On the use of time–temperature superposition in multicomponent/multiphase polymer systems

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In view of the fact that log G' *versus* log G'' plots for homogeneous polymer systems are virtually independent of temperature, we have suggested that before attempting to apply time–temperature superposition to multicomponent and/or multiphase polymer systems, one must first observe whether or not plots of log G' *versus* log G'' show temperature independence. We have demonstrated that log G' *versus* log G'' plots are very sensitive to a variation in the morphological state of multicomponent/multiphase polymer systems (e.g. immiscible polymer blends, microphase-separated block copolymers, liquid crystalline polymers). We have pointed out that whereas the so-called Cole–Cole plot is strictly an empirical correlation, plots of log G' *versus* log G'' have a basis of molecular viscoelasticity theory and thus the two are *not* related to each other.

(Keywords: time–temperature superposition; compatible polymer blends; block copolymers; liquid-crystalline polymers)

INTRODUCTION

Time–temperature superposition has long been used to obtain temperature-independent master curves for polymer systems by shifting values of steady-state shear viscosity (η) along the shear rate ($\dot{\gamma}$) axis or by shifting values of dynamic storage modulus (G') and/or dynamic loss modulus (G'') along the frequency (ω) axis. Here, one chooses a reference temperature and shifts the rheological properties of interest, which were obtained at other temperatures, to the corresponding values at that temperature. There is a shift factor, a_T, which is a function of temperature, that enables one to obtain these master curves (i.e. $\log \eta_r$ *versus* $\log \dot{\gamma} a_T$, $\log G'_r$ *versus* $\log \omega a_T$, and $\log G''_r$ *versus* $\log \omega a_T$ plots, where $\eta_r = \eta \rho_0 T_0 / a_T \rho T$, $G'_r = G' \rho_0 T_0 / \rho T$, and $G''_r = G'' \rho_0 T_0 / \rho T$ in which the subscript 0 denotes a reference state). Using the Williams–Landel–Ferry (WLF) equation, one can relate the shift factor a_T to the glass transition temperature (T_g) of a polymer and two constants, C_1 and C_2, which have been found to be characteristic of the polymer's molecular structure[1].

It should be pointed out that the use of time–temperature superposition is meaningful as long as the morphology of the polymer remains the same over the temperature range of interest, thus it has been used primarily for homopolymers. However, in recent years time–temperature superposition has been applied to compatible polymer blends[2–7], where compatibility was judged on the basis of a single T_g, to microphase-separated block copolymers[8–13], and also to thermotropic liquid-crystalline polymers[14]. It should be mentioned that there is *no* theoretical guideline as to how the values of a_T for compatible polymer blends (multiphase polymer systems in general) may be obtained from the WLF equation. Thus, the values of a_T for compatible polymer blends are usually obtained by shifting the values of G' (or G'') along the frequency ω axis.

Han and coworkers[15–19] favour the use of $\log G'$ *versus* $\log G''$ plots over $\log G'_r$ (or $\log G''_r$) *versus* $\log \omega a_T$ plots in obtaining temperature-independent correlations for polymer systems. The purpose of this paper is to point out some advantages of using $\log G'$ *versus* $\log G''$ plots over $\log G'_r$ (or $\log G''_r$) *versus* $\log \omega a_T$ plots for multicomponent/multiphase polymer systems.

BACKGROUND

Han and Jhon[17] have shown, using the tube model of Doi and Edwards[20], that in the terminal region (where $\omega \tau_d \ll 1$ holds, τ_d being the tube disengagement time) of linear, flexible, *entangled* monodisperse homopolymers, the following expression†:

$$\log G' = 2 \log G'' + \log (6/5G_N^\circ) \tag{1}$$

holds where G_N° is the plateau modulus. Notice that G_N° is related to temperature through the relationship[1,21,22]:

$$G_N^\circ = \rho R T / M_e \tag{2}$$

where ρ is the density, R is the universal gas constant, T is the absolute temperature and M_e is the entanglement molecular weight. Substitution of equation (2) into equation (1) gives:

$$\log G' = 2 \log G'' + \log (6M_e/5\rho R T) \tag{3}$$

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†This expression is for all odd values of p, whereas ref. 15 presented an expression for $p = 1$

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indicating that plots of $\log G'$ *versus* $\log G''$ are independent of molecular weight and virtually independent of (or very weakly dependent upon) temperature. For linear, flexible, *unentangled* monodisperse homopolymers, using the Rouse model[23] the following expression can be obtained:

$$\log G' = 2\log G'' + \log(5M/4\rho RT) \qquad (4)$$

where M is the molecular weight. Equation (4) indicates that for *unentangled* homopolymers, $\log G'$ *versus* $\log G''$ plots are dependent upon molecular weight and virtually independent of (or very weakly dependent upon) temperature.

