Breakdown of time–temperature superposition in miscible polymer blends

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The empirical principle of time–temperature superposition has been found to fail for a miscible blend of 20 weight% poly(ethylene oxide) in poly(methyl methacrylate). Oscillatory shear rheometry data is reported for this blend at four temperatures well above the glass transition temperature of the blend. The longest relaxation time of each component in the blend is obtained from the frequency dependence of the loss modulus. The temperature dependence of the longest relaxation time of each component in the blend is found to obey the empirical WLF equation of the pure component referenced to the glass transition temperature of the blend.

(Keywords: miscible blends; rheology; thermorheological complexity; time–temperature superposition; poly(ethylene oxide); poly(methyl methacrylate))

INTRODUCTION

Miscible (single-phase) polymer blends are becoming increasingly important for industrial use of polymers because of the unique combinations of properties that are possible with blends. An understanding of the rheological properties of such blends is crucial for prediction of processing behaviour. For multiphase blends, the empirical principle of time–temperature superposition is known to fail in dramatic fashion[1,2]. However, the limited available data on single-phase blend systems[3–8] indicates that time–temperature superposition is applicable for miscible blends. The purpose of this report is to demonstrate that time–temperature superposition is, in fact, invalid for a miscible blend. The exact nature of the breakdown of superposition is shown to be quite simple, and provides significant insight into the temperature dependence of rheology of all single-phase polymer systems.

I have chosen to study a blend of poly(ethylene oxide) and poly(methyl methacrylate), which is a model blend system in two respects. First of all, both polymers can be prepared by anionic polymerization techniques yielding narrow molecular weight distributions. Secondly, the enthalpic interaction between these polymers is weakly attractive. This makes the blend miscible without strong specific interactions between the components, which might complicate the blend rheology.

Because the enthalpic interaction is so weak in this particular blend system, numerous studies in the literature[9–22] have focused on verifying that PEO and PMMA form a single-phase blend above the melting point of PEO ($T_m = 65$°C). A variety of techniques have been employed: glass transition temperature from differential scanning calorimetry[9–12], PEO melting point depression[10–15], PEO crystallization kinetics[9,10,14,16], ^{13}C n.m.r.[17], inverse gas chromatography[18], and small angle neutron scattering[19–22]. The general consensus is that PEO and PMMA form a single-phase blend. However, the reported values of the Flory–Huggins interaction parameter χ are so small that miscibility cannot be claimed to have been irrefutably proven. I.r. spectroscopy results indicate that specific interactions between PEO and PMMA are very weak[23]. Cloud points have been measured for PEO/PMMA blends[12,24,25], and a lower critical solution temperature of 230°C was reported for a blend of polydisperse polymers with $M_w(\text{PEO}) = 300\,000$ and $M_w(\text{PMMA}) = 130\,000$. I conclude from the literature results that PEO and PMMA form a marginally miscible system, with apparent miscibility over a wide temperature range even though $|\chi|$ is quite small. I therefore determine the phase behaviour of the blend using light scattering.

EXPERIMENTAL

The poly(methyl methacrylate) sample was synthesized by standard techniques[26] and has a weight-average molecular weight of 107 000 by size exclusion chromatography. The poly(ethylene oxide) sample was obtained from Polymer Laboratories, and has a weight-average molecular weight of 235 000 (obtained from the manufacturer). Size exclusion chromatography indicates that $M_w/M_n < 1.2$ for both of these samples.

Tacticity of PMMA has been shown to be a critical factor controlling miscibility in PEO/PMMA blends, because blends with highly isotactic PMMA have been reported to be incompatible[27,28]. Triad analysis[26] of ^{1}H-n.m.r. on our PMMA sample gave 78% syndiotactic, 21% heterotactic, and 1% isotactic.

