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Dedicated to Prof. Edith A. Turi in recognition of her leadership in education

DSC AND p-V-T STUDY OF PVC/PMMA BLENDS

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Abstract

Poly(vinyl chloride)/Poly(methyl methacrylate) – PVC/PMMA – blends were investigated by comparative p-V-T and differential scanning calorimetry (DSC) measurements. The study was concentrated on the glass transition range of the blends, and it was found that the blends are characterized by a single glass transition temperature suggesting miscibility of the blend components. It is shown that the glass temperature of the blends increases with both increasing heating rate and pressure. In parallel hereto one observes a decrease in the volume expansion coefficients, which is more accentuated for the polymeric melts than for the polymeric glasses. The dependence of the glass temperature on the composition of the polymer blends shows a sigmoidal behaviour which is due to the fact that positive deviations of the glass temperature from values predicted by additivity rules are observed in the high PVC concentration range, whereas in the high PMMA range negative deviations occur. This suggests a denser packing of the blends and thus a stronger interaction between the blend components in the high PVC concentration range. These packing differences increase with increasing pressure and decreasing heating rate and are generally more accentuated for the glass temperatures evaluated from p-V-T measurements.

Keywords: amorphous PVC/PMMA blends, DSC and p-V-T measurements, miscibility and composition dependence of the glass temperature

Introduction

Conflicting data have been presented in literature concerning the compatibility of poly(vinyl chloride) – PVC – and poly(methyl methacrylate) – PMMA. Thus, Schurer *et al*. [1] reported PVC/PMMA to be miscible only in blends having a PVC content greater than 60% w/w, whereas Razinska *et al*. [2] claimed PVC/PMMA to be immiscible. On the other hand, Parmer *et al.* [3] asserted PVC/PMMA to be miscible over the whole range of composition showing a single glass transition, T_g, in the second DSC heating rate traces. Misciblility of PVC/PMMA has also been confirmed by Albert *et al*. [4] by non-radiative energy transfer and NMR.

It is well known that miscibility of polymers is dependent of sample preparation and molecular weight as well as of the tacticity of the polymers. Additionally, due to the kinetic character of the glass transition, the reported glass transition temperatures depend on the mode of definition of T_g for a given method of measurement (DSC, dynamic mechanical methods or p-V-T, for instance) as well as the operating conditions

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during the measurement (heating/cooling rates, frequency and pressure, respectively).

Taking into account that Parmer *et al.* [3] reported miscibility for PVC, M_w=62000 and PMMA, M_w=102000, in the present investigation we used polymers of similar molecular weight, i.e., PVC, M_w=83500 and PMMA, M_w=108000. To study the influence of the operating conditions (heating rate and pressure, respectively) on the glass transition of the PVC83500/PMMA108000 blend, we applied two different methods of measurement, i.e., differential scanning calorimetry – DSC – and p-V-T. A single glass temperature was observed by both methods, thus confirming the misciblity of this PVC/PMMA blend.

Experimental

The PVC (M_w=83500, M_n=37400) was supplied by Aldrich Chemical Co., whereas the PMMA (M_w=108000, M_n=100000) synthesized by group transfer polymerization was obtained from Röhm/Darmstadt. Polymer blends of an overall weight of 3g for each case were prepared by dissolution of the components in 60 ml THF. At first, the appropriate amount of PVC for a given blend composition was dissolved using as stabilizer a 1% w/w di-*n*-octylin-S,S'-bis(isooctylmercapto acetate) supplied by Ciba-Geigy. The accessory part of PMMA was then added and dissolved by stirring at 50–60ºC. After dissolution, the polymer blend was precipitated with methanol and dried at 50ºC to constant weight.

About 10 mg of each amorphous blend sample obtained by precipitation from the THF solutions as well as of the components were used directly for DSC measurements. Samples of 1.2 g were prepared for p-V-T measurements by press-moulding in vacuum, assuring the samples to be absolutely free of solvent and/or air bubbles.

DSC measurements at different heating rates using samples quenched from the melt were carried out on a Perkin Elmer DSC-7. Indium and high-purity cyclohexane were used for temperature calibration. The reported T_g values were estimated from the second heating scans as the transition midpoint (1/2 Δc_p) temperatures.

