parameter approach. The miscibility parameter calculated for the PS/ P(MMA-co-St) - 20/80 blend is 0.0002 and much lower than the critical value, 0.0027, i.e. the blend should be miscible and transparent. On the other hand, the PMMA/ P(MMA-co-St) - 70/30 blend was rated immiscible (χ12 = 0.0019, χc =0.0011), but the blends are completely transparent in the entire composition range. A detailed explanation of these effects can be found in Refs. 15 and 16. However, the main difficulty is to express transparency as a number or parameter, which can be related to component interaction. Beside the size of the particles, which depends on miscibility, transparency is influenced also by the relative refractive indices of the components. The comparison of the PVC/PS or the PMMA/PS blends further emphasizes these difficulties. Neither of the blends transmits light at any composition. However, their predicted miscibility parameters differ significantly, they are 0.0314 and 0.0054, respectively, and their mechanical properties are also dissimilar. These results demonstrate sufficiently that generally transparency cannot be used as a measure of miscibility.

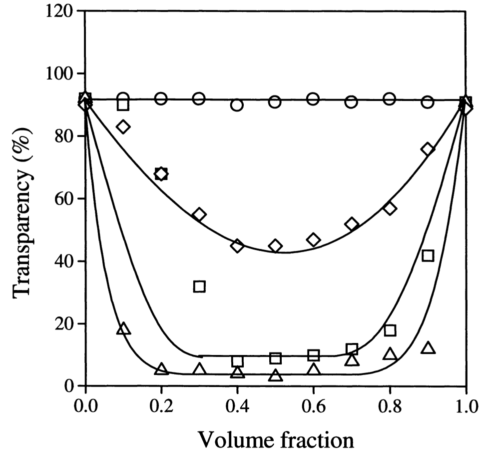

Fig. 1: *Composition dependence of the transparency of various polymer blends; (o) PMMA/Co - 70/30, (◊) PS/Co - 20/80, (□) PMMA/Co - 50/50, (Δ) PMMA/Co -20/80*

One of the most frequently used experimental techniques to estimate miscibility of polymer pairs is the determination of their glass transition temperature in the blend. Partial miscibility results in two phases with slightly changing T_g of the matrix polymer of the given phase, as shown by Fig. 2 for the PMMA/PS and the PVC/PS blends. The T_g of the components shifts slightly toward that of the other polymer in both blends. Blending has a somewhat larger effect on T_g in the PVC/PS than in the PMMA/PS blends indicating a stronger interaction of the components (Fig. 2). Partial miscibility is proved also by the behavior of the PS component of the blends. The same polymer was used in both blends, thus the T_g of the PS rich phases is the same at low second polymer content. The change in the glass transition temperature of PS increases with composition and its direction depends on the T_g of the other polymer. The strength of the inter action is clearly stronger in the PVC/PS blend than in the other as indicated by the shift in T_g. However, this result is in contradiction with prediction, since χ_{12} values of 0.0054 and 0.0314 were obtained for the PMMA/PS and the PVC/PS blends, respectively. For partially miscible blends the Flory-Huggins interaction parameter can be calculated from the shift in the T_g values of the components by the approach of Kim and Burns[17,18]. The calculations yielded χ_{12} values of 0.0113 and 0.0028 for the above mentioned two blends, which are in complete agreement with the observed composition dependence of T_g, with experience and also with our expectations. This result proves again the inability of the simple group contribution approach to predict small differences between blends of slightly differing miscibility. Although the measurement of glass transition temperature is a convenient way to predict miscibility,

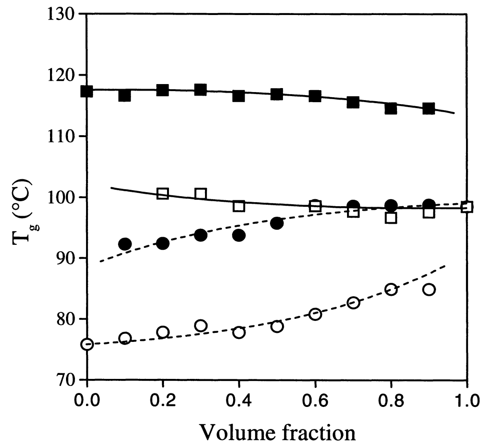

Fig. 2: *Composition dependence of conjugate phases in the partially miscible blends of PMMA(■)/PS(□) and PVC(O)/PS(●)*

it cannot be used when the difference between the T_g values of the components is very small. As shown in Table 2, ΔT_g was less than 20 °C for most of the studied blends.

