

# Mechanical relaxation in miscible polymer systems: the glass transition regime in poly(vinylmethylether) (PVME)-cross-polystyrene (PS) semi-interpenetrating networks

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Miscible semi-interpenetrating polymer networks (semi-IPN) of varying composition are prepared by crosslinking polystyrene containing few maleic anhydride groups with a diamine in the presence of linear poly(vinylmethylether) (PVME). The resulting PVME-c-P(ScoMA) semi-IPNs are characterized by their thermal and thermomechanical behaviour. Comparison with the corresponding uncrosslinked material proves that weak crosslinking has a negligible effect on the location of the glass transition as measured by d.s.c. Both the  $T_g$  data and the temperatures of the loss modulus maximum  $E''$  (at 1 rad/s) show the same non-linear curved composition dependence. Contrary to this the  $\tan \delta$  maximum varies linearly with composition. These experimental results, in combination with frequency dependent measurements show that the temperature dependence of the mechanical response in the glass transition region is thermorheological complex. The results are interpreted by different segmental mobilities of PS and PVME chain segments in the glass transition region.

**(Keywords: polyvinylmethylether-polystyrene; miscible semi-IPNs; glass transition; dynamic mechanical analysis; thermorheological complex behaviour)**

## INTRODUCTION

The glass transition behaviour of miscible multicomponent polymer systems has been subject to a great number of studies<sup>1–3</sup>. Most often differential scanning calorimetry (d.s.c.) is used as an experimental method to probe miscibility via analysis of the glass transition behaviour. Several attempts have been reported to describe glass transition temperatures of miscible or partially miscible polymer blends as a function of blend composition. We have recently demonstrated<sup>4</sup> that both the popular Gordon–Taylor equation<sup>5</sup> and the Kwei equation<sup>6</sup> are special cases of a more fundamental treatment of the glass transition given by Kanig in 1963<sup>7</sup>.

Both the Gordon–Taylor equation and the corresponding equation by Kanig have been derived for the concentration dependence of the glass transition of copolymers. The glass transition of the copolymer according to Kanig is related to the free energy of hole formation, i.e. the energy required to generate holes by separating polymer–polymer contacts. In the case of a copolymer consisting of A and B units three types of contacts A:A, B:B and A:B are taken into account. If the energy to separate an A:B contact is given by the arithmetic mean of the corresponding A:A and B:B

contacts, Kanig's theory reduces to the Gordon–Taylor approach.

Though these equations are rather successful in describing the concentration dependence of many copolymer systems as well as miscible polymer blends, questions remain concerning the physical significance of such mixing rules in polymer blends, because the situation on a molecular level might be more complicated.

In the present paper we report calorimetric and dynamic-mechanical data of the glass transition in a miscible semi-interpenetrating polymer system. The purpose of the paper is to demonstrate that d.s.c alone only gives a very crude description of the glass transition behaviour of multicomponent polymer systems. The present study is based on one of the most intensively studied miscible polymer blend systems, namely polystyrene (PS) and polyvinylmethylether (PVME). As part of a project where the influence of crosslinking on the phase behaviour of polymer blends is studied, semi-IPNs were prepared for this system. In the first part of the paper the preparation of the semi-IPNs is discussed. Further experiments are restricted to the characterization of the glass transition region in these materials. The results on the phase behaviour will be published elsewhere<sup>8,9</sup>. A neutron scattering study on PVME-c-PS-semi-IPNs prepared in a different way has been published recently<sup>10</sup>.

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## EXPERIMENTAL

## Preparation of PVME-c-P(ScoMA) semi-interpenetrating networks

**Materials.** Laboratory grade PVME (Aldrich) ( $M_n = 16\,000$ ,  $M_w/M_n = 3$ ) was fractionated to obtain materials of narrower molecular weight distribution (MWD). Technical grade P(ScoMA) copolymers of varying maleic anhydride (MA) content<sup>11</sup> were used. Some analytical data on the starting materials are given in Table 1. Hexamethylenediamine was purchased from Merck. Analytical grade THF was used as received.