Note in equation (3) that an increase in temperature from T_1 to T_2 will shift the value of $\log G'$ by the amount $\log(\rho_1 T_1/\rho_2 T_2)$, which may not be noticeable in $\log G'$ *versus* $\log G''$ plots. Note that the density is inversely proportional to temperature. To illustrate the point, *Figure 1* gives plots of $\log G'$ *versus* $\log G''$ for a nearly monodisperse polystyrene (PS), having a weight-average molecular weight (M_w) of 1.95×10^5 and a polydispersity (M_w/M_n) of 1.07, at various temperatures ranging from 160 to 230°C (ref. 24). Indeed the temperature dependency of $\log G'$ *versus* $\log G''$ plots is not discernible in *Figure 1*, as equation (3) suggests. Earlier, similar observations were made by Han and coworkers[15–19].

For *polydisperse* polymers, assuming that the log normal distribution function represents the molecular distribution of a polymer and that the relaxation modulus of the polymer is expressed by the 3.4-power law in terms of the constituent fractions, it can be shown that the following expression[24]:

$$\log G' = 2\log G' + \log(6/5G_N^\circ) + 3.4\log(M_z/M_w) \qquad (5)$$

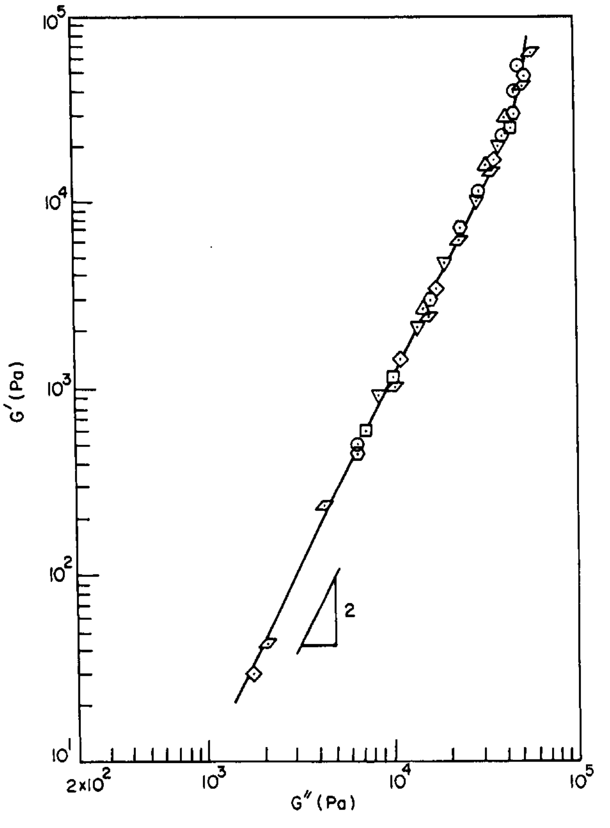

Figure 1 Plots of $\log G'$ *versus* $\log G''$ for a nearly monodisperse polystyrene having a weight-average molecular weight of 1.95×10^5 and polydispersity of 1.07 at various temperatures (°C)[24]: ⊙, 160; ◬, 170; ⊡, 180; ▽, 200; ⟐, 210; ⬡, 220; ▱, 230

holds, where M_z and M_w are z-average and weight-average molecular weights, respectively. Notice that equations (1) and (5) indicate that in the terminal region the slope of $\log G'$ *versus* $\log G''$ plots is 2 for both monodisperse and polydisperse polymers, and that the values of G' will be shifted upward by the amount $3.4\log(M_z/M_w)$ above the values of G' for monodisperse polymers; thus, the shift will be greater with increasing polydispersity, M_z/M_w.

In the linear region (where $0 < \omega\tau_d \approx 1$) of flexible, entangled polydisperse polymers, Han and Kim[25] obtained the expression:

$$\log G' = x\log G'' + (1-x)\log(8G_N^\circ/\pi^2) \qquad (6)$$

where $1 < x < 2$, indicating that the slope of $\log G'$ *versus* $\log G''$ plots is less than 2.

It is appropriate to mention at this juncture that using the ordinary coordinate system, in 1941 Cole and Cole[26] plotted the imaginary part ε'' of the complex dielectric constant against the real part ε' for a number of polar materials at various temperatures. The so-called Cole–Cole plots fall on a circular arc; a different arc is obtained for each temperature, with the shape of the circular arc *varying* with temperature. In the past, some investigators[27–29] applied Cole–Cole plots to interpret dynamic mechanical properties of polymeric materials in the solid state.

In 1983 Han and Lem[15] first reported that plots of $\log G'$ *versus* $\log G''$ are virtually independent of temperature for viscoelastic homopolymers. Having made a similar observation, in 1984 Harell and Nakajima[30] called $\log G'$ *versus* $\log G''$ plots 'modified' Cole–Cole plots. It should be pointed out that the Cole–Cole plot is strictly an empirical correlation, whereas $\log G'$ *versus* $\log G''$ plots have the basis of a molecular viscoelasticity theory, described by equations (1)–(6). It should be pointed out that plots of $\log G'$ *versus* $\log G''$ for polymeric liquids have *no* relation with an empirical correlation, Cole–Cole plot.