The p-V-T measurements were performed by the hydrostatic method using the GNOMIX p-V-T device of Zoller. The data were recorded in the isobaric mode of operation, being acquired at selectable time intervals during controlled heating of the sample with a heating rate of 4 K min^{-1}. After the self-driven cooling to room temperature, the pressure was increased to reach the next selected isobaric pressure. The data are presented in isobaric form, i.e., specific volume *vs.* temperature for the selected pressures in the range 10–200 MPa (Fig. 1).

To prevent thermal degradation during the p-V-T measurements the thermal stability of the less stable PVC was proved isothermally at 220°C. Although the p-V-T runs were stoped at 160°C for PVC and the PVC containing blends the observed deviation from the expected behaviour at the highest pressure of 200 MPa suggested a possible degradation of the blend with the highest 87.5 w/w% PVC content.

Shown in Fig. 1 for illustration are the p-V-T data for the 75/25 w/w% PVC/PMMA and 25/75 w/w% PMMA blends, respectively. With increasing pressure, a decrease of the specific volume and a shift of the glass temperatures to higher temperatures is observed. At the same time, an enlargement of the 'relaxation zones' situated between glassy state and melt develops. These 'relaxation zones' are characterized by a less steep increase (or even decrease) of the specific volume with temperature and they are generally enlarged in the polymer blends. It is, however, interesting to note that the 'relaxation zones', situated within the glass transition range, are much more accentuated in the PVC rich blends.

As indicated in Fig. 1, the p-V-T glass temperatures are defined as the temperatures obtained through the intersection of the extrapolated lines of the specific volumes of the melt and of the glass, or at higher pressures of the appropriate 'relaxation zones', respectively. Thus the glass temperatures evaluated by p-V-T unlike the DSC T_g, characterize the temperatures corresponding to the 'end' of the glass transition ranges.

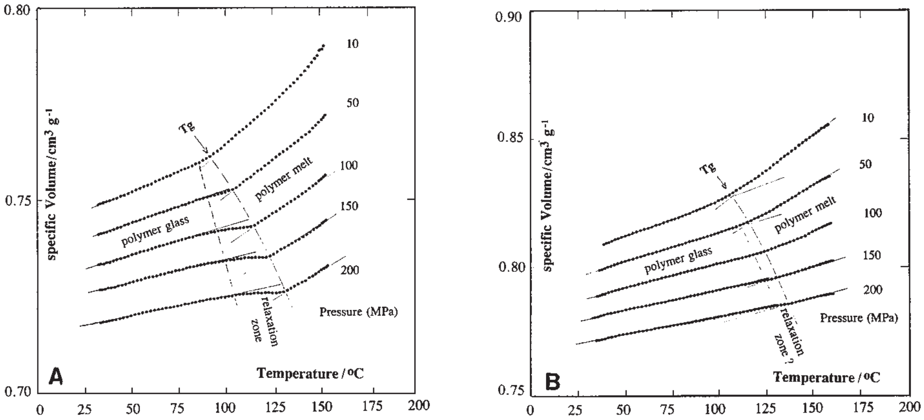

Fig. 1 Isobaric p-V-T diagrams of PVC/PMMA blends, (heating rate: 4 K min^{-1}).
A – 75 w/w% PVC/25 w/w% PMMA; B – 25 w/w% PVC/ 75 w/w% PMMA

The slopes of the respective specific volume vs. temperature lines (as well their intersections defining T_g) were evaluated by linear last square regression using the accessory Gnomix p-V-T software. The straight lines shown in Figs 1A and 1B were manually drawn to visualize the different extent of the respective 'relaxation zones' within the glass transition range. They were not used to evaluate the T_g's.

Subsequently, for a comparative discussion of the composition dependence of the glass temperatures of the studied PVC/PMMA blends, p-V-T data obtained in the isobaric mode of operation at a heating rate of 4 K min^{-1} are used in addition to DSC data scaned at different heating rates situated between 16 and 36 K min^{-1}.

Results and discussion

p-V-T data obtained in the isobaric mode of operation at a heating rate of 4 K min^{-1}

Generally, an increase of the glass temperature with increasing pressure is observed. The pressure dependence of the glass temperatures of PVC, PMMA and of the studied PVC/PMMA blends is shown in Fig. 2. The pressure dependent shift of the glass temperature to higher temperatures is larger the higher the T_g at the lowest applied pressure of 10 MPa. Accordingly, an enlargement is observed of the temperature range between the blend components PVC and PMMA (i.e., 29 K at 10 MPa and 51 K at 200 MPa). On the other hand, the expansion coefficients decrease with increasing pressure, the decrease being larger in the melt and smaller in the glassy blends (Fig. 3).

