TIME-TEMPERATURE SUPERPOSITION FOR POLYMERIC BLENDS

Marnix van Gurp and Jo Palmen
DSM Research
PO. Box 18
6160 MD Geleen, The Netherlands

INTRODUCTION

Time-temperature superposition (TTS, also frequency-temperature superposition or the method of reduced variables) is a well-known procedure frequently applied, either to determine the temperature dependence of the rheological behavior of a polymeric liquid or to expand the time or frequency regime at a given temperature at which the material behavior is studied. For elementary models of polymers under deformation, it is not too difficult to show that the principle is indeed valid [1]. This is due to the fact that the various relaxation times belonging to a given relaxation process have the same temperature dependence. For example, the modified Rouse model has a relaxation spectrum:

$$G_i = \frac{\rho RT}{M} \qquad \tau_i = \frac{6M\eta_0}{\pi^2 i^2 \rho RT} = \frac{\tau_1}{i^2}$$

in which all G_i and all τ_i have the same temperature dependence. If we now define shift factors

$$a_T = \frac{\tau_i(T)}{\tau_i(T_0)} \quad \text{and} \quad b_T = \frac{G_i(T)}{G_i(T_0)}, \text{ we will find}$$

$$G'(\omega) = b_T \Sigma G_i(T_0) \frac{(\omega a_T)^2 \tau_i^2(T_0)}{1+(\omega a_T)^2 \tau_i^2(T_0)}$$

so that $G'(\omega)/b_T$ and similarly $G''(\omega)/b_T, G_d(\omega)/b_T$, and $\delta = \text{atan}(G''/G')$ as a function of (wa_T) yield temperature independent curves. Note that the product of the horizontal and vertical shift factors equals the shift factor determined from the zero shear viscosity:

$$a_T b_T = \frac{\eta_0(T)}{\eta_0(T_0)}$$

According to Ferry 'ITS holds when: (i) exact matching of shapes of adjacent (time or frequency dependent) curves is obtained; (ii) a_T has the same value for all viscoelastic functions; (iii) the temperature dependence of a_T has a reasonable form (WLF, Arrhenius).

In practice, however, many reasons why the principle should fail are conceivable, like the occurrence of more than one relaxation mechanisms with distinct temperature dependences [2]. For example, in the vicinity of the glass transition temperature both energetically and entropically induced relaxations play a role, and in general TTS will not hold. Obviously, materials which change (chemically or physically) during the rheological measurement will not obey TTS.

In the case of inhomogeneous polymeric materials, in particular polymeric blends, the different components of the material will in general display a different temperature-dependent rheology, so that TTS will not hold for blends. Surprisingly, for many blends the principle is still reported to hold [3], see also Table 1. The question arises why this is the case. Furthermore, if indeed TTS fails, further inspection of this failure might give information on specific interactions present in the inhomogeneous system.

Table 1:

	TTS holds	TTS fails
Miscible	**PS/PVME [1,25,26]** **SAN/SMA [2, own]** **SAN/PCL [30]** **PMMA/PVDF [2,3]** **PPO/PS [2,4,5,3 1]** **sPS/mPA2,10 [29]** **PS/PCHMA [32]**	**PEO/PMMA [21,27,own]** **1,2PB/PIP [18-20,28]**
Immiscible	ABS **[6,7,** own] **SB/PB [14]** **PS/PC [9,10]** **HDPE/LDPE [11]** **LLDPE/LDPE** [own] **PA6/EVA [2]** PS-co-SSA/PEA-co-VP **[12]** **PS/PB [8]** **PE/PP [13,own]** **PP/EVA [23]**	**PS/PMMA [22]** **PS/LDPE** [own] **PE/EVA [15]** **PS/PEA [12]** **SAN/PMMA** [own]