BREAKDOWN OF TIME–TEMPERATURE SUPERPOSITION FOR MULTICOMPONENT AND/OR MULTIPHASE POLYMER SYSTEMS

It has been amply demonstrated in the literature[31,32] that the rheological properties of an immiscible polymer blend depend very much on its morphological state, which in turn is determined by, among many factors, the rheological properties of the constituent components, the type and the intensity of flow field applied, and interfacial tension. Thus one would expect time–temperature superposition to break down in immiscible polymer blends, forming liquid–liquid (e.g. dispersed two-phase or cocontinuous two-phase) mixtures.

Figure 2 gives $\log G'$ *versus* $\log G''$ plots for a 30/70 PS/poly(methyl methacrylate) (PMMA) blend at 210, 220 and 230°C. Surprisingly the plots of $\log G'$ *versus* $\log G''$ given in *Figure 2* show little or no discernible temperature dependence. This seemingly peculiar observation can be explained by the fact that the temperatures (200–230°C) at which the rheological measurements were taken are very far from the critical temperature at which the mixture can form a single, homogeneous phase, and thus the morphological state of the blends changed little over the range of temperatures employed for the rheological measurements.

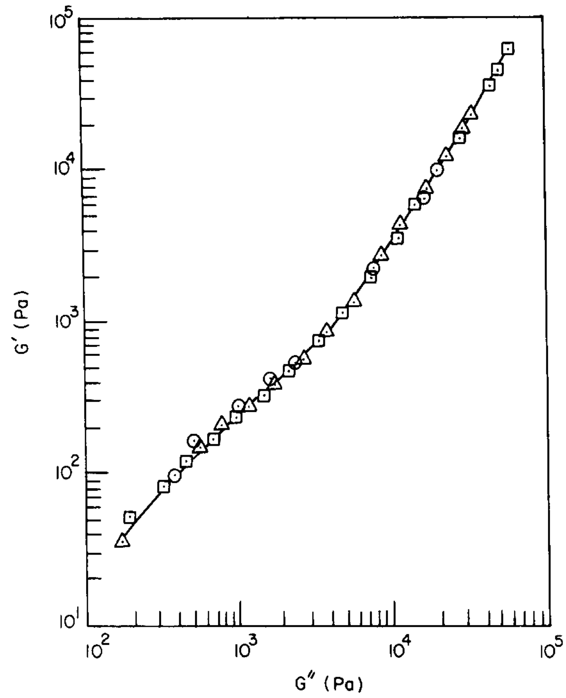

Figure 2 Plots of log G' *versus* log G'' for the 30/70 PS/PMMA blend at various temperatures (°C): ○, 210; △, 220; □, 230

An important point to be made from *Figure 2*, however, is that plots of log G' *versus* log G'' exhibit an inflection point. Note that such an inflection point in log G' *versus* log G'' plots is not observed for homopolymer systems (see *Figure 1*). Hence the temperature independence of log G' *versus* log G'' plots alone does not warrant that time–temperature superposition may be used for multicomponent and/or multiphase polymer systems. It is well known that PS/PMMA blends form dispersed two-phase mixtures. Thus, the use of time–temperature superposition with such mixtures is not valid.

Today there is general agreement among researchers that whether a polymer blend may be regarded as miscible or immiscible depends very much on the experimental techniques employed. A polymer blend is commonly regarded as miscible when it exhibits a single T_g on the basis of differential scanning calorimetry (d.s.c.) or dynamic mechanical analysis (d.m.a.). Note that the smallest size that these experimental techniques can detect is about 50 nm, meaning that the presence of microheterogeneity with sizes smaller than 50 nm in a polymer blend cannot be detected by these techniques. Thus the presence of a single T_g in a polymer blend is not sufficient to confirm that the blend is miscible on a molecular (or segmental) level.

Recently, using dynamic viscoelastic data for a blend consisting of 20.2 wt% poly(ethylene oxide) (PEO) and 79.8 wt% PMMA, hereafter referred to as the 20/80 PEO/PMMA blend, which exhibited a single T_g, Colby[33] reported that time–temperature superposition failed over a certain range of angular frequencies. Specifically, when shifting the G'' data at 120, 137 and 174°C, plotted on a rectangular coordinate, along the logarithmic ω axis to superimpose with the data at 155°C, Colby found that time–temperature superposition did not work at values of $\omega \geq 0.1$ rad s^{-1}, while it did work at values of ω between 0.001 and 0.1 rad s^{-1}. He attributed the observed failure of time–temperature superposition at $\omega \geq 0.1$ to the differences in the temperature dependence of the relaxation times (or the friction factors) of PMMA and PEO in the blend. Subsequently, Ngai and Plazek[34] offered an interpretation of Colby's experimental observation, using a theoretical coupling scheme[35].

Using data supplied by Colby, we have prepared plots of log G' *versus* log G'' for the 20/80 PEO/PMMA blend, and they are displayed in *Figure 3*. It can be seen in *Figure 3* that in the terminal region the temperature dependence is not discernible, but the log G' *versus* log G'' plot has a curvature somewhat resembling the shape of log G' *versus* log G'' plots for the 30/70 PS/PMMA blend, given in *Figure 2*. On the basis of this observation, we tentatively suspect that the 20/80 PEO/PMMA blend might have had *microheterogeneity* with sizes less than about 50 nm. The suspicion can be proven or disproven using solid-state nuclear magnetic resonance (n.m.r.) spectroscopy. In other words, the fact that log G' *versus* log G'' plots are virtually independent of temperature for a binary polymer blend, which exhibits a single value of T_g, does not warrant that time–temperature superposition should work. Below we shall elaborate on this, using the dynamic viscoelastic data for blends of PS and poly(vinyl methyl ether) (PVME) reported by Schneider and Wirbser[36].

