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Modelling Segmental Dynamics in Miscible Polymer Blends

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Summary: The complex thermorheological behaviour observed in miscible polymer blends is modelled by combining two existing theoretical approaches: The Thermal Concentration Fluctuation model (A. Zetsche, E.W. Fischer, *Acta Polymer.* **1994**, *45*, 168) and the Effective Concentration model (T.P. Lodge, T.C.B. McLeish, *Macromolecules* **2000**, *33*, 5278), giving rise to a simple model with only one adjustable parameter. This model is then tested in the case of two model blends allowing to show its abilities and limitations to describe how the respective segmental dynamics of lowest or highest T_g component are affected by blending.

Keywords: amorphous, blends, glass transition, modelling, thermoplastic polymers

Introduction

Miscible polymer blends tend to present a much more complex thermorheological behaviour than pure polymers, especially when the difference between the glass transition temperatures (ΔT_g) of the blend components is large. The broadening of the relaxation time distribution of each component is one of the key phenomena observed. Fischer and Zetsche[1] showed that it could be formally related to *Thermal Concentration Fluctuations* (TCF). In their model, a blend sample of average composition ϕ_0 is supposed to be divided into small subvolumes V_i in which the local concentration ϕ is different from average composition due to the TCF. In the temperature range where this spatial distribution of compositions is quasi-stationary at the time scale of the segmental α-relaxation, it gives rise to a distribution of local mobilities. Base on these ideas, Fischer and Zetsche propose to describe the broadening of the relaxation time distribution of each blend component by considering that each subvolume relaxes with the same non-exponential behaviour as the pure polymer, but with a different characteristic times τ. The relaxation broadening due to blending is then described by a distribution $H(\log\tau)$ of these characteristic relaxation times, which allows them to calculate the dielectric relaxation of one blend component:

$$\varepsilon''(\log\omega) = \int_{-\infty}^{\infty} H(\log\tau)\cdot \mathrm{Im}\left[\varepsilon^*(\log\omega + \log\tau)\right] d\log\tau \qquad (1)$$

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Where ε^* is given by the Havriliak-Negami (HN) function:

$$\varepsilon^*(\omega)=\varepsilon_\infty+\Delta\varepsilon\cdot\frac{1}{\left(1+(i\omega\tau)^\alpha\right)^\gamma} \tag{2}$$

where the relaxation strength $\Delta\varepsilon$ and the exponents α and γ are those experimentally obtained from pure polymer's dielectric relaxation curves analysis.

The key idea of Fischer and Zetsche is to obtain the distribution $H(\log\tau)$ starting from a *gaussian distribution* of concentration $P(\phi)$:

$$P(\phi)\propto\exp\left[\frac{-(\phi-\phi_0)^2}{2\left\langle(\Delta\phi)^2\right\rangle}\right] \tag{3}$$

Where the variance $<(\Delta\phi)^2>$ depends of the size of the subvolumes V_i.

They then assume that the composition dependence of blend's macroscopic glass transition temperature (obtained by Dynamic Scanning Calorimetry): $T_g(\phi_0) = F(\phi_0)$, is not modified at the microscopic level, so that one can calculate the glass transition of each subvolume as $T_g(\phi)=F(\phi)$, the function F being for example the Brekner equation:

$$T_g(\phi)=T_{gA}+\left(T_{gB}-T_{gA}\right)\left[(1+K_1)\cdot\phi-(K_1+K_2)\cdot\phi^2+K_2\cdot\phi^3\right] \tag{4}$$

Where T_{gA} and T_{gB} are the pure components glass transition temperatures and K_1 and K_2 are fitting parameters determined from Differential Scanning Calorimetry (DSC) measurements.

That leads to a new distribution $N(T_g)$, which in turn can be transformed into $H(\log\tau)$ using the William-Landel-Ferry (WLF) equation:

$$\log\left(\frac{\tau}{\tau_g}\right)=\frac{C_1\cdot\left[T-T_g(\phi)\right]}{C_2+\left[T-T_g(\phi)\right]} \tag{5}$$