A typical experimental procedure is given for the preparation of a semi-IPN of 50 wt% of PVME: 0.5 g of PVME and 0.5 g of P(ScoMA) ( $= 4.8 \times 10^{-3}$  mol of repeating units) are dissolved in 10 ml of THF. To get a degree of crosslinking of 1 mol% with respect to the P(ScoMA), 5.6 mg hexamethylenediamine (HMDA) ( $= 4.8 \times 10^{-5}$  mol) are dissolved in THF and the two solutions are mixed and poured into a flat bottomed petri dish. After about 5 min gelation occurs (Figure 1). The solvent is slowly removed, the resulting film further dried in a vacuum oven and heated to 80°C for imide formation from the amide-acid intermediate. The films thus obtained are suitable for d.s.c. small angle light scattering, dynamic-mechanical, i.r. dichroism and swelling experiments<sup>8</sup>. Films of different thickness between 0.02 and 0.6 mm are available by this technique.

## Differential scanning calorimetry

D.s.c. measurements were made using a Perkin-Elmer DSC 7 instrument. The block temperature was kept at  $-100^\circ\text{C}$ . The instrument was calibrated using standard procedures. Several runs at different heating rates (10, 20, 40 K/min) were recorded.

## Dynamic mechanical analysis

The dynamic mechanical spectra were made on a Rheometrics Solid Analyser RSAII in the temperature step mode. The temperature normally was varied from about  $T_g - 50\text{ K}$  to  $T_g + 100\text{ K}$ . Tests were made at every three degrees. Films were measured in the dynamic tensile testing mode. Pretension and dynamic deformation were kept low within the limits of linear viscoelastic behaviour. The strain amplitude was adapted to obtain optimum experimental resolution. The standard frequency of measurement was 1 rad/s. Additional frequency sweep experiments were made in the frequency range between 0.1 and 100 rad/s.

## RESULTS

## Synthesis of the semi-interpenetrating networks

Different synthetic routes are reported for the synthesis of semi-interpenetrating networks of linear chains A dissolved in a network of B chains (Poly(A-c-B))<sup>12</sup>. These include crosslinking polymerization of B (+ small

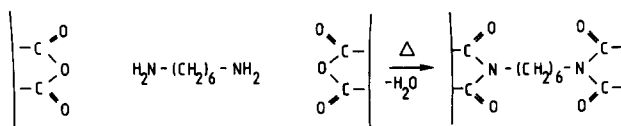
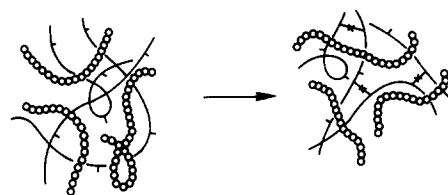


Figure 1 Schematic representation of the crosslink reaction of P(ScoMA) copolymers in the presence of diamines

amount of multifunctional crosslinker) in the presence of Poly-A; swelling of network Poly-c-A with monomer B and polymerization of the latter; and crosslinking of Poly-B in the presence of Poly-A.

To synthesize PVME-c-PS semi-IPNs we first tried the thermally induced radical copolymerization of styrene and divinylbenzene in the presence of PVME. In most of the experiments turbid samples were obtained, indicating phase separation. In addition, radical polymerization in bulk in the presence of PVME might result in considerable amount of chain transfer to PVME and thus a material, where both PS and PVME are part of the network could result or where graft copolymers are formed partially. In the recent paper of Bauer *et al.*<sup>10</sup>, the semi-IPNs were prepared in this way. These authors used thermally induced radical polymerization and report the formation of phase separated materials for a highly crosslinked sample. The authors argued that phase separation might occur when the amount of PVME exceeds the equilibrium degree of swelling of the network. Thus it should be expected that phase separation occurs predominantly at large amounts of PVME and high crosslink densities. Bauer *et al.* only prepared semi-IPNs with equal amounts of PS and PVME.

To crosslink PS in the presence of PVME by a non-radical process to ensure that the PVME is not attached covalently to the network, a copolymer of PS with crosslinkable comonomer units can be used. In the present study poly(styrene-co-maleic anhydride) (P(ScoMA) copolymer with a MA content of 4.7 wt% was used. In a recent work Min and Paul<sup>11</sup> have reported that the onset of phase separation in PVME/P(ScoMA) blends is slightly shifted to higher temperatures for MA contents below 20 wt%, which has been interpreted by the 'copolymer' effect. Contrary to that in a parallel study from this laboratory the results indicate that incorporation of MA groups decreases the miscibility window<sup>12</sup>, which also was predicted by equation of state theories. Nevertheless the effect of few MA groups on the miscibility apparently is rather small.