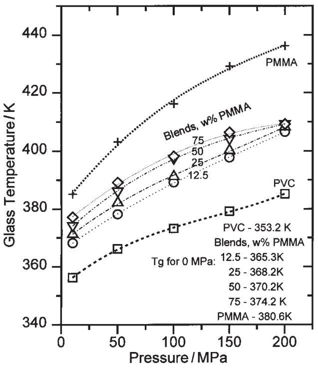

Fig. 2 Pressure dependence of the glass temperature of PVC/PMMA blends (isobaric p-V-T data, heating rate: 4 K min^{-1})

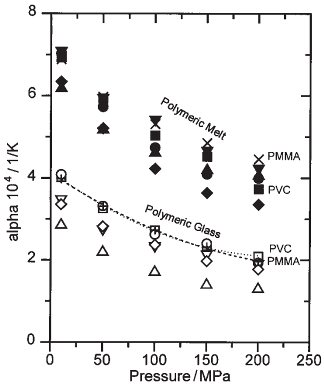

Fig. 3 Pressure dependence of the volumic extension coefficients, α, of PVC/PMMA blends. (heating rate: 4 K min^{-1}). Significance of signs: ■ – PVC ; ○ – 0.875/0.125 w/w% PVC/PMMA ; Δ: upward – 0.75/0.25 PVC/PMMA ; downward – 0.5/0.5 PVC/PMMA; ◆ – 0.25/0.75 PVC/PMMA; + – PMMA, glass; × – PMMA, melt

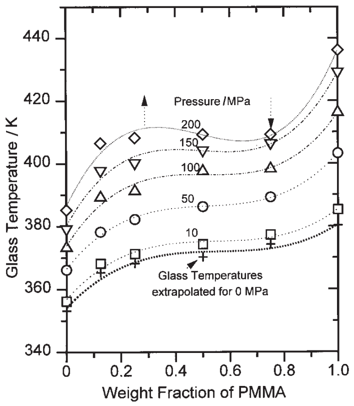

Fig. 4 Pressure influence on the composition dependence of the glass temperature of PVC/PMMA blends (heating rate: 4 K min^{-1})

The composition dependence of the p-V-T glass temperatures of PVC/PMMA blends obtained in the isobaric mode of measurement at a heating rate of 4 K min^{-1} is illustrated in Fig. 4. Taking into account that the glass temperatures of the blends exhibit deviations from additivity, the T_g-data were adapted using the third order T_g *vs.* composition equation of Brekner *et al.* [5], which accounts for both the effects of the claimed thermodynamic hetero-interaction in miscible polymer blends as well as of conformational rearrangements due to hetero-contact formation between the blend components. It is interesting to emphasize that in the high PVC concentration range the glass temperatures of the blends show positive deviations from a linear interpolation according to the Fox relation increasing with pressure, whereas in the high PMMA concentration range, increasing negative deviations are observed. This becomes more evident if the data are presented by the difference $\Delta T_g=(T_{g,\mathrm{blend}}-T_{g,\mathrm{add.Fox}})$ *vs.* composition as shown in Fig. 5. The third order T_g *vs.* concentration equation

$$(T_{g,\mathrm{blend}}-T_{g,1})/(T_{g,2}-T_{g,1})=(1+K_1)w_{2c}-(K_1+K_2)w_{2c}^2+Kw_{2c}^3 \qquad (1)$$

was deduced by extension of the Gordon–Taylor equation [6] for volume additivity so as to account for both the energetic effects of the favoured hetero-interaction imposed by the thermodynamics of polymer miscibility and for entropic effects due to conformational rearrangements induced by the hetero-contact formation. $w_{2c}=K_{w2}/(w_1+K_{w2})$ with $(w_1+K_{w2})=1$, is the weight fraction of the component with the higher glass temperature, $T_{g,2}$, corrected for additive behaviour [7].