1. Stadler et al. Polymer 29, 1643 (1988), 2. Han & Chuang, JAPS 30, 4431 (1985), 3. Wu, JPS:B:PP 25,557 (1987), 4. Prest & Porter, JPS A2 10, 1639 (1972), 5. Schmidt, JAPS 23, 2469 (1979), 6. Aoki, J. Soc. Rheol. Jpn. 7, 20 (1979), 7. Masuda et al. Pure & Appl. Chem. 56, 1457 (1984), 8. Wang & Lee, JAPS 33,431 (1987), 9. Wisniewski et al. Eur. Polym. J. 21,479 (1985), 10. Lipatov et al. JAPS 26,499 (1981), 11. Curto et al. Rheol. Acta 22,197 (1983), 12. Bazuin & Eisenberg, JPS:B:PP 24, 1021 (1986), 13. Alle & Lyngaae-Jorgensen, Rheol. Acta 19, 94 (1980), 14. Watanabe & Kotake, Mcromol. 16,769 (1983), 15. Fujimura & Iwakura, Kobunshi Ronb., Eng. Ed. 3 1864 (1974), 16. Yanovski, Chem. Eng. Comm. 32,219 (1984), 17. Cavaille et al. JPS:B:PP 25, 1847 (1987), 18. Kannan & Komfield, J. Rheol. 38, 1127 (1994), 19. Zawada et al. Macromol. 27, 6861 (1994), 20. Roovers & Toporowski, Macromol. 25, 3454 (1992), 21. Colby, Xth Int. Congr. Rheol. p 278 (1988), 22. Han & Rim, Polymer 34, 2533 (1993), 23. Cassagneau et al. JAPS 58, 1393 (1995), 24. Zom et al. Macromol. 28, 8552 (1995), 25. Ajji et al. JPS:B:PP 29, 1573 (1991), 26. Mani et al. J. Rheol. 36, 1625 (1992), 27. Colby, Polymer 30, 1275 (1989), 28. Arendt et al. Rheol. Acta 33,322 (1994), 30. Han & Yuang, JAPS 33, 1199 (1987), 3 1. Stadler & De Araujo, Makromol. Chem. Macromol. Symp. 38,243 (1990), 32. Friedrich et al. Polymer 37, 2499 (1996).

HOMOGENEOUS BLENDS

Homogeneous polymeric materials with a distribution of chain lengths are the simplest class of blends to consider. In general, the chain length will not influence the relaxation mechanism, and in practice no influence of chain length on the activation energy is found. Branched polymers are a separate class, since they may be considered as blends of polymers with various amounts of branching. In most cases more branching is found for longer chains, while in addition the longest chains are responsible for the longest relaxation times. Since branching does affect the temperature sensitivity of the rheology [4], an inhomogeneous branching distribution may cause failure of the TTS principle. LDPE for example needs a considerable vertical shift in the superposition procedure (in steady shear this can equally well be explained by a stress-dependent activation energy) and TTS is sometimes slightly violated. A more pronounced example of this effect is branched EPDM. Figure 1 shows the master curves of the storage and loss moduli G' and G" of a long chain branched EPDM as a function of the reduced angular frequency **ω** at 125 *°C*. In addition we have plotted the phase angle **δ** = atan(G"/G') versus the absolute value of the complex modulus. This way of plotting eliminates the effect of shifting along the frequency axis, and yields temperature independent curves when ITS holds. Furthermore, direct insight into the amount of a resulting vertical shift (here along the G_d -axis) is readily observed, which cannot be seen from a G'-G" plot. Therefore, failure of TTS can conveniently be read from the plot. Indeed, failure of TTS is clear for this example of a long-chained branched EPDM.

Interestingly, in some cases, e.g. for materials in which branching is introduced by peroxide or electron beam irradiation, it is possible to shift the long times side of the relaxation time spectrum using one activation energy (related to the branched polymer) and the other side with a lower activation energy (the linear components).