The blend was 20.2% by weight PEO, prepared by dissolution in warm (40°C) acetone, and dried in a rotary evaporator at 35°C. Further drying was accomplished at room temperature under vacuum for three weeks (less than 0.01 g weight loss in the final week of drying). Solvents that are capable of hydrogen bonding with PEO or PMMA (such as acetone) cannot be entirely removed from these polymers even under vacuum at temperatures near T_g. For this reason, the following procedure was used to prepare all samples for rheological study. First the vacuum-dried sample was moulded in a vacuum-assisted compression mould at 50°C above T_g or T_m, resulting in a

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bubble-free disc. This disc was then placed in the rheometer (under flowing nitrogen gas) and allowed to bubble at a temperature slightly above the highest temperature of measurement. The sample was then remoulded, and the procedure was repeated as needed to provide a disc which remained almost entirely bubble-free even at the highest temperature of measurement.

Glass transition temperatures were measured using a DuPont 1090 differential scanning calorimeter. The glass transitions of the pure PMMA and the blend were taken to be the midpoint in an upwards temperature scan at 10°C/min (measured immediately after cooling at -10°C/min from the liquid state). The PMMA sample has a T_g of 129°C, which is consistent with other high molecular weight PMMA samples of this tacticity[26]. The blend has a single T_g of 75°C. The PEO sample had to be quenched in liquid nitrogen (from 100°C to -78°C) in order to inhibit crystallization enough to allow the glass transition to be measured. A 10°C/min heating rate immediately following the quench gave a T_g of -52°C, which is consistent with literature results[10]. The width of the transition in the d.s.c. for the blend was ~ 30 K, which is twice as large as the transition widths of the pure components (~ 15 K).

The blend was transparent at all temperatures, but was not perfectly clear, as reported previously for similar PEO/PMMA blends[24]. Light scattered (at a 90° angle) from a thin film on a microscope slide was used to determine the phase behaviour of the blend up to 300°C. The blend remained transparent at all temperatures, indicating that if concentration fluctuations occur in my blend, they are limited to length scales which are smaller than the wavelength of light. I conclude from the d.s.c. and light scattering results that my blend is miscible between 75°C and 300°C.

Oscillatory shear rheometry using a Rheometrics System Four rheometer was used to study the viscoelastic response of the pure components and the blend at temperatures well above T_g (the lowest temperature of measurement for pure PEO was 66°C due to crystallization problems below that temperature). Temperature control was achieved via a steady flow of heated nitrogen gas through the sample chamber. Parallel plates (25 mm in diameter) were used with 1–2 mm gap heights. Linear viscoelastic response was demonstrated at all frequencies by varying the strain amplitude by at least a factor of two. Strain was increased at low frequencies to keep the magnitude of the torque above 10 dyne cm. The highest frequency used was always 100 rad/s (due to limitations of the dynamic motor) and the lowest frequency was determined by either relaxation of the sample or prohibitively long times to acquire additional data (the lowest frequency used was 2.5×10^{-4} rad/s). All samples were run at the lowest temperature first, with successive runs at higher temperatures. Finally the lowest temperature response was checked again to ensure that no degradation of the sample had occurred.

RESULTS AND DISCUSSION

The empirical principle of time–temperature superposition[2] states that the frequency dependences of the complex modulus $G^*(\omega; T)$ at two temperatures are related by a simple scale change:

$$G^*(\omega; T) = b_T G^*(a_T \omega; T_0) \qquad (1)$$

This principle was found to be valid for both pure components and was utilized to make master curves. a_T and b_T are adjustable parameters which are functions of temperature, but not frequency. The modulus scale shifts b_T were found to be very small and are not discussed here. The temperature dependence of the frequency scale shifts for both pure components was found to obey the empirical WLF equation[2]. (Because the reference temperature T_0 in equation (1) is arbitrary, following Ferry[2], I take $T_0 = T_g$.)

$$\log a_T = -\frac{C_1(T - T_g)}{C_2 + T - T_g} \qquad (2)$$

For the PMMA sample, data at six temperatures between 136°C and 200°C were used to determine $C_1 = 11.9$ and $C_2 = 69$ K. Plazek[29–31] has reported that the temperature dependence of rheology for PMMA samples of various tacticities is the same when compared at the same $T - T_g$. My data for $\log a_T$ vs $T - T_g$ on PMMA are consistent with Plazek's data. Plazek has also pointed out that the WLF equation does not hold for PMMA if the temperature range is very broad and includes data below T_g. All of Plazek's data with $T > T_g + 10$°C are consistent with equation (2) with C_1 and C_2 given above.