The parameter K_1 depends essentially on the difference between the interaction energies of binary hetero- and homo-contacts. Due to the asymmetry of the third order T_g *vs.* composition Eq. [1] (w_{2c} being used as the only one independent variable) included in K_1 are, however, partial contributions of the energetic effect caused by conformational entropy changes. They are induced by the conformational rearrangements imposed by the binary hetero-contact formation. Accordingly, positive values

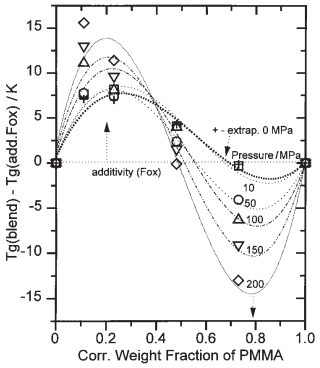

Fig. 5 Pressure influence on the composition dependence of $\Delta T_g = T_{g(blend)} - T_{g(add)}$, the deviation from additivity of the glass temperature of PVC/PMMA blends (heating rate: 4 K min^{-1})

of K_1 suggest predominant energetic contributions of the hetero interaction, whereas negative values indicate prevailing conformational entropy effects. K_2 accounts exclusively for the effects of the conformational entropy. Because of the asymmetry of Eq. [1] the difference (K_1–K_2) includes besides the difference between the interaction energies of binary hetero- and homo-contacts the complementary contributions of the energetic effect caused by conformational entropy changes which are not included in K_1. Unfortunately there is no way to separate the energetic interaction effects from the conformational entropy effects. For details see [5, 8].

For the specific volume additivity assumed by Gordon-Taylor [6] as well as for the 'flexible' bond additivity suggested by DiMarzio [9], a Gordon–Taylor like equation is obtained

$$T_{g,\mathrm{blend}} = (w_1 T_{g,1} + K w_2 T_{g,2})/(w_1 + K w_2) \tag{2}$$

with K a parameter specific for the assumed additivity. It has been shown that in a first approximation, this parameter can be substituted with the ratio of the glass temperatures of the blend components, i.e., $K = T_{g,1}/T_{g,2}$ valid for both specific volume and 'flexible bond' additivity [8]. The result of the substitution is the well known Fox equation [10]

$$1/T_{g,\mathrm{blend}} = w_1/T_{g,1} + w_2/T_{g,2} \tag{3}$$

which thus can be considered to be effectively representative for the weighted additivity of the glass temperatures of the components in miscible polymer blends, i.e., $T_{g,\mathrm{add.Fox}}$. As a consequence, the corrected weight fraction of the blend component with the higher glass temperature may be defined as

$$w_{2c} = w_2 T_{g,1}/(w_1 T_{g,2} + w_2 T_{g,1}) \tag{4}$$

and the Gordon–Taylor equation may thus be reformulated:

$$(T_{\mathrm{g,add.Fox}}-T_{\mathrm{g,1}})/(T_{\mathrm{g,2}}-T_{\mathrm{g,1}})=w_{2\mathrm{c}} \tag{5}$$

Accordingly, the deviation from additivity of the glass temperature of miscible polymer blends may be expressed as

$$\Delta T_{\mathrm{g}}=(T_{\mathrm{g,blend}}-T_{\mathrm{g,add.Fox}}=(T_{\mathrm{g,2}}-T_{\mathrm{g,1}})[K_1w_{2\mathrm{c}}-(K_1+K_2)w_{2\mathrm{c}}^2+K_2w_{2\mathrm{c}}^3] \tag{6}$$

DSC data obtained at different heating rates

The influence of the heating rate on the T_g data evaluated from the second heating DSC-scans is illustrated in Fig. 6. As expected, the glass transition temperatures are shifted to higher temperatures which increasing heating rate, the temperature shift being larger the higher the glass temperature of the polymer. As a consequence, the difference between the glass temperatures of the blend components increases with increasing heating rate (Fig. 7).

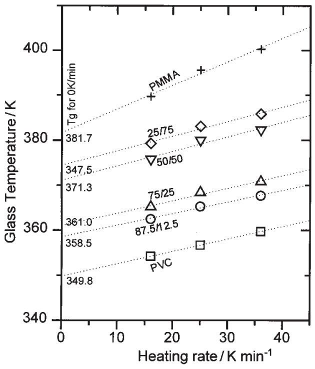

Fig. 6 Heating rate dependence of the glass temperature of PVC/PMMA blends (T_g by DSC measurements)

Although the influences of heating rate and pressure on the glass temperatures are similar, the possible explanations are quite different. The increasing heating rate accentuates the kinetic character, i.e., increases due to the time lag the distance form equilibrium of the glass transition, whereas the increasing pressure reduces the ‘free volume’ of the system.