According to Schneider and Wirbser[36], blends of PS ($M_w = 73\,500$ and $M_w/M_n = 1.08$) and PVME ($M_w = 97\,500$ and $M_w/M_n = 2.06$) had very broad, single T_gs, as shown in *Figure 4* in which the arrow pointing upward denotes the temperature at which the glass transition begins and the arrow pointing downward denotes the temperature at which the glass transition ends. In order to facilitate the following discussion, *Figure 5* is prepared to show the dependence of T_g on blend composition for the PS/PVME blends employed, where T_{gi} denotes the onset point, T_{gm} the midpoint and T_{gf} the final point of the glass transition as determined by d.s.c. *Table 1* gives a summary of the T_{gi}, T_{gm} and T_{gf} for the PS/PVME blends. Also plotted in *Figure 5* is a turbidity curve reported by Yang *et al.*[37] who used a PVME having $M_w = 99\,000$ and

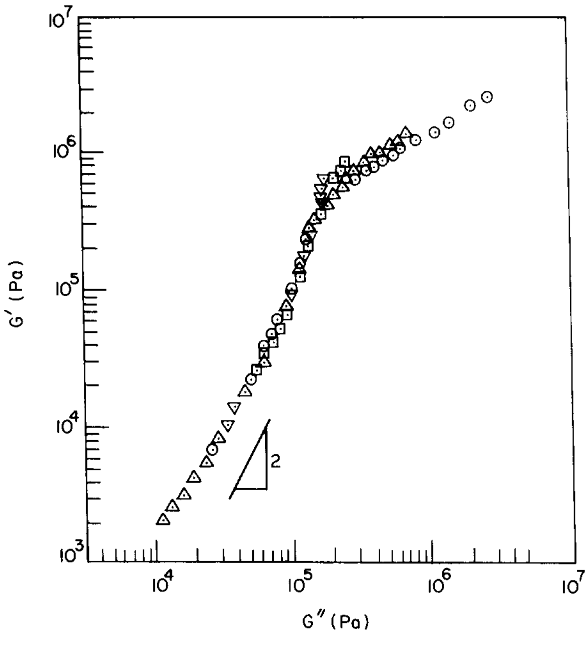

Figure 3 Plots of log G' *versus* log G'' for the 20/80 PEO/PMMA blend at various temperatures (°C): ○, 120; △, 137; □, 155; ▽, 174

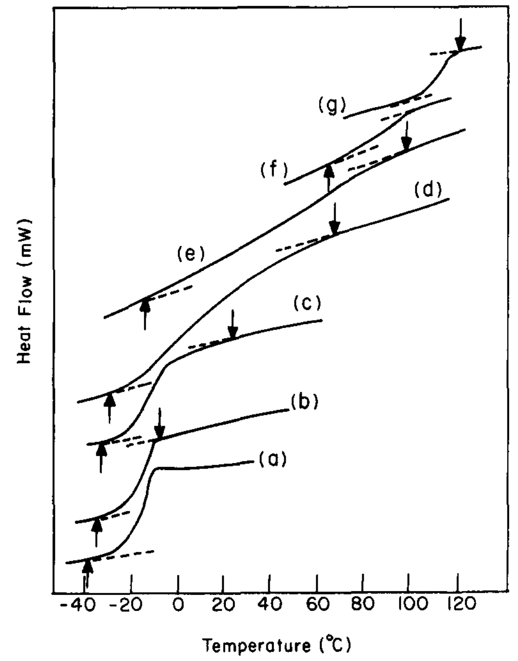

Figure 4 Traces of d.s.c. thermograms for PS/PVME blends[36]: (a) homopolymer PVME; (b) 90/10 PVME/PS blend; (c) 75/25 PVME/PS blend; (d) 50/50 PVME/PS blend; (e) 25/75 PVME/PS blend; (f) 10/90 PVME/PS blend; (g) homopolymer PS

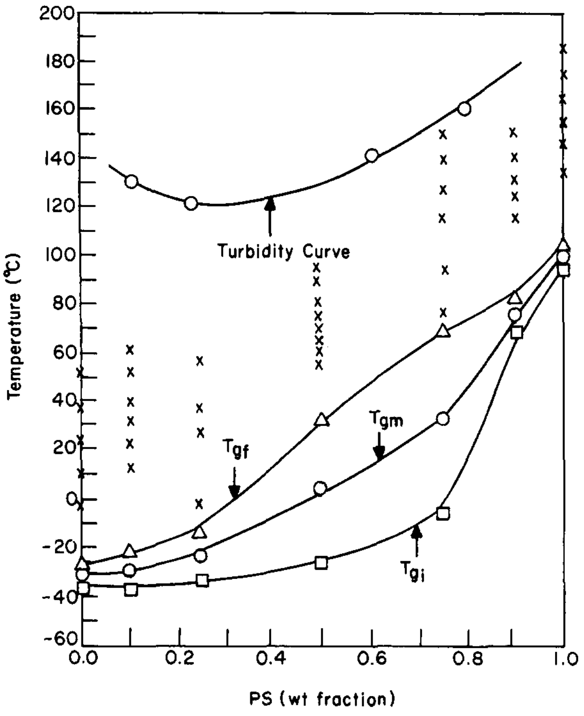

Figure 5 Composition dependence of glass transition temperature for PS/PVME blends: ×, temperatures at which oscillatory shear experiments were performed. The turbidity curve is taken from ref. 37