For the PEO sample, data at three temperatures between 66°C and 138°C were used to determine $C_1 = 6.9$ and $C_2 = 88$ K. At temperatures this far above T_g ($= -52$°C) the temperature dependence of relaxation times are often reported to follow Arrhenius behaviour[2]. Our data could be fit to an Arrhenius equation, with an activation energy of 6.4 kcal/mole. This value is much smaller than the value reported by Ferry[32] for PEO in this temperature range (11.7 kcal/mole), but is quite consistent with the value reported by Fujita[33] of 6 kcal/mole. However, there is WLF curvature in a plot of $\log a_T$ vs $1/T$ for the data on PEO, and I therefore use equation (2) with the coefficients given above to describe the temperature dependence of rheology for PEO.

In sharp contrast to the data on the pure components, time–temperature superposition failed dramatically for the blend, as shown in *Figure 1*. The loss modulus data at 120°C, 137°C and 174°C have been shifted along the frequency axis to superimpose with the data at 155°C at

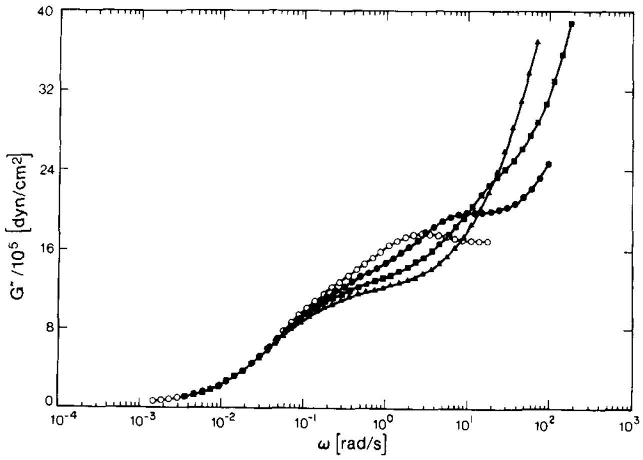

Figure 1 Loss modulus data at four temperatures for the blend, shifted on the frequency scale to superimpose with the 155°C data at low frequency. ○, 174°C data; ●, 155°C data; ■, 137°C data; ▲, 120°C

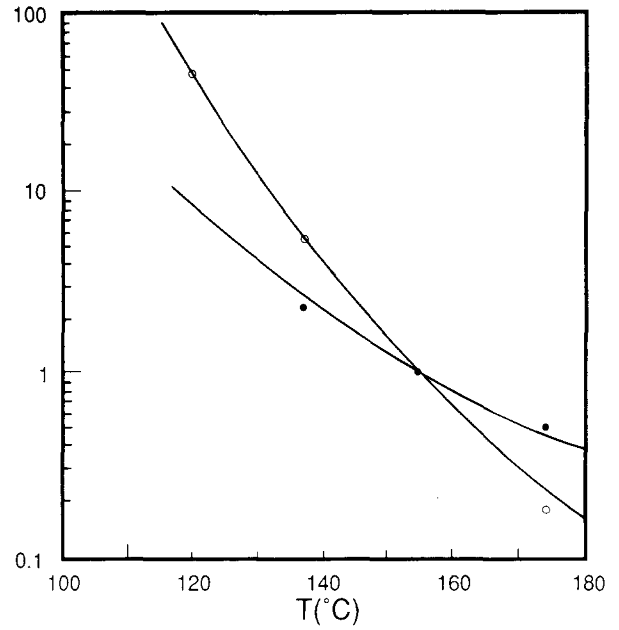

Figure 2 Temperature dependence of shift factors for both components in the blend. ○, PMMA; ●, PEO. Solid curves are equation (2) with C_1 and C_2 of each pure component and T_g of the blend

low frequencies, but the data at high frequencies cannot be superimposed. We have studied a number of PEO/PMMA blends of different molecular weights and compositions, and time–temperature superposition failed for all of these blends[34].