The maleic anhydride groups are crosslinked by the reaction with a diamine. In the present study hexamethylenediamine (HMDA) has been used as a crosslinker. The reaction scheme is shown in Figure 1.

More details on the preparation of the semi-IPNs are given in the experimental section. For low degrees of crosslinking (1 and 2%) the samples are transparent in the whole composition range. For high degrees of crosslinking translucent or turbid samples were obtained.

Table 1 Characterization of the starting materials

Sample	$M_n$	$M_w/M_n$	$T_g$
PVME-0	16 000	3	-27
PVME-1	33 000	2.2	-27
PVME-2	66 000	1.25	-26
P(ScoMA)-4.7	80 000	2.4	108

Phase separated films were obtained for a crosslink density of 4%. Details on the mechanical properties of these materials will be reported elsewhere. The discussion of the present paper focuses on samples with low degree of crosslinking. Due to the fact that the small amount of MA does not drastically influence the phase behaviour, the materials will be designated as PVME-c-PS-semi IPNs rather than PVME-c-P(ScoMA). Table 2 gives the characterization of the samples used in this study. The amount of crosslinker was kept constant at 1.1 wt% with respect to the P(ScoMA). This corresponds to one junction per 100 repeating units along the polymer chain. The concentration of PVME was varied between 0 and 90 wt%. It is possible to extract the PVME chains quantitatively out of these semi-IPNs. Upon immersing the semi-IPNs in water in most cases phase separation occurs and only a part of the PVME can be extracted. Details of these studies and the characterization of the properties of the resulting microfoams will be reported in a forthcoming paper<sup>13</sup>.

#### Differential scanning calorimetry

In Figure 2a and b two series of d.s.c. traces for blends and semi-IPNs are shown for a heating rate of 20 K min<sup>-1</sup>.

**Table 2** Characterization of the semi-IPNs

Sample	Wt% P(ScoMA)	Crosslink density	$T_g$	$T_{max}(E'')$ (°C)	$T_{max}(\tan \delta)$
1	10	1	-24	-26	-16
2	20	1	-20	-22	-7
3	30	1	-16	-19	+8
4	40	1	-7	-12	+20
5	50	1	+5	-3	+41
6	60	1	+23	+19	+55
7	70	1	+35	+42	+69
8	80	1	+55	+53	+86
9	90	1	+76	+69	+99
10	100	1	+110	+111	+120

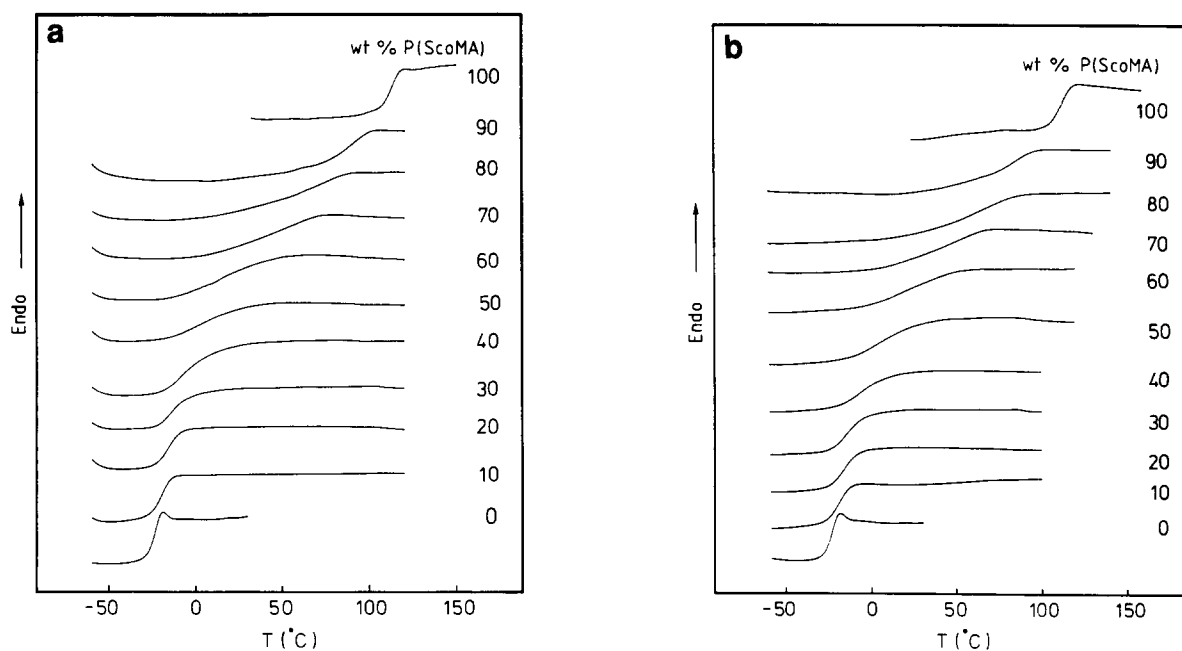
In all cases a single glass transition region is observed, indicating mixing on a molecular level. In the intermediate range of compositions from 40 to 80 wt% of PS the glass transition region is rather broad while a narrow glass transition is observed at high PVME concentrations.