Where $\log\tau_g$, C_1 and C_2 depend on the polymer component considered, these two latter being in a first approximation linear interpolations of the pure component's parameters. It is noteworthy that in the first formulation of the Fischer's model[1], it is not clear how the Jacobian term ($d\log\tau\,/\,d\phi$) - involved in the transformation from $P(\phi)$ to $H(\log\tau)$ – is taken into account. In the later formulation given by Kumar et al.[3] this Jacobian was explicitly considered and some refinements were also introduced trying to account for another key issue of miscible blends dynamics: the observation of distinctly different segmental mobilities for the two components observed with a wide range of experimental techniques [4-10]. Based on the assumption that the fluctuation subvolumes are equal to the cooperative volumes of Donth, which introduces a strong composition and temperature dependence of $<(\Delta\phi)^2>$, Kumar's model allows a near quantitative description of the behaviour of various miscible polymer blends near T_g. Nevertheless, it seems to fail in explaining the persistence of the different component segmental mobilities well above the glass transition temperature, where the presence of concentration fluctuations does not play a significant role on the dynamic features[5, 9]

This latter point can be addressed by introducing the *Effective Concentration concept*:[2] In a miscible blend of polymers A and B, chain connectivity imposes that the local environment of a segment of polymer A is (on average) necessarily richer in polymer A compared to the *bulk composition* ϕ. The *Effective Concentration* ϕ_{eff} sensed by a polymer segment is thus given by:

$$\phi_{eff} = \phi_{self} + \left(1 - \phi_{self}\right) \cdot \phi \tag{6}$$

where ϕ_{self} is the *Self Concentration* of the considered polymer segment, which was recently expressed by Lodge and McLeish[2] as:

$$\phi_{self} = \frac{C_\infty M_0}{k \rho N_{av} l_k^3} \tag{7}$$

where: C_∞ is the characteristic ratio, M_0 is the molar mass of repeat unit, k is the number of backbone bonds per repeat unit, ρ is the density, N_{av} is the Avogadro number and l_k is the length of a Kuhn statistical segment. This concept rationalizes the dynamic heterogeneities observed well above T_g where TCF contribution vanishes: As we have shown in a recent experimental study[11], it allows to quantitatively predict the two different effective glass transition temperatures $T_{g\ eff\, A}$ and $T_{g\ eff\, B}$ corresponding to each component in the miscible blend and which are linked to their respective average segmental mobilities

In the present paper, we will describe how the combination of the TCF model with the Effective Concentration concept leads to a simple model where TCF variance $<(\Delta\phi)^2>$ is the only adjustable parameter. As an application, this model will be used to account for the dielectric relaxation behaviour of two model miscible polymer blends in which only one component is dielectrically active, this component being either the one having the lower glass transition temperature (PVME in PVME/PS blends) or the higher one (PoClS in PS/PoClS blends). This particularity will allow us to study selectively the efficiency and limitations of the model to describe the effect of blending on the dynamics of the lower or higher T_g component of the blend.

After discussing the results, we will propose some future improvements of the model.

Modelling

The introduction of the Effective Concentration concept in Fischer's formalism can be carried out as follows. We consider the same local concentration distribution induced by TCF, but inside each relaxing subvolume V_i of composition ϕ. We then introduce two different effective local concentrations ϕ_{effA} and ϕ_{effB} corresponding to the local environments of polymer segments A and B. Under this assumption we implicitly consider that the size of each subvolume V_i is much larger than l_k^3 (the volume where the self-concentration is relevant). On these grounds, $P(\phi)$ yield two distinct local concentration distributions, depending on the component considered:

$$P(\phi_{eff\,A}) = \frac{1}{1-\phi_{self\,A}} P(\phi) \qquad (8a) \qquad \text{and} \qquad P(\phi_{eff\,B}) = \frac{1}{1-\phi_{self\,B}} P(\phi) \qquad (8b)$$

This is illustrated in Figure 1, for a representative example in which the average composition of the blend ϕ_0 would be equal to 0.5 ; TCF would be characterized by $<(\Delta\phi)^2> = 0.1$ and the self concentrations ϕ_{selfA} and ϕ_{selfB} would be both equal to 0.25.

Following the same procedure as Fischer, but now replacing T_g in the WLF equation by T_{geff}, these distributions can be easily transformed into two distinct characteristic relaxation times distributions $H(log\tau_A)$ and $H(log\tau_B)$ of each component in the blend, which in turn allow to calculate the dielectric relaxation curves $\varepsilon''(\omega, T)$. The parameters C_1 and C_2 of each subvolume might be different for each polymer component and following Fischer will be taken, in a first approximation, as linear interpolations of pure polymers parameters, at the respective effective concentrations ϕ_{effA} and ϕ_{effB}. In addition, the value of $\tau_g = \tau(T_{geff})$ will be taken fixed to the τ_g value determined for the pure component.