The superimposed drop in $G''(\omega)$ at low frequency in *Figure 1*, corresponding to the terminal relaxation of the blend, is due to relaxation of the PMMA at each temperature. (Assignments of relaxations to specific components in the blend were made by the crude rule of thumb that a given component generally relaxes at roughly the same time $(1/\omega)$ at a given $T-T_g$ regardless of composition. This empirical rule has been found to be valid for a number of other PEO/PMMA blends[34], within about a factor of 3 (see *Figure 3*).) The local maximum in $G''(\omega)$ near 6 rad/s at 155°C is due to relaxation of the PEO, as is the peak in the 174°C data at lower frequency and the bump in the 137°C data at higher frequency. The terminal relaxation time of the PEO is taken as the reciprocal of the frequency at which this relaxation occurs. Apparently the relaxation times of the two components are moving apart as the temperature is lowered. This fact is demonstrated more clearly in *Figure 2*, where I plot the temperature dependence of the shift factors for each component in the blend, using a reference temperature of 155°C. For PMMA, a_T is simply the frequency scale shift used to generate *Figure 1*. For PEO, I calculate a_T from the apparent relaxation times of the PEO in the blend at various temperatures. The solid curves in *Figure 2* are WLF equations, using C_1 and C_2 of the pure components and T_g of the blend (75°C) in equation (2). The data fit these WLF equations within experimental error, although this error is admittedly rather large in the case of the PEO relaxation due to the difficulty associated with precisely determining the relaxation time from the loss modulus data. There is also a potential systematic error in the PEO WLF equation due to the uncertainty in the T_g of pure PEO. Values of T_g for PEO have been reported[35] in the range $-115°\mathrm{C} \leqslant T_g \leqslant -40°\mathrm{C}$, reflecting the uncertainty in determining an accurate glass transition for a crystalline polymer.

Current molecular theories of polymer relaxation[36] are built around the confining tube picture, in which any single chain is surrounded by an effective tube made up of other chains. The temperature dependence of rheology in these models (and others) is embodied in an effective friction coefficient[2,36]. As is obvious from *Figures 1* and *2*, each component in this miscible blend has an individual friction coefficient. However, the friction coefficients are apparently separable into two parts: one associated with the surrounding chains making up the tube, and the other associated with some intrinsic properties of the chain itself. In the context of equation (2), the entire effect of the surrounding chains is manifested in T_g, while the parameters C_1 and C_2 are apparently intrinsic properties of a given chain, independent of the environment of surrounding chains making up the tube.

It is not clear at present whether the breakdown of time–temperature superposition is general for all miscible blends, or is specific to miscible blends with very small enthalpic interactions. The fact that χ is indistinguishable from zero[21] (within experimental error) means that concentration fluctuations are quite large in this blend. We estimate the correlation length scale for concentration fluctuations in the blend to be ~ 50 Å using the random phase approximation[37]. Knowledge of unperturbed dimensions and entanglement molecular weights of polymers allows us to calculate an effective tube diameter[36,38]. For each of the pure components, the tube diameter is ~ 40 Å. Because the correlation length of concentration fluctuations is of the same order as the tube diameter, each chain will see a very heterogeneous environment. It is conceivable that this heterogeneous environment could make time–temperature superposition fail. The question of generality of the breakdown of time–temperature superposition in miscible blends must await further studies on rheology of miscible blends of model polymers with stronger enthalpic interactions.