$M_w/M_n=2.13$ and a PS having $M_w=119000$ and $M_w/M_n=1.05$. In view of the fact that the turbidity curve depends on the molecular weights of the constituent components and that the molecular weights of the PVME and PS used for constructing the turbidity curve in *Figure 5* are slightly higher than those used for the T_g measurements, the turbidity curve is expected to be shifted slightly upward for the PS/PVME blend system used for the T_g measurements. Symbol × in *Figure 5* denotes the temperatures at which oscillatory shear measurements were reported in ref. 36. From *Figure 5* it suffices to state that all the rheological data were taken at temperatures in the single-phase region as determined by cloud point measurements.

Plots of log G' *versus* log G'' for the 50/50 PS/PVME blend are given in *Figure 6*, in which a solid line is drawn through the data points to guide the eye. Although a very weak temperature dependence of log G' *versus* log G'' plots is seen in *Figure 6*, the following observations are worth noting: (a) the slope of the log G' *versus* log G'' plot in the terminal region is much smaller than 2; and (b) an inflection point is seen in the log G' *versus* log G'' plot. Plots of log G' *versus* log G'' for the 75/25 PS/PVME blend are given in *Figure 7*, showing a rather strong temperature dependence. In *Figure 7* solid lines are drawn through the data points to guide the eye. It should be remembered that each of these two blends has a single, broad glass transition (see *Figure 4*). The quality of the correlation displayed in *Figures 6* and *7* suggests that the PS/PVME blends might *not* have been miscible at dimensions (say below 50 nm) that d.s.c. could not detect. The validity of this observation can be confirmed or disproven using solid-state n.m.r. spectroscopy. We can conclude from the above observations that the use of

Table 1 Glass transition temperatures[a] of the PVME/PS blend system investigated by Schneider and Wirbser[36]

Polymer blend	T_{gi} (°C)	T_{gm} (°C)	T_{gf} (°C)	ΔT_g (°C)
PVME	−35	−31.0	−26	9
90/10 PVME/PS	−37.6	−33.6	−22	15.6
75/25 PVME/PS	−34	−30.4	−13	21
50/50 PVME/PS	−26	−3.0	33	59
25/75 PVME/PS	−6	34.0	69	75
10/90 PVME/PS	67	74.0	84	17
PS	93	98.0	105	12

[a] T_g data extrapolated for zero heating rate

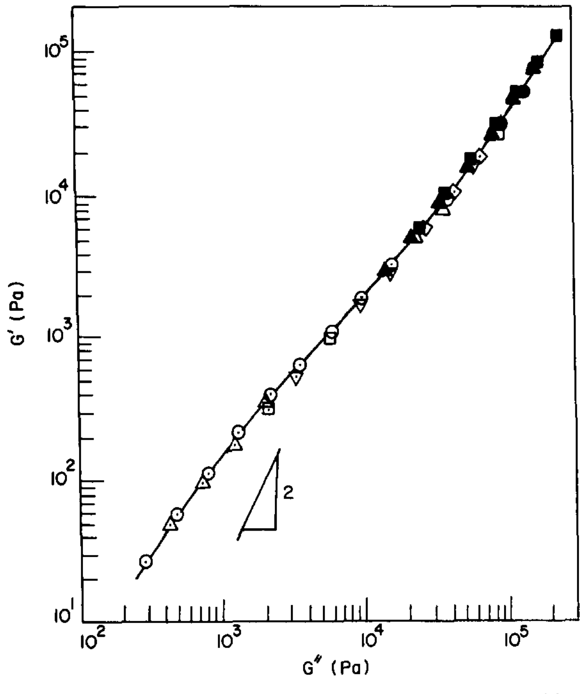

Figure 6 Plots of log G' *versus* log G'' for the 50/50 PS/PVME blend at various temperatures (°C): ○, 95; △, 90; □, 80; ▽, 75; ◇, 70; ●, 65; ▲, 60; ■, 55