The same behaviour is observed in blends of PVME with pure PS (without maleic anhydride)<sup>14</sup>. The 'static' glass transition temperatures obtained from the d.s.c. measurements after extrapolation to heating rate zero, are plotted in Figure 3a as a function of composition for the blends of PVME with the P(ScoMA) and two series of semi-IPNs with different crosslink density (1% and 2%). The data for the blend and the miscible semi-IPNs fall on a single curve. The data are very much the same as for PS-PVME blends and the  $T_g$ -composition curve is strongly non-linear. It cannot be described by the Gordon-Taylor relation.

However, as is shown in Figure 3b, linearization of the d.s.c. data is possible using the recently proposed generalized formulation<sup>4</sup>. It must be concluded from these thermoanalytical data that low degrees of crosslinking have no extra influence on the glass transition behaviour in these semi-IPNs as compared to the uncrosslinked blends. The system is still homogeneous. Small angle light scattering experiments show that the observation of the onset of phase separation (turbidity) is extremely dependent on the heating rate<sup>8,9</sup>. According to the work of Bauer *et al.*<sup>10</sup>, the binodal (turbidity curve) and spinodal curves might show different shapes, depending on the crosslink density, junction functionality and network topology.

#### Dynamic mechanical analysis

The dynamic mechanical properties of the glass transition region were analysed in the dynamic tensile testing mode at 1 rad/s. In Figure 4,  $E'$ ,  $E''$  and  $\tan \delta$  are plotted as a function of temperature for crosslinked P(ScoMA) copolymer without PVME. As for other amorphous polymers and lightly crosslinked polymer



**Figure 2** D.s.c. traces at 20 K/min for various sample compositions; (a) blends from PVME and P(ScoMA); (b) semi-IPN PVME-c-P(ScoMA) 1% crosslink density