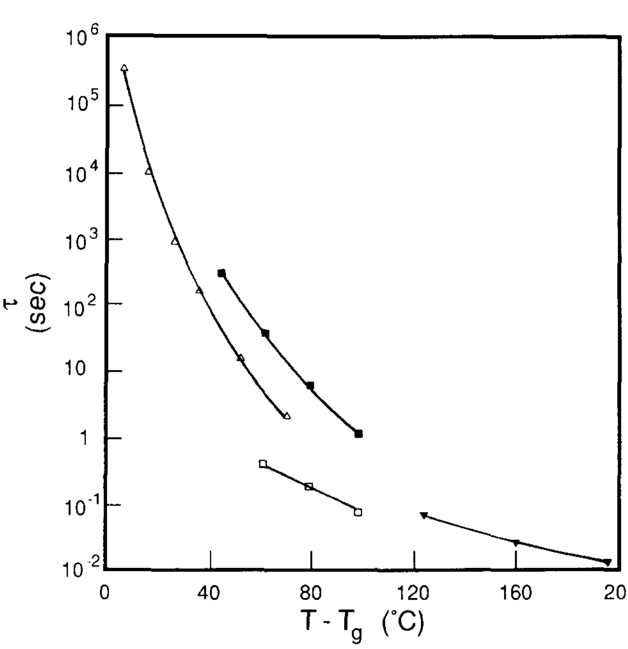

Figure 3 Temperature dependence of terminal relaxation times. △, Pure PMMA; ▲, pure PEO; ■, PMMA in the blend; □, PEO in the blend

The reported validity of time–temperature superposition for PEO/PMMA blends[7], as well as for other miscible blends[3–8], is presumably due to a combination of three factors. First of all, the WLF parameters C_1 and C_2 are generally quite similar for different polymers[2]. If these parameters were exactly the same for the two components in a blend, time–temperature superposition would be valid. If the WLF parameters are nearly the same for the two components, time–temperature superposition might work within experimental error over a relatively narrow frequency range. Past workers have used considerably narrower ranges of frequency because they assumed time–temperature superposition did work, and thus were not trying to test it *per se*. Also, past workers made their blends with polydisperse components. Polydispersity of the pure components acts to smear out the oscillatory response because the low molecular weight species will dominate the relaxations in the rubbery plateau. As a result, $G^*(\omega)$ is relatively featureless for blends of polydisperse polymers (there are no local maxima in $G''(\omega)$ in any of the data in refs 3–8, for instance).

While the temperature dependence of rheology is described by the WLF equations of the pure components shifted to the T_g of the blend, the magnitudes of the relaxation times are not predicted so simply. *Figure 3* shows the dependence of terminal relaxation time on $T-T_g$ for the pure components and the blend. The PMMA relaxes slower in the blend than in pure PMMA (at the same $T-T_g$), while the PEO relaxes faster in the blend. The discrepancy in the relaxation times of PEO may be due to our uncertainty in the T_g of pure PEO. A shift in the glass temperature of PEO to higher temperatures (by $\sim 10°C$) would bring the relaxation times of pure PEO and blended PEO into good agreement. However, there is a real difference in the relaxation times of the pure PMMA and the blended PMMA. The PMMA in the blend takes longer to relax at the same $T-T_g$, and this represents new physics which has yet to be explained.

An individual friction factor for each component in a blend would at least partly explain the tracer diffusion coefficient data reported by Composto *et al.*[39,40] on polystyrene poly(2,6-dimethyl 1,4-phenylene oxide) blends, which show polystyrene ($M = 255\,000$) diffusing more than an order of magnitude faster than PPO ($M = 35\,000$) for blends rich in PPO. Details of both the temperature and composition dependence of the terminal relaxation times are needed in order to develop a better understanding of diffusion and rheology of miscible polymer blends.

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REFERENCES

1 Kaplan, D. and Tschoegl, N. W. *Polym. Eng. Sci.* 1974, **14**, 43

2 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn, Wiley, New York (1980)