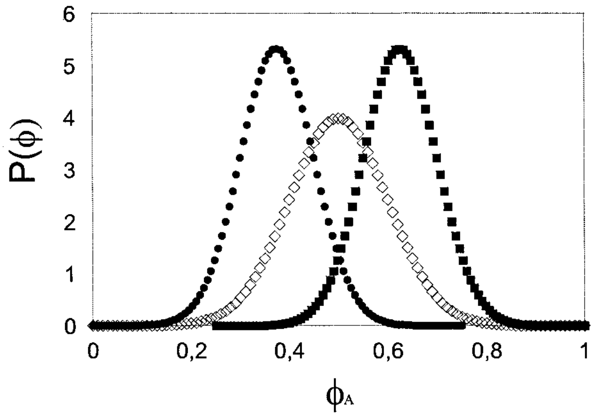

Figure 1. Example of local concentration distributions: Gaussian distribution due to TCF(◊, equation 3) and corresponding local environments of polymer A segments (■, equation 8) and polymer B segments (●, equation 8b) is due to chain connectivity

Experimental

One blend was studied for each polymer pair: a poly(vinyl methyl ether)/Polystyrene blend of weight composition (35/65) and a Poly-o-chlorostyrene/Polystyrene blend of weight composition (50/50). Poly-o-chlorostyrene ($\overline{M}_w$=225000 g/mol; $\overline{M}_w/\overline{M}_n$ =1.7) and poly(vinyl methyl ether) ($\overline{M}_w$=21900 g/mol; $\overline{M}_w/\overline{M}_n$ =3) were obtained from Lark Enterprises and Aldrich Chemical respectively. For PVME/PS blend, a Polystyrene ($\overline{M}_w$=66000 g/mol; $\overline{M}_w/\overline{M}_n$ =1.03), obtained from Polymer Laboratories was used. In contrast, a Polystyrene oligomer ($\overline{M}_w$=740 g/mol; $\overline{M}_w/\overline{M}_n$ =1.06) purchased Polymer Source was used for PS/PoClS blends in order to increase the difference between the T_g of the components. Blends were prepared by solution casting using toluene as solvent. Obtained films were carefully dried under vacuum, above their glass transition temperatures during 72 hours, in order to remove the solvent completely. Reference samples of PVME, PoClS and PS were prepared in a similar way.

Dielectric relaxation measurements were performed on two different set-ups supplied by Novocontrol GmbH. For the frequency range from 10^{-3} to 10^{7} Hz the set-up consisted of a Solartron-Schlumberger frequency response analyser SI 1260 supplemented by a high-impedance preamplifier of variable gain. For the frequency range from 10^{6} to 10^{9} Hz a Hewlett-Packard impedance analyser HP4191A was used. For both ranges the sample was kept between two condenser plates (gold-plated electrodes, 20 and 5 mm diameter, respectively) that were maintained at a fixed distance. Frequency sweeps were performed at constant temperature with temperature stability better than 0.05 K.

Results

In order to have all the parameters required by the model to describe the blends' dielectric relaxation, we first focus on the analysis and modelling of pure components' behaviour. Actually, the dielectric relaxation of PVME, PS and their blends were already studied in detail by our team in a previous paper[6]. The α-relaxation of pure PVME was successfully described by an HN function (Equation 2) with the condition:

$$\gamma(\alpha) = 1 - 0.812 \cdot (1-\alpha)^{0.387} \qquad (9)$$

This imposed relationship between the parameters α and γ allows to calculate the corresponding parameters of the Kohlrausch-Williams-Watts (KWW) time function as:

$$\beta = [\alpha \cdot \gamma(\alpha)]^{1/1.23} \qquad (10)$$

$$\log \tau_{KWW} = \log \tau_{HN} - 2.6 \cdot (1-\beta)^{0.5} \exp(-3\beta) \qquad (11)$$

Therefore the dielectric relaxation of PVME at a given distance from T_g is described by only two parameters, β and $log\ \tau_{KWW}$, plus the relaxation strength which temperature dependence was found to be well described by:

$$\Delta\varepsilon(T) = -0.0125 + 0.23438 \cdot 1000/T \qquad (12)$$

Parameter β was found to increase slightly with temperature above T_g, reaching a stable value of 0.5 at higher temperatures. This behaviour has been observed for different polymers[12]. For our calculation of PS/PVME blend's behaviour, we will consider a fixed value β = 0.5. The relaxation time of pure polymers followed the WLF equation with $log\ \tau_{g\ PVME}$ = 0.159; $C_{1\ PVME}$ = 13.20; $C_{2\ PVME}$ = 49.5 K ; $log\ \tau_{g\ PS}$ = -0.769 ; $C_{1\ PS}$ = 11.75 and $C_{2\ PS}$ = 47.0 K.