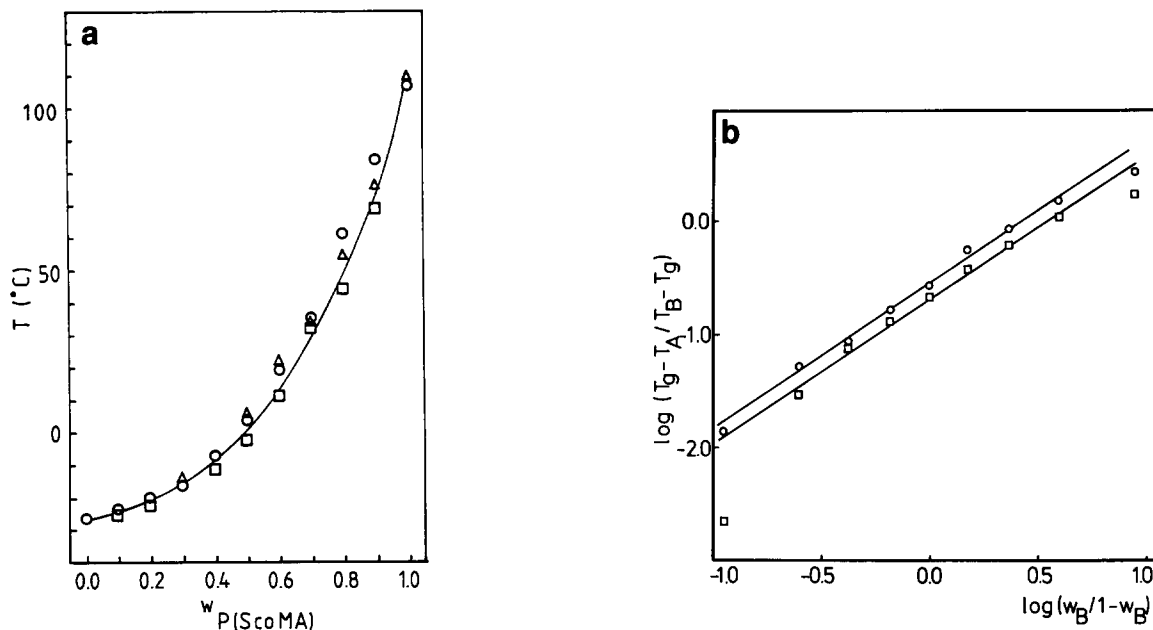


Figure 3 (a) Glass transition temperatures for PVME/P(ScoMA) blends and two series of semi-interpenetrating networks of different crosslink density as a function of composition:  $\circ$ , blend;  $\triangle$ , semi-IPN 1%;  $\square$ , semi-IPN 2%. (b) Representation of the glass transition data of the PVME-c-P(ScoMA) semi-IPNs in the linearized formulation (equation 15 in ref. 4) ( $B = \text{PVME}$ ,  $A = \text{P(ScoMA)}$ );  $\circ = 1\%$  crosslinker,  $\square = 2\%$  crosslinker)

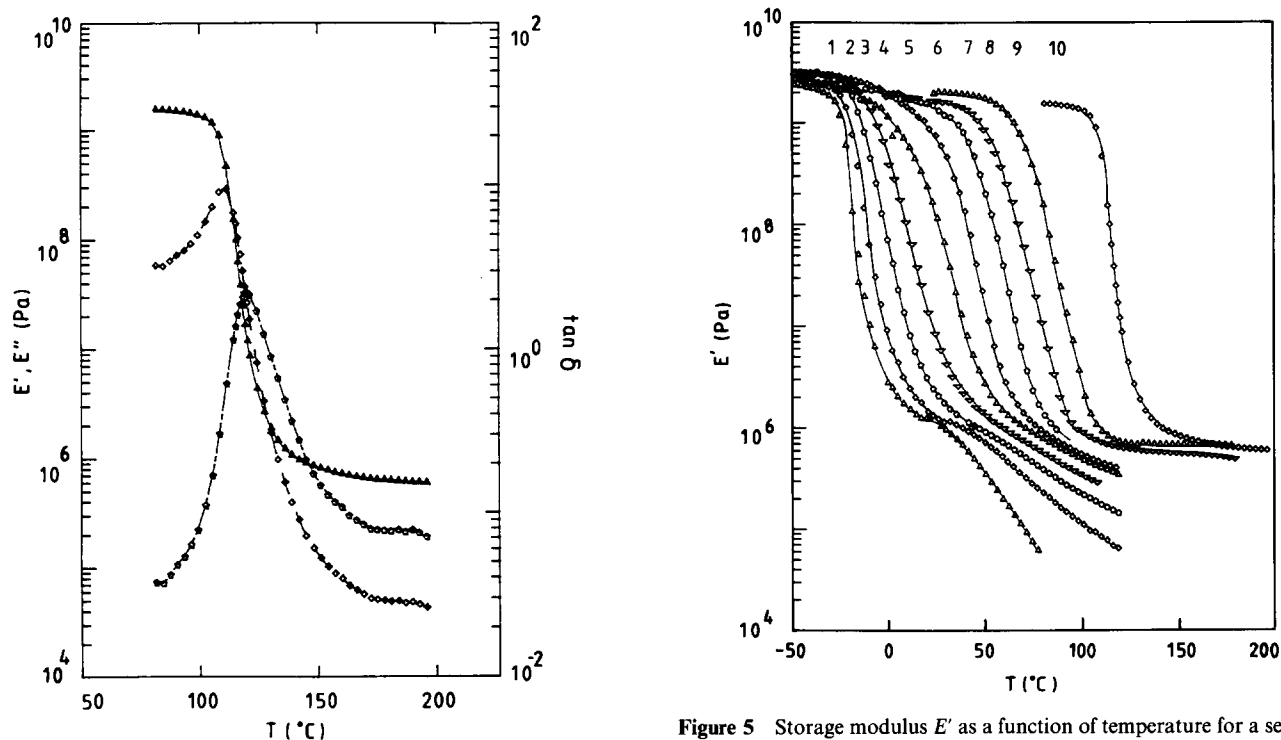


Figure 4 Storage modulus  $E'$  ( $\triangle$ ), loss modulus  $E''$  ( $\diamond$ ) and  $\tan \delta$  ( $\circ$ ) as a function of temperature for a P(ScoMA) network (1% crosslinkage) at 1 rad/s