The composition dependence of the DSC glass temperatures of the PVC/PMMA blends is illustrated in Fig. 8. Although the behaviour of the glass temperatures is similar to that observed for the p-V-T glass temperatures, the deviations from additivity are less accentuated. Again, large positive deviations from additivity are observed in the high PVC concentration range. The negative deviations in the high PMMA concentration range are, however, less accentuated. It is interesting to note that the positive deviations from additivity decrease with increasing heating rate, whereas the negative deviations increase (Fig. 9).

Finally, illustrated in Fig. 10 are the ΔT_g *vs*. composition curves of PVC/PMMA blends obtained by extrapolation of the p-V-T T_g data to zero pressure (0 MPa) and of

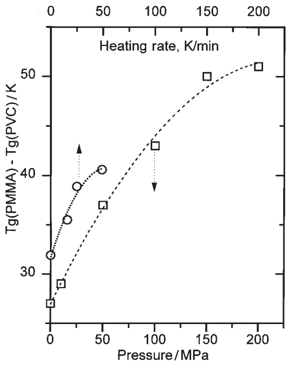

Fig. 7 Influence of pressure and heating rate on ($T_{g,PMMA}$–$T_{g,PVC}$), the difference between the glass temperatures of the PVC/PMMA blend components

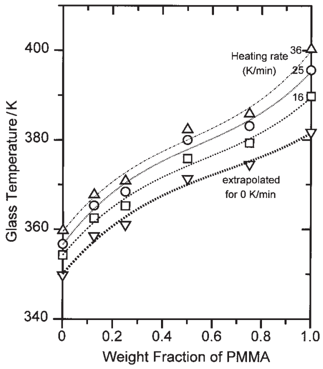

Fig. 8 Heating rate influence on the composition dependence of the glass temperature of PVC/PMMA blends

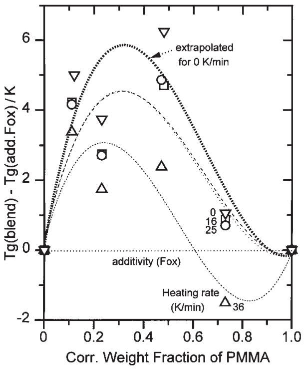

Fig. 9 Heating rate influence on the composition dependence of $\Delta T_g = T_{g(blend)} - T_{g(add)}$, the deviation from additivity of the glass temperature of PVC/PMMA blends

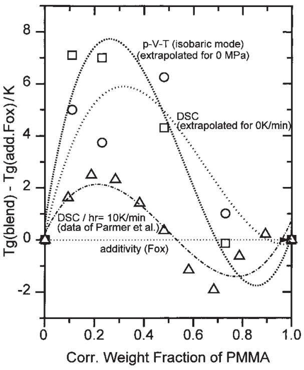

Fig. 10 Comparison of pressure and heating rate influence on $\Delta T_g = T_{g(\text{blend})} - T_{g(\text{add})}$ (ΔT_g data extrapolated for zero MPa and zero K min^{-1}) – are included DSC data for 10 K min^{-1} of Parmer *et al.* [3]

the DSC T_g data to zero heating rate. DSC T_g data of Parmer *et al.* [3] obtained at a heating rate of 10 K min^{-1} are included for comparison.

General discussion

Although there is a surprising similarity between the influence of the heating rate and the pressure on the composition dependent sigmoidal T_g behaviour of the studied PVC/PMMA blend, essential differences may be pointed out (Figs 5 and 9, respectively).

Firstly, the observed deviations from addtivity of the glass temperatures of the PVC/PMMA blends increase with increasing pressure, whereas they decrease with increasing heating rate. Additionally, both the sigmoidal character of the T_g *vs*. composition curves and the negative deviations from additivity of the blend T_g in the high PMMA concentration range are much more accentuated in p-V-T.