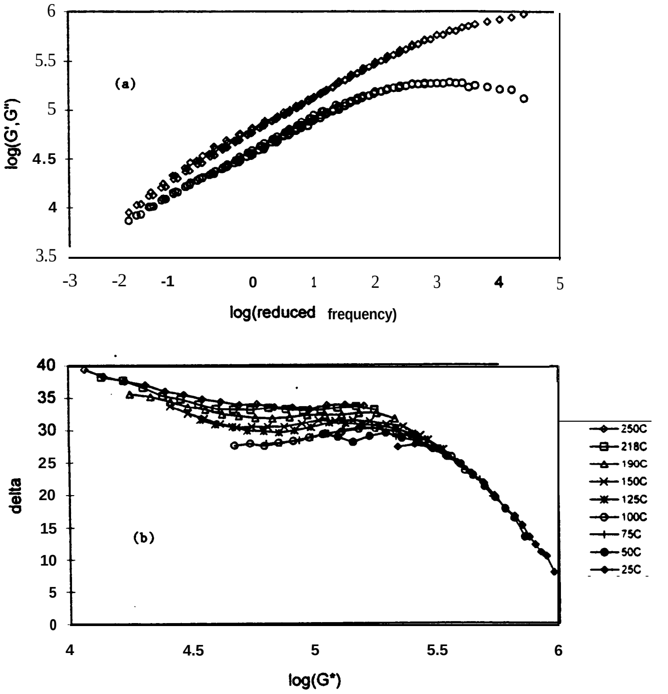

Figure 1 Dynamic mechanical results of a long chain branched EPDM. a) Storage and loss moduli as a function of reduced angular frequency at a reference temperature of 125 °C . b) Phase angle as a function of dynamic modulus at various temperatures.

MISCIBLE BLENDS

Until the end of the 1980's it was thought that for miscible blends of chemically differing polymers the dynamics of the two components would have the same temperature dependence [5], due to their intimate mixing. However, measurements on PEO/PMMA blends, assumed to be miscible, showed a clear failure of the TTS principle [6]. It was suggested that the components retain their own temperature sensitivity in the blend due to heterogeneities on a very small scale, while the local dynamics may be influenced by each component's surroundings [7]. When strong interactions between components play a role, it is thought that the strong coupling may result in one single temperature dependence [8]. Obviously, when the temperature sensitivities of both components are comparable (close T_g 's), TTS will also hold. The occurrence of local heterogeneities, and therefore failure of TTS, is reported to be very sensitive to the difference in glass temperature of the blend components [9]. Interestingly, a miscible SAN-SMA blend with ΔT_g =47 °C , seems to obey TTS quite well, see Figure 2.

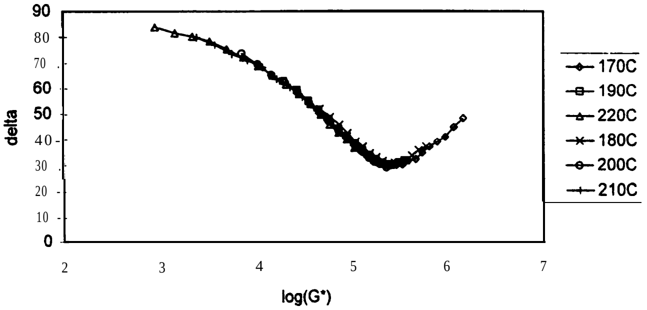

Figure 2 Phase angle as a function of dynamic modulus for a 40:60 SAN/SMA blend at various temperatures.

IMMISCIBLE BLENDS

In principle, immiscible blends will not obey TTS due to the different temperature dependencies of both components. Surprisingly, however, for many blends successful application of TTS is reported, see Table 1. The simplest reason may be that the activation energies or WLF parameters .of the components are not too far apart. On the other hand, the experimental accuracy with which a measurement is performed may well be a factor affecting the decision whether or not TTS is thought to hold. It should be realized that in many cases the only criterion is the visual inspection of the experimental results on a certain (most often logarithmic) scale. Consequently, the same blend may be found to obey TTS on the basis of capillary measurements while it fails if dynamic mechanical results are used. Furthermore, measurements at large deformations like capillary experiments are suspect due to the fact that the blend morphology may change during flow.

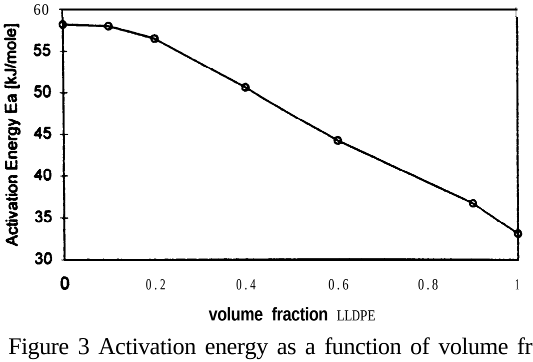

Figure 3 Activation energy as a function of volume fraction LLDPE in a LDPE/LLDPE blend.