networks, a sharp transition is observed in the glass transition region.

The loss modulus  $E''$  as well as the loss tangent  $\tan \delta$  show sharp maxima which are separated by about 8–10 degrees. In many other single phase systems, including networks, the maxima of the loss modulus and  $\tan \delta$  are even more close. For the P(ScoMA) the maximum of  $E''$  is located at the glass transition as measured by d.s.c., while the maximum of  $\tan \delta$ , which often is used as a

Figure 5 Storage modulus  $E'$  as a function of temperature for a series of PVME-c-P(ScoMA) semi-IPNs at 1 rad/s (sample designation as in Table 2)

measure of the glass transition is located at slightly higher temperatures. From comparison with other crosslinked materials, i.e. polybutadiene networks where the maxima are separated only by 3–6 degrees, it must be concluded, that the slightly larger difference between the maxima of  $\tan \delta$  and  $E''$  must have a different origin.

In Figures 5–7 the storage modulus  $E'$ , the loss modulus  $E''$  and the loss tangent ( $\tan \delta$ ) are plotted as a function of temperature for the semi-IPN samples of varying composition.

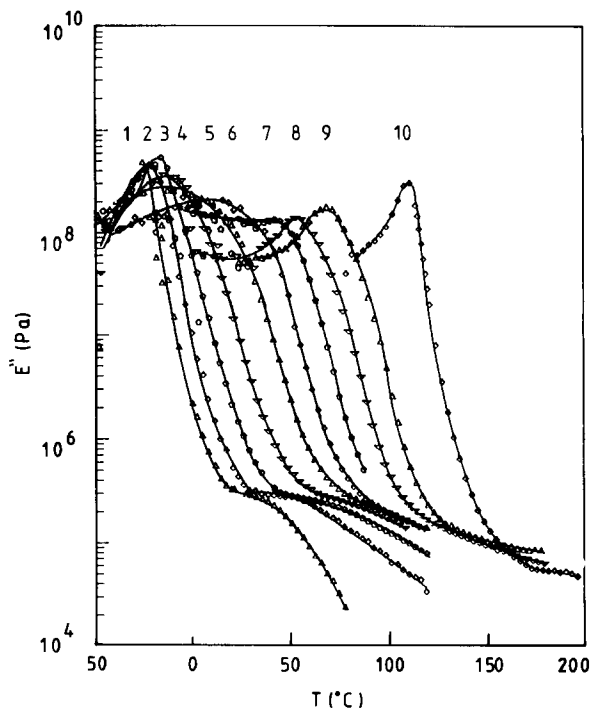


Figure 6 Loss modulus  $E''$  as a function of temperature for a series of PVME-c-P(ScoMA) semi-IPNs at 1 rad/s (sample designation as in Table 2)

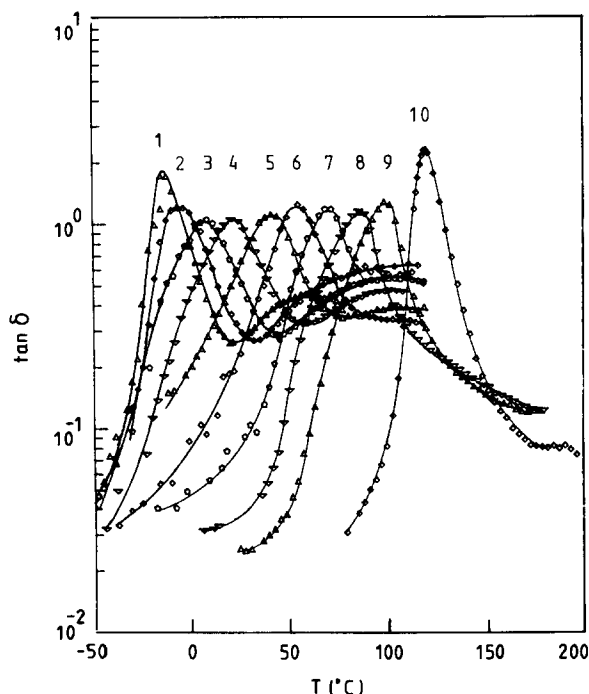


Figure 7  $\tan \delta$  as a function of temperature for a series of PVME-c-P(ScoMA) semi-IPNs at 1 rad/s (sample designation as in Table 2)