Due to the kinetic character of the glass transition, the ‘frozen in’ glass is a thermodynamically metastable state and depending on the history situated more or less distant from equilibrium characterized by ‘zero-conformational’ entropy as predicted by the thermodynamic theory of the glassy state of Gibbs and DiMarzio [11]. During heating across the glass transition range, the system tends to regain the equilibrium state through ‘relaxation’. Because of the time lag between the rate of relaxation and heating rate, the ‘relaxation zone’ spreads out with increasing heating rate. As a consequence, the glass temperature is shifted to higher temperatures. But an increasing heating rate simultaneously decreases the time available for formation by conformational rearrangement of all residual binary hetero-contacts not yet realized between the blend components during development of the ‘frozen in’ glassy state. This explains the decrease with increasing heating rate of the observed positive deviations from additivity of the T_g in the high PVC concentration range as a result of prevailing hetero-contact contacts. A reduced probability of hetero-contact formation permits an ‘apparent’ increase of the ‘free volume’ allowing additional conformational rearrangements with increasing heating rate, in the neighborhood of the fewer hetero-contacts. This explains an increase of conformational entropy and of the increasing negative deviations in the high PMMA concentration range of the blends.

It is, however, interesting to note that hetero-contact formation is favored in the high PVC concentration range, i.e. hetero-contact interaction prevails by dissolution of PMMA in a PVC matrix. In contrast to that, the dissolution of PVC in a PMMA matrix, facilitates ‘conformational rearrangements’, because of a smaller tendency for hetero-contact interaction. Unfortunately, we must confess that we are not yet able to explain this difference in the interaction behaviour of the blend components in the high concentration ranges of PVC and PMMA, respectively. The same behaviour is observed for the pressure influence on the glass temperature of PVC/PMMA blends.

Assuming that an increasing part of the ‘frozen in’ metastable excess ‘free volume’ of the glassy state is squeezed out by increasing pressure, it may be supposed that hetero-contact interaction between the blend components is enhanced because of the accompanying approach of the interacting sites. Thus generally, binary hetero-contact formation will be amplifyed by increasing pressure, promoting in miscible polymer blends the tendency of positive deviations from additivity of the glass temperature. It thus seems surprising that in the PVC/PMMA blends are observed with increasing pressure beside increasing positive deviations from additivity of the glass temperature in PVC rich blends also strong decreasing negative deviations in PMMA rich blends. This could be attributed to the important differences observed in the extension of the ‘relaxation zones’ situated between the polymeric glass and melt (Fig. 1 for the 75/25 and 25/75 w/w% PVC/PMMA blends, respectively). For illustration the pressure dependent extension of the ‘relaxation zones’ observed in the glass transition range of the studied PVC/PMMA blends is shown in Fig. 11.

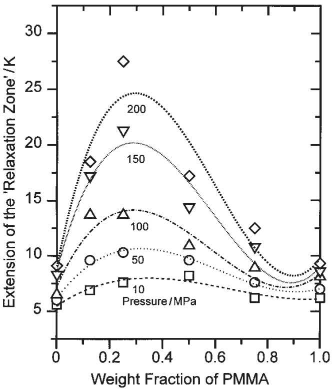

Fig. 11 Pressure influence on the extension of ‘relaxation zones’ within the glass transition range of PVC/PMMA blends

It is, however, astonishing that the shape of the ΔT_g *vs*. composition curves of PVC/PMMA blends (Fig. 5) reflects roughly the shape of the respective 'relaxation zone' curves shown in Fig. 11. It may thus be supposed that the recovery of the equilibrium hetero-contact arrangement in miscible PVC/PMMA blends is more complete the larger the 'relaxation zone' within the glass transition range. This could be the explication why the glass temperatures of PVC rich blends exhibit positive deviations, whereas those of PMMA rich blends are characterized by negative deviations from additivity.

It may thus be assumed that the observed increasing positive deviations in the PVC rich blends, are related to the increasing enlargement of the 'relaxation zones' with increasing pressure, whereas the negative deviations in the PMMA rich blends are caused by the comparatively substantial reduction of the 'relaxation zones'.

In conclusion, it seems that optimal hetero-contact formation in miscible polymer blends depends not only on the time lag between the rates of conformational rearrangement and of crossing the glass transition range, but also on the size of 'relaxation zones' at a given glass transition rate.

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