Even if activation energies of the two components in the blend are different, failure of TTS may be subtle and therefore experimentally unseen, e.g. when the contribution of one of the two components to the measured stress signal is small. This may be due either to small volume fractions or low viscosity of one of the components, or to the fact that the relaxation of one of the components falls outside the experimental time regime. Furthermore, broad molar mass distributions yield structureless dynamic spectra, which may in practice result in successful application of TTS. In the latter case, it is possible to find the activation energy of the blend using a simple mixing rule, see Figure 3. The subtleness of failure of TTS is illustrated in Figure 4, where the phase angle δ is plotted versus G_d for a 40:60 LDPE/LLDPE blend at three different temperatures. The experimental symbols indicate that within small scatter TTS seems to hold, while calculated curves at the three different temperatures using a simple log additive blending rule indicates failure (i.e. the three drawn curves do not superpose). Interestingly, although the activation energies of LDPE and LLDPE are differing by about a factor of two, the calculated curves almost perfectly superpose between moduli of 10^4 and 10^5 Pa. Obviously, the arguments to explain the successful application of 'ITS in practice to immiscible blends are equally well applicable to miscible blends. In fact, a nice example is the 1,2-PB/PI system, for which TTS is reported to hold **[10]** and -- after close inspection-- to fail [7,11].

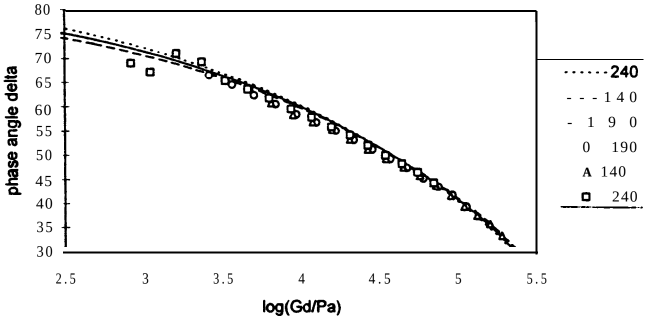

Figure 4 Phase angle as a function of dynamic modulus for a 40:60 LDPE/LLDPE blend at three different temperatures. Symbols indicate experimental results, drawn lines are calculations based on a log-additive mixing rule applied to the two components.

Interfacial effects can be seen as a relaxation mechanism with its own temperature dependence and therefore accountable for the failure of TTS. Figure 5 shows results of dynamic mechanical measurements on a PE/PS blend at various temperatures. Failure is apparent, in particular at reduced temperatures where the effect of interfacial tension is more pronounced. Blends undergoing a phase transition upon a change of temperature will, in principle, not obey the TTS principle [12]. Here the physical microstructure of the material changes with temperature.

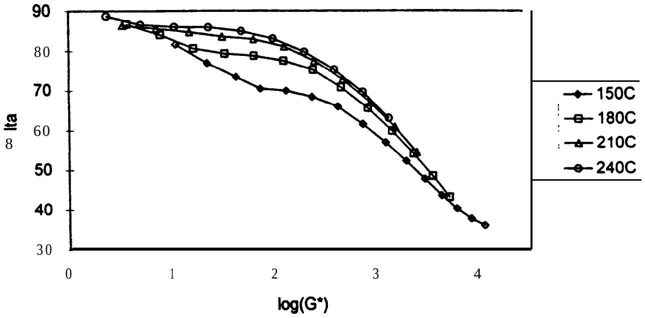

Figure Phase angle versus complex modulus for a 20:80 blend at various temperatures.

TTS AS AN INDICATOR

In many cases, rheology (in particular dynamic spectra at various temperatures) can be used as an indicator of molecular structure. The most obvious example is the relation set up between molar mass distribution and the relaxation time spectrum. Furthermore, the activation energy may be used as an indicator of the type of material [13] or the amount of branching [14]. Also, the vertical shift factors may yield information on chain stiffness, or branching, although not much work has been devoted to these relations.

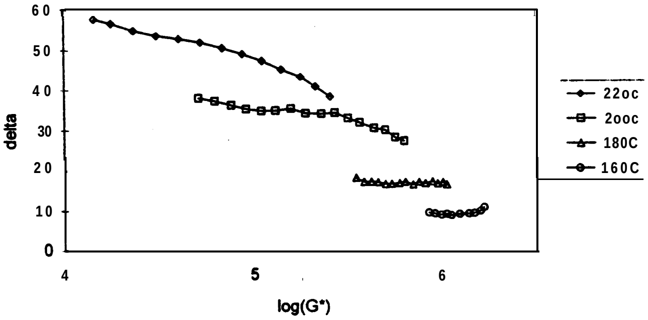

Figure 6 Phase angle as a function of dynamic modulus for PVC at different temperatures.