3 Prest, W. M. and Porter, R. S. *J. Polym. Sci. Part A-2* 1972, **10**, 1639

4 Wisniewsky, C., Marin, G. and Monge, P. *Eur. Polym. J.* 1984, **20**, 691

5 Brekner, M.-J., Cantow, H.-J. and Schneider, H. A. *Polym. Bull.* 1985, **14**, 17

6 Wu, S. *J. Polym. Sci., Polym. Phys. Edn.* 1987, **25**, 557

7 Wu, S. *J. Polym. Sci., Polym. Phys. Edn.* 1987, **25**, 2511

8 Roland, C. M. *J. Polym. Sci., Polym. Phys. Edn.* 1988, **26**, 839

9 Hoffman, D. M. *PhD Thesis*, University of Massachusetts, 1979

10 Li, X. and Hsu, S. L. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 1331

11 Liberman, S. A., Gomes, A. de S. and Macchi, E. M. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 2809

12 Fernandes, A. C., Barlow, J. W. and Paul, D. R. *J. Appl. Polym. Sci.* 1986, **32**, 5481

13 Cortazar, M. M., Calahorra, M. E. and Guzman, G. M. *Eur. Polym. J.* 1982, **18**, 165

14 Martuscelli, E., Pracella, M. and Yue, W. P. *Polymer* 1984, **25**, 1097

15 Martuscelli, E., Silvestre, C., Addonizio, M. L. and Amelino, L. *Makromol Chem.* 1986, **187**, 1557

16 Calahorra, E., Cortazar, M. and Guzman, G. M. *Polymer* 1982, **23**, 1322

17 Martuscelli, E., Demma, G., Rossi, E. and Segre, A. L. *Polym. Commun.* 1983, **24**, 266

18 Elorza, J. M., Fdz-Berridi, M. J., Iruin, J. J. and Guzman, G. M. *Polym. Eng. Sci.* 1984, **24**, 287

19 Lefebvre, J.-M. R., Porter, R. S. and Wignall, G. D. *Polym. Eng. Sci.* 1987, **27**, 433

20 Russell, T. P., Ito, H. and Wignall, G. D. *Mater. Res. Soc. Symp. Proc.* 1987, **79**, 87

21 Ito, H., Russell, T. P. and Wignall, G. D. *Macromolecules* 1987, **20**, 2213

22 Russell, T. P., Ito, H. and Wignall, G. D. *Macromolecules* 1988, **21**, 1703

23 Ramana Rao, G., Castiglioni, C., Gussoni, M., Zerbi, G. and Martuscelli, E. *Polymer* 1985, **26**, 811

24 Fernandes, A. C. *PhD Thesis*, University of Texas, 1986

25 Min, K. E., Chiou, J. S., Barlow, J. W. and Paul, D. R. *Polymer* 1987, **28**, 1721

26 Long, T. E. *PhD Thesis*, Virginia Polytechnic Institute, 1987

27 Cimmino, S., Martuscelli, E. and Silvestre, C. *J. Calorimetry* 1986, **17**, 188

28 Silvestre, C., Cimmino, S., Martuscelli, E., Karasz, F. E. and MacKnight, W. J. *Polymer* 1987, **28**, 1190

29 Plazek, D. J., Tan, V. and O'Rourke, V. M. *Rheol. Acta* 1974, **13**, 367

30 Plazek, D. J. and Raghupathi, N. *Polym. Preprints* 1974, **15**, 53

31 Plazek, D. J. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 729

32 Yin, T. P., Lovell, S. E. and Ferry, J. D. *J. Phys. Chem.* 1961, **65**, 534

33 Teramoto, A. and Fujita, H. *Makromol. Chem.* 1965, **85**, 261

34 Colby, R. H. in 'Tenth International Congress on Rheology' (Ed. P. H. T. Uhlherr), Australian Society of Rheology, Sydney, Australia, 1988, **1**, 278

35 Brandrup, J. and Immergut, E. H. (Eds), 'Polymer Handbook', 2nd Edn, Wiley, New York (1975)

36 Doi, M. and Edwards, S. F. 'The Theory of Polymer Dynamics', Clarendon Press, Oxford (1986)

37 deGennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca (1979), p. 110

38 Graessley, W. W. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 27

39 Composto, R. J., Mayer, J. W., Kramer, E. J. and White, D. M. *Phys. Rev. Lett.* 1986, **57**, 1312

40 Composto, R. J., Kramer, E. J. and White, D. M. *Macromolecules* 1988, **21**, 2580