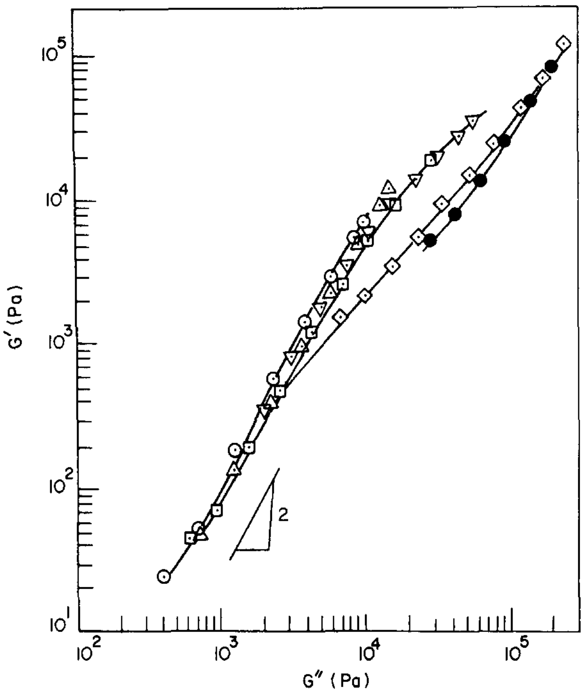

Figure 7 Plots of log G' *versus* log G'' for the 75/25 PS/PVME blend at various temperatures (°C): ○, 150; △, 140; ⊡, 127.2; ▽, 115.3; ◇, 90.1; ●, 75.2

time–temperature superposition for polymer blends, which may be judged to be miscible on the basis of T_g measurements alone, is not justifiable unless plots of log G' *versus* log G'' show temperature independence and furthermore the absence of *microheterogeneity* on a molecular level is confirmed.

It is well established today that a block copolymer forms microdomains, depending on the molecular weight, block length ratio and temperature. There exists a critical temperature, commonly referred to as an order–disorder transition (or microphase separation transition) temperature (T_r), at which a homogeneous block copolymer begins to form microdomains as the temperature is decreased or a microphase-separated block copolymer becomes homogeneous as the temperature is increased[38]. A number of investigators[8–13] have used time–temperature superposition to obtain reduced (or master) curves from dynamic viscoelastic data for microphase-separated block copolymers. As pointed out by Han and coworkers[39,40], the use of such a practice is not valid.

Let us illustrate this point by presenting in *Figure 8* the dynamic viscoelastic data for a polystyrene-*block*-polyisoprene (SI) copolymer ($M_w = 17\,870$ and $M_w/M_n = 1.07$) having equal weight fractions of polystyrene and polyisoprene blocks[41]. It can be seen in *Figure 8* that log G' *versus* log G'' plots for this block copolymer become virtually independent of temperature at 120°C and above, and the slope is very close to 2. According to the criterion presented above, this block copolymer is homogeneous at temperatures of 120°C and above, so that in this case time–temperature superposition is applicable only at 120°C and above. We thus conclude that time–temperature superposition breaks down for microphase-separated block copolymers. Han and coworkers[39,40,42] have suggested the use of log G' *versus* log G'' plots to determine the T_r of microphase-separated block copolymers.

In thermotropic liquid-crystalline polymers (TLCP), there exists a temperature, commonly referred to as the clearing (or isotropization) temperature (T_{cl}) at which an anisotropic–isotropic phase transition takes place as the temperature is increased from the anisotropic region or an isotropic–anisotropic phase transition takes place as the temperature is decreased from the isotropic region[43]. The morphology of the anisotropic phase in a TLCP can be nematic, smectic or cholesteric.

Recently, Han and Kim[44] synthesized an aromatic polyester, poly[(phenyl sulfonyl)-*p*-phenylene 1,10-decamethylene-bis(4-oxybenzoate)] (PSHQ10) having $M_w = 40\,000$ and $M_w/M_n = 1.54$, which is based on a triad ester mesogenic unit containing an arylsulfonyl-substituted hydroquinone alternated with a decamethylene spacer[45]. PSHQ10 has (a) a T_g of 88°C, (b) a normal melting temperature of 115°C, and (c) a nematic–isotropic transition temperature (T_{NI}) of 175°C. *Figure 9* gives plots of log G' *versus* log G'' for PSHQ10 at 190°C in the isotropic region and at various temperatures (below 175°C) in the nematic region. In obtaining the results displayed in *Figure 9*, a solvent-cast specimen of PSHQ10 was first heated to 190°C, subjected to steady-state shear flow at a very low shear rate ($\dot{\gamma} = 0.08\ \text{s}^{-1}$) for 4 min to ensure that all previous thermal histories associated with the specimen preparation were erased, and then cooled slowly to a predetermined temperature (130, 140, 150 or 160°C) in the nematic region before taking oscillatory shear flow measurements. A fresh specimen was used for each temperature. It is of great interest to observe in *Figure 9* that in the isotropic region (i.e. $T > 175$°C) log G' *versus* log G'' plots become independent of temperature and have a slope very close to 2, but in the nematic region (i.e. at $T < 175$°C) log G' *versus* log G'' plots depend on temperature and have a slope less than 2 in the terminal