Another important aspect of this previous work[6] on dielectric behaviour of PS, PVME and their blends was the successful modelling of the *β-relaxation* of PVME which was shown not to be affected by blending. The model obtained allowed us to calculated the contribution of this secondary relaxation in the dielectric curves and to subtract it from experimental curves in order to observe only the *α-relaxation* contribution which we intend to model.

The relaxation behaviour of pure PoClS was studied following the same procedure as for pure PVME. The modified HN function described above successfully fitted the dielectric relaxation curves. The parameter β was found to vary much more near T_g than for PVME. Nevertheless, a few degrees above T_g, β reaches a rather constant value (β = 0.46), that we will use for calculations. Also the relaxation strength $\Delta\varepsilon$ was found to vary strongly with temperature near T_g and reaches at nearly constant value at high temperature. We will consider this high temperature limit value $\Delta\varepsilon = 1.2$ for the calculations. The relaxation time of pure PoClS and PS oligomer follows the WLF equation with $log\ \tau_{g\ PoClS} = -0.132$; $C_{1\ PoClS} = 12.36$; $C_{2\ PoClS} = 67.1$ K; $log\ \tau_{g\ PSo} = -0.632$; $C_{1\ PSo} = 14.37$ and $C_{2\ PSo} = 53.7$ K.

The self concentration values ($\phi_{selfPVME}$=0.25 and $\phi_{selfPOCLS}$ = 0.22), as well as the pure components T_g and parameters K_1 and K_2 for the two blends were taken from our previous publication[11] . These latter parameters are listed in Table 1.

Let us now focus on the relaxation behaviour of the blends: Figures 2 and 3 show the relaxations of PVME in the (35/65) PS/PVME blend and PoClS in the (50/50) PS/PoClS blend, respectively. One can clearly observe the relaxation broadening due to blending, which is much more important in the case of the PS/PVME blend.

Discussion

The model was fitted to the experimental curves with $<(\Delta\phi)^2>$ as the only adjustable parameter. Figure 2 shows that a near quantitative prediction of dielectric relaxation curves is obtained for PVME/PS blend using a fixed value of $<(\Delta\phi)^2>=0.04$ on the whole temperature range. This result is different from those obtained by Fischer and Zetsche for the same system, whose model, in order to fit experimental curves, needed much lower and clearly temperature dependent values of $<(\Delta\phi)^2>$, together with an adjustment of $\Delta\varepsilon$, C_1 and C_2.

Regarding the accuracy of model predictions, three points have to be enlighten: First, the position of peak maximum and height are reasonably well described despite of the simple assumption made on the values of $\Delta\varepsilon$, C_1 and C_2. The use of $\Delta\varepsilon$ as a free parameter for each temperature and the adjustment C_1 and C_2 via the iterative procedure proposed by Fischer and Zetsche in their paper would of course lead to even better predictions. Second, the description of relaxation broadening toward low frequencies (i.e., slow part of the response) is very good. Nevertheless, the third point we shall stress is that the broadening toward high frequencies (i.e., fast part of the response) is not so well described near T_g. This failure was actually predictable as a previous study of PS/PVME blends[6] showed that close to T_g, the dynamics of the PVME segments in the blend extends to high frequencies more than in pure polymer at the same temperature. This phenomenon, which can be interpreted as the result of a lack of packing of the blend leading to regions with greater "free volume" than in pure PVME, is obviously not taken into account by the simple model we are considering here.