Failure of TTS may now be an indication of several things:
1. The most trivial of these is thermal instability of the material at elevated temperatures. This can simply be checked by performing time-dependent measurements, since in most cases kinetics will play a role. Furthermore, physical changes may take place in the vicinity of a phase transition. These are, however, reversible. A nice example is PVC in which it takes very long for all microcrystals to vanish at elevated temperatures, see Figure 6.
2. A priori it is expected that application of TTS fails in the case of blends. It is not too difficult to apply a blend rule to the dynamic spectra of both components of the blend and check the resulting curves at various temperatures. This is indeed illustrative, since this reveals if the extent of failure agrees with the experimental results, or, alternatively, that TTS is strictly speaking not applicable, but only to such a minor extent that the experimental results are superposable.

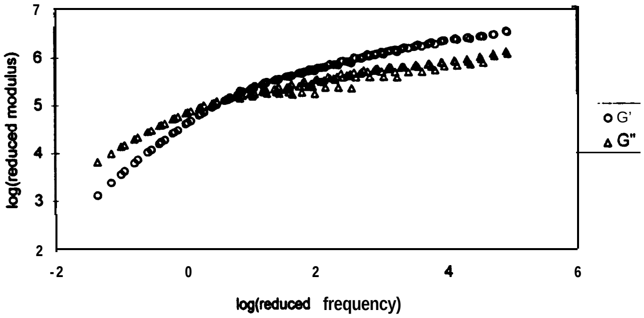

Figure 7 Storage and loss modulus of a 35:65 PEO/PMMA blend at a reference temperature of 190 °C, measured at 70,90,110, 130, 150, 170,190 and 210 °C.

3. In some cases other temperature-dependent phenomena may be anticipated, like the influence of interfacial stresses, e.g. to be calculated using Palierne's model, or the effect of an equilibrium modulus, which can simply be subtracted before the shifting procedure [15]. Interestingly, both effects are purely elastic, and therefore appear to show up predominantly in the storage modulus. Shifting of both G' and G" may now be used to have an indication of the existence of either additional elastic or frictional forces. Figure 7 shows a 3565 PEO/PMMA blend, where the shifting of G' seems to be reasonable, while G" is not shiftable. Although, in principle, G' and G" are related according to the Kramers-Kronig relations, one might argue that in this case mostly local frictional interactions influence the temperature-dependent dynamics.

REFERENCES

1. J.D. Ferry, Viscoelastic Properties of Polymers, Wiley, New York, 1980.
2. D.J. Plazek, J. Rheol. **40**, 987 (1996).
3. L.A. Utracki, Polymer Alloys and Blends, Hanser, Munich, 1989.
4. W.W. Graessley, Macromol. **15**, 1164 (1982).
5. C. Tsenoglou in: New Trends in Physics and Physical Chemistry of Polymers, L.-H. Lee (ed.), Plenum Press, New York, 1989, pp 375-383.
6. R.H. Colby, Polymer **30**, 1275 (1989).
7. B.H. Arendt, R.M. Kannan, M. Zewail, J.A. Komfield, and S.D. Smith, Rheol. Acta **33**, 322 (1994).
8. R. Hagen and R.A. Weiss, Polymer **36**, 4657 (1995).
9. S.K. Kumar, R.H. Colby, S.H. Anastasiadis, and G. Fytas, J. Chem. Phys. **105**, 3777 (1996).
ld. C.M. Roland, J. Polym. Sci., Part B **26**, 839 (1988).
11. J. Roovers and PM. Toporowski, Macromol. **25**, 3454 (1992).
12. S. Mani, M.F. Malone and H.H. Winter, J. Rheol. **36**, 1625 (1992).
13. R.S. Porter, H.H. Chuah and J.-S. Wang, J. Rheol. **39**, 649 (1995).
14. B.H. Bersted, J. Appl. Polym. Sci. **30**, 375 1 (1985).
15. B.J.R. Scholtens, J. Polym. Sci., Part B **22**, 317 (1984).