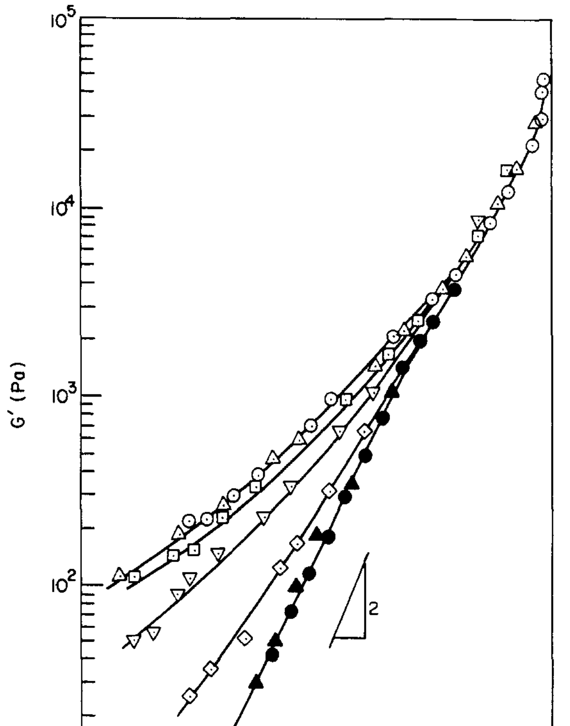

Figure 8 Plots of log G' *versus* log G'' for an SI diblock copolymer at various temperatures (°C): ○, 100; △, 105; ⊡, 110; ▽, 115; ◇, 117; ●, 120; ▲, 125

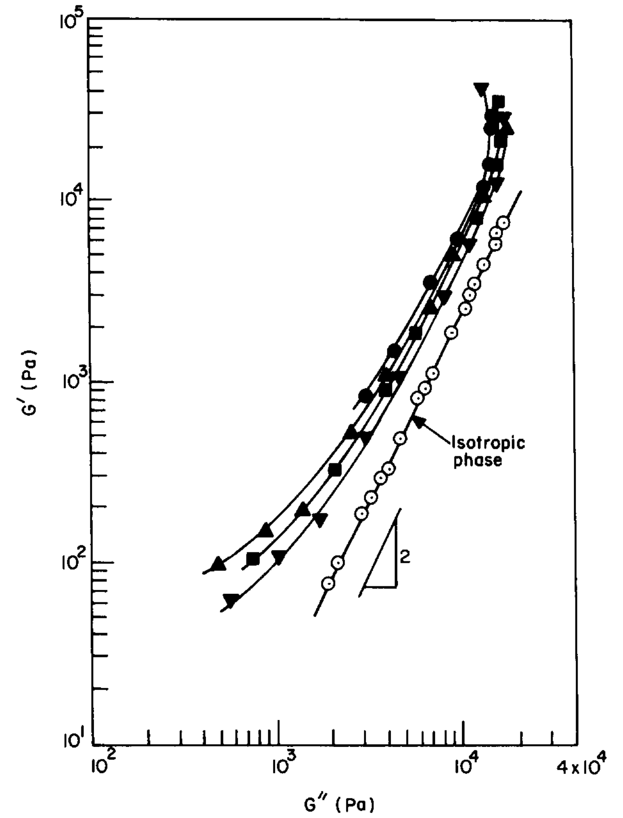

Figure 9 Plots of log G' *versus* log G'' for PSHQ10 at various temperatures. Isotropic phase at 190°C (⊙). Nematic phase at 130°C (●), 140°C (▲), 150°C (■), and 160°C (▼). Measurements in the nematic region were taken using a fresh specimen at each temperature

region. Notice in *Figure 9* that as the temperature is increased, the log G' *versus* log G'' plot approaches that for the isotropic phase, an observation very similar to that made for an SI diblock copolymer (see *Figure 8*). We thus conclude that time–temperature superposition breaks down for anisotropic liquid-crystalline polymers. The above observation suggests that the isotropic–anisotropic transition temperature (T_{NI}) of a TLCP can be determined using log G' *versus* log G'' plots.

CONCLUDING REMARKS

In this paper, we have pointed out that whereas the so-called Cole–Cole plot is strictly an empirical correlation, plots of log G' *versus* log G'' have a basis of molecular viscoelasticity theory and thus the two are *not* related to each other. We have shown further that before attempting to apply time–temperature superposition to multicomponent and/or multiphase polymer systems, one must first observe whether or not plots of log G' *versus* log G'' show temperature independence. While the use of a log G'_{r} *versus* log ωa_{T} plot enables us to determine the plateau modulus G_{N}°, the use of a log G' *versus* log G'' plot gives the following advantages: (1) it requires no data manipulation or data reduction in obtaining temperature-independent correlation; (2) for entangled homopolymers, it gives a correlation which is independent of molecular weight; (3) for multicomponent/multiphase polymer systems (e.g. microphase-separated block copolymers, liquid-crystalline polymers), it is very sensitive to a variation in the morphological state.

We have pointed out that temperature independence of log G' *versus* log G'' plots does not warrant the use of time–temperature superposition in multicomponent and/or multiphase polymer systems. This has been elaborated on for polymer blends, microphase-separated block copolymers and thermotropic liquid-crystalline polymers. We are of the opinion that when dealing with polymer blends, a criterion for compatibility solely based on a single glass transition temperature obtained from, for instance, d.s.c., may not warrant the use of time–temperature superposition, because d.s.c. cannot detect the presence of microheterogeneity in a blend with domain sizes less than about 50 nm.