For the PoClS/PS blend (Figure 3), the model seems to describe reasonably well the relaxation broadening using a value of $<(\Delta\phi)^2>=0.0036$. Nevertheless, the prediction of the dielectric curve maximum position is not correct. This evidence that the time scale of the dynamics of PoClS in the blend calculated in the model is far from that in the experiment. A possible reason for this failure is the fact that we fixed τ_g of the component in blend to be the same than that of the pure polymer. This condition is approximately verified for the PVME/PS blend studied (the temperature where $1/\omega_{max}$ equals τ_g (261.5 K) is almost the same that $T_{geff\ PVME}$ = 258.7 K), but clearly it is not for the PoClS/PS blend (in that case the temperature where $1/\omega_{max}$ equals τ_g (345.0 K) is clearly different from $T_{geff\ PoClS}$ = 332.5 K). In order to illustrate the effect of this difference of 12.5 K we have plotted as a dashed line in Figure 3 the curve predicted by the model at T=350 – 12.5 = 337.5 K. One can see that the obtained curve describes quite well the experimental data of the blend at 350 K.

Table 1. Parameters of Brekner's equation used for calculations

Blend A/B	T_{gA}	T_{gB}	K_1	K_2
PVME/PS	249.5	373	-0.707	0.462
PSo/PoClS	280	402	-0.296	0.792

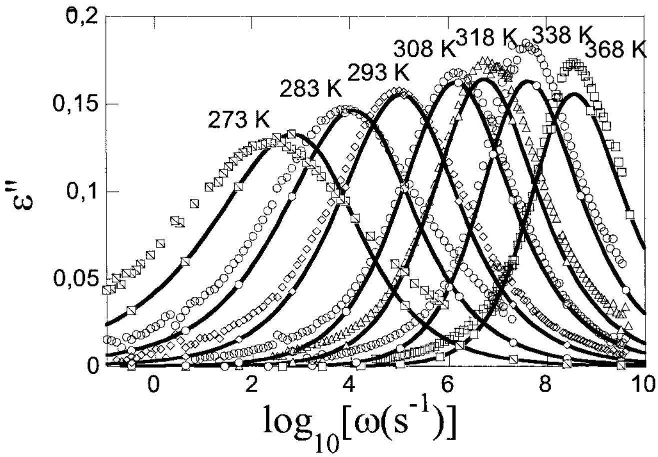

Figure 2. Dielectric relaxation of a PS/PVME (35/65) blend: lines show model predictions

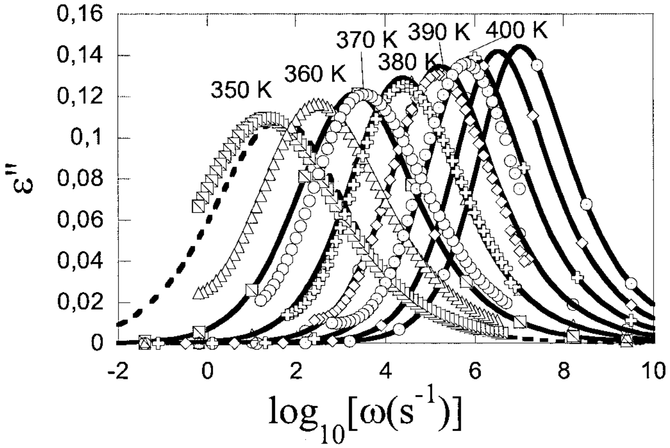

Figure 3. Dielectric relaxation of the PoClS/PSo (50/50) blend: solid lines with points show model predictions at each experimental temperature (solid line with circles on the right side is the prediction for the 400 K experiment in circles), dashed line show model prediction at 337.7 K

Conclusion

The introduction of the *Effective Concentration concept* into the Concentration Fluctuation Model of Fischer lead to a simple model in which *Thermal Concentration Fluctuation* variance $<(\Delta\phi)^2>$ is the only adjustable parameter. As a test, such a model was used to calculate the dielectric α-relaxation curves of two model polymer blends. The results obtained for the

PVME/PS blend, showed that the model seems to give a quite satisfactory description of how the dynamics of the lowest T_g component of the blend (PVME in that case) is affected by blending, except for high frequencies and temperatures close to blend's glass transition, where some additional consideration on blend packing should be introduced. As an opposition with the previous work of Fischer on the same polymer binary blend, we shall point out that, apart from requiring only the adjustment of $<(\Delta\phi)^2>$, our model did not show any apparent need for a strong temperature dependence of this latter.

The results obtained for the second blend studied (PoClS/PS) shown that the model seems to be able to describe the relaxation broadening effect of blending on the highest T_g component of the blend (here PoClS), but not the evolution of relaxation peak maximum with temperature. Apparently, this problem lies in how the isothermal relaxation time is calculated from the glass transition. The refinement of this part of the model is now in progress.

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