The solubility and diffusion of small molecular weight materials in polymers depends on the morphology of the polymer, on the chemical structure and physical properties of the compound and on the interactions prevailing in the system$^{19-22)}$. The absorption of a solvent can be also used to estimate the miscibility of two polymers$^{23-25)}$. If the interaction between components is strong, less solvent is absorbed by the blend than by the individual components. Solvent absorption can easily be measured by immersing the polymer into a solvent and measuring weight gain as a function of time. The interaction of the components can be estimated from the value of equilibrium solvent uptake by the Flory-Huggins theory$^{23-25)}$. The calculated interaction parameters are plotted as a function of composition in Fig. 3 for the PS/P(MMA-co-St) - 70/30 and the PS/P(MMA-co-St) - 20/80 blends. The results completely agree with expectation and also correspond to the prediction of the simple solubility parameter approach. The experiments were carried out for all the blends and an interaction parameter could be determined in spite of the relatively large scatter of the experimental points (see Fig.

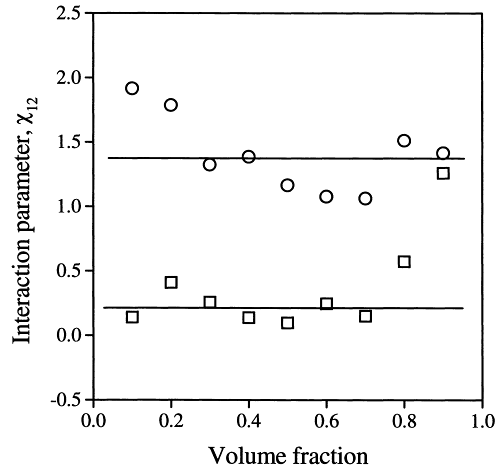

Fig. 3: *Composition dependence of the Flory-Huggins parameter derived from methanol absorption measurements for blends (O) PS/Co - 70/30, (□) PS/Co - 20/80*

3); they provide an apparently reasonable estimate of component interaction in the studied blends.

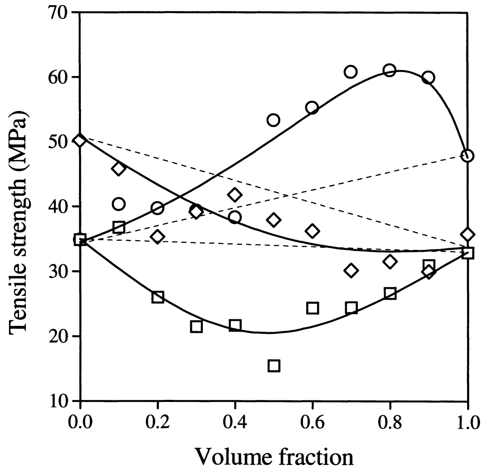

Fig. 4: *Composition dependence of the tensile strength of various glassy amorphous polymer blends;* (○) *PVC/PMMA,* (◊) *PMMA/PS,* (□) *PVC/PS*

Properties

The mechanical properties measured at large deformations, like yield and ultimate properties, depend strongly on composition. This is especially valid for blends of poor miscibility. The composition dependence of tensile strength is plotted for three blends in Fig. 4. The strength of the blends deviates from additivity and the deviation varies both in extent and direction. Although we may conclude from these results that component interaction is stronger in the PVC/ PMMA blend than in the other two, a quantitative estimate of interaction or miscibility is impossible in this way. The data obviously must be reduced to a single number, which then