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REFERENCES

1 Ferry, J. D. 'Viscoelastic Properties of Polymers' 3rd edn, Wiley, New York, 1980
2 Prest, W. M. and Porter, R. S. *J. Polym. Sci., Polym. Phys. Edn* 1972, **10**, 1639
3 Wu, S. *J. Polym. Sci., Part B: Polym. Phys.* 1987, **25**, 557, 2511
4 Wu, S. *Polymer* 1988, **28**, 1144
5 Ajii, A., Coplin, L. and Prud'homme, R. E. *J. Polym. Sci., Part B: Polym. Phys.* 1988, **26**, 2279
6 Stadler, R., Freitas, L. L., Krieger, V. and Klots, S. *Polymer* 1988, **29**, 1643
7 Roland, C. M. *J. Polym. Sci., Part B: Polym. Phys.* 1988, **26**, 839
8 Chung, C. I. and Gale, J. C. *J. Polym. Sci., Polym. Phys. Edn* 1976, **14**, 1149
9 Guinlock, E. and Porter, R. S. *Polym. Eng. Sci.* 1977, **17**, 535
10 Futamura, S. and Meinecke, E. A. *Polym. Eng. Sci.* 1977, **17**, 563
11 Widmaier, J. M. and Meyer, G. C. *J. Polym. Sci., Part B: Polym. Phys.* 1980, **18**, 2217
12 Bates, F. S. and Hartney, M. A. *Macromolecules* 1985, **18**, 2478
13 Bates, F. S., Rosedale, J. H. and Fredrickson, G. H. *J. Chem. Phys.* 1990, **92**, 6255
14 Driscoll, P., Masuda, T. and Fujiwara, K. *Macromolecules* 1991, **24**, 1567
15 Han, C. D. and Lem, K. W. *Polym. Eng. Rev.* 1983, **2**, 135
16 Chuang, H. K. and Han, C. D. *J. Appl. Polym. Sci.* 1984, **29**, 2205
17 Han, C. D. and Jhon, M. S. *J. Appl. Polym. Sci.* 1986, **32**, 3809
18 Han, C. D., Ma, Y. J. and Chu, S. G. *J. Appl. Polym. Sci.* 1986, **32**, 2478
19 Han, C. D. *J. Appl. Polym. Sci.* 1988, **37**, 167
20 Doi, M. and Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* 1978, **74**, 1802, 1818
21 Graessley, W. W. *Adv. Polym. Sci.* 1982, **47**, 67
22 Doi, M. and Edwards, S. F. 'The Theory of Polymer Dynamics', Clarendon, Oxford, 1986
23 Rouse, P. E. *J. Chem. Phys.* 1953, **21**, 1272
24 Kim, J. K. PhD Dissertation, Polytechnic University, Brooklyn, 1990
25 Han, C. D. and Kim, J. K. *Macromolecules* 1989, **22**, 4292
26 Cole, K. S. and Cole, R. H. *J. Chem. Phys.* 1941, **9**, 341
27 Nolle, A. W. *J. Polym. Sci.* 1950, **5**, 1
28 Takahashi, S. *J. Colloid. Sci.* 1954, **9**, 313
29 Kanakkanatt, S. V. *J. Cell. Plast.* 1973, **9**, 54
30 Harell, E. R. and Nakajima, N. *J. Appl. Polym. Sci.* 1984, **29**, 995
31 Han, C. D. 'Rheology in Polymer Processing, Academic Press, New York, 1976, Ch. 7
32 Han, C. D. 'Multiphase Flow in Polymer Processing', Academic Press, New York, 1981, Ch. 4
33 Colby, R. H. *Polymer* 1989, **30**, 1275
34 Ngai, K. L. and Plazek, D. J. *Macromolecules* 1990, **23**, 4182
35 Ngai, K. L., Rajagopal, A. K. and Teitler, S. J. *J. Chem. Phys.* 1988, **88**, 5086
36 Schneider, H. A. and Wirbser, J. *New Polym. Mater.* 1990, **2**, 149

37 Yang, H., Shibayama, M., Stein, R. S., Shimizu, N. and Hashimoto, T. *Macromolecules* 1986, **19**, 1667

38 Hashimoto, T., in 'Thermoplastic Elastomers' (Eds N. R. Legge, G. Holden and H. E. Schroeder), Hanser, Munich, 1987, Ch. 12, Sect. 3

39 Han, C. D. and Kim, J. *J. Polym. Sci., Part B: Polym. Phys.* 1987, **25**, 1741

40 Han, C. D., Kim, J. and Kim, J. K. *Macromolecules* 1989, **22**, 383

41 Han, C. D. and Baek, D. M. Unpublished research, 1992

42 Han, C. D., Baek, D. M. and Kim, J. K. *Macromolecules* 1990, **23**, 561

43 Ober, C. K., Jin, J. I., Zhou, Q. and Lenz, R. W. *Adv. Polym. Sci.* 1981, **59**, 103

44 Han, C. D. and Kim, S. S. Unpublished research, 1992

45 Furukawa, A. and Lenz, R. W. *Macromol. Chem., Macromol. Symp.* 1986, **2**, 3