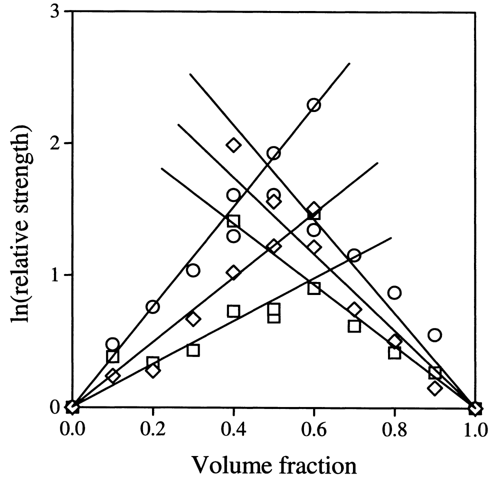

Fig. 5: *Linear representation of the composition dependence of tensile strength for the blends of the previous figure. Symbols are the same as in Fig. 4*

can be related to χ_{12} or any other quantity characterizing interaction. This reduction of the data can be made through the application of Eqs. 1 and 2. Eq. 1 can be rearranged to calculate relative strength, i.e. $\sigma_{Trel} = [\sigma_T/(\sigma_{T0}/\lambda^n)][(1 + 2.5\varphi_d)/(1 - \varphi_d)]$, and if $\ln\sigma_{Trel}$ is plotted against φ_d a straight line must be obtained. Since we assume a dispersed phase structure and phase inversion, we obtain two lines, one for each matrix polymer. The primary data of Fig. 4 are plotted in this form in Fig. 5. Relatively good linear correlations are obtained for all the blends, which allow the calculation of parameters *B* and *C*. The measurements and the calculation could be carried out for all the blends except the PS/P(MMA-co- St) - 70/30 pair, which proved to be too brittle and the specimens broke upon gripping them into the tensile testing machine.

Correlation

It has been shown above that diffusion experiments provide a quantitative measure of miscibility, while Parameter *C* gives an estimate of component interaction based on mechanical properties. The two quantities are plotted against each other in Fig. 6. A clear and surprisingly close correlation exists between *C* and $\chi_{1,2}$. The results prove that the general correlation mentioned in the introductory part exists, indeed, and it can be expressed quantitatively through the approach presented here.

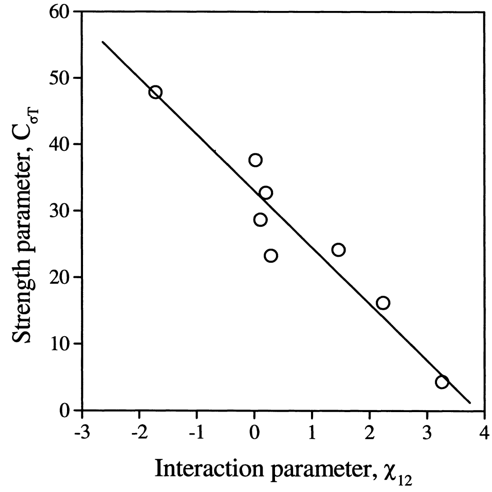

Fig. 6: *Correlation of miscibility (χ_{12}) and mechanical properties (strength, C) of various glassy amorphous blends*

Attention must be called here to the deficiencies of the theory as well. The limitations of the Flory-Huggins theory are well known, moreover the blends usually are not in equilibrium. One of the basic assumptions of the correlation expressed by Eq. 1 is that the blends possess heterogeneous structure; some of the studied blends were clearly homogeneous. Special attention must be called here to the oversimplification of the expression for the size of the dispersed particles[3,4)] and to the fact that Eq. 2 usually gives unrealistic C values for polymer/elastomer blends. These correlations must be definitely revised in the future. In spite of these deficiencies the simple approach presented in this paper works surprisingly well and offers a possibility for the quantitative evaluation of the performance of new polymer blends.

Conclusions

The experiments carried out on 9 polymer pairs of varying miscibility proved that a general correlation exists between the miscibility and properties of polymer blends. The solubility parameter approach gives only a rough estimate of interaction, it cannot express fine differences and completely fails in the case of specific interactions. The other, relatively simple methods used for the estimation of miscibility work surprisingly well. Although the measurement of transparency and glass transition temperature has limitations, solvent absorption can be determined easily for practically all blends, thus the method offers a quantitative measure of component interaction if the solvent is selected properly. After appropriate data reduction, the composition dependence of mechanical properties also supplies a quantitative estimate of compatibility. Although the approach presented in this paper reflects well the general correlation between miscibility and properties, it must be refined and improved in order to obtain a reliable estimate of blend performance.

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