A single transition from the glassy region to the rubbery plateau is observed, which is very broad for mixtures in the intermediate composition range. For mixtures rich in PS, the storage modulus  $E'$  is still in the order of  $5 \times 10^8$  Pa at the glass transition temperature determined by d.s.c.

The most interesting observation is the relative location of the  $E''$  and the  $\tan \delta$  maximum. For samples with low amount of PS or PVME, the maxima of  $E''$  and  $\tan \delta$  are rather sharp and separated by less than 10 degrees.

For intermediate compositions (40–70 wt% of polystyrene), the two maxima are separated by about 30–35 degrees. The distinct maximum of the  $E''$ , which is observed at compositions rich in one of the components, becomes extremely broad and difficult to locate at these intermediate compositions.

At higher temperatures, far above  $T_g$  an additional maximum is observed in the  $\tan \delta$  curve which decreases in intensity with decreasing PVME content. This maximum can be associated to the reptation of the PVME chains within the PS network. Its location strongly depends on the molecular weight and molecular weight distribution of the PVME chains. This is shown in Figure 8, where the  $\tan \delta$  curves of two semi-IPNs of the same composition and crosslink density but different PVME chain characteristics are compared. A more detailed analysis of the relaxation of the PVME chains in the PS network is presently in progress.

In Figure 9 the location of the maxima of  $E''$  and  $\tan \delta$  are plotted as a function of semi-IPN composition and compared to the glass transition temperatures obtained from d.s.c. It is evident that the loss modulus maximum, though difficult to locate for intermediate compositions, is directly related to the glass transition temperatures measured by d.s.c. Contrary to this, the  $\tan \delta$  maximum varies linearly with composition. This is in contrast to the behaviour of homopolymers or homogeneous statistical copolymers where the loss modulus maximum and the  $\tan \delta$  maximum are closely related.

Another interesting observation can be made upon closer inspection of the  $\tan \delta$ -T curves. In the semi-IPNs with PS content  $> 20$  wt%, a shoulder is observed at low temperatures, located close to the temperature of the  $E''$  maximum.

These observations show that the glass relaxation in this miscible polymer system shows a very complex

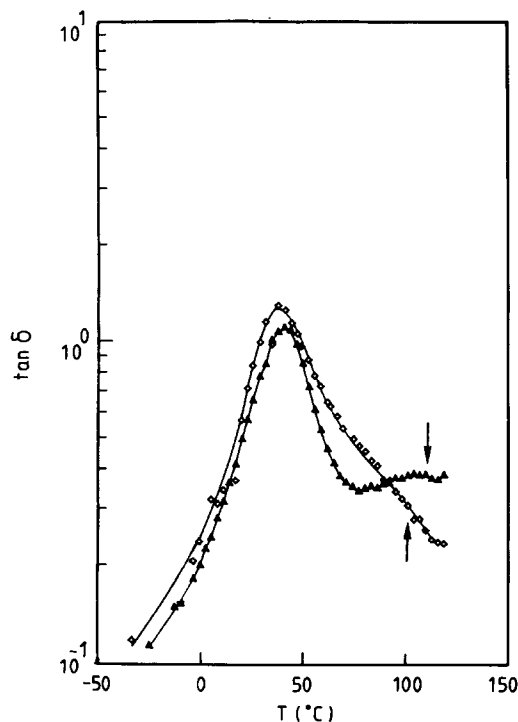


Figure 8  $\tan \delta$  as a function of temperature (1 rad/s) for two PVME-c-P(ScoMA) semi-IPNs for two different PVMEs:  $\triangle$ , PVME-1;  $\diamond$ , PVME-2 (see Table 1), arrows indicate location of the terminal relaxation of the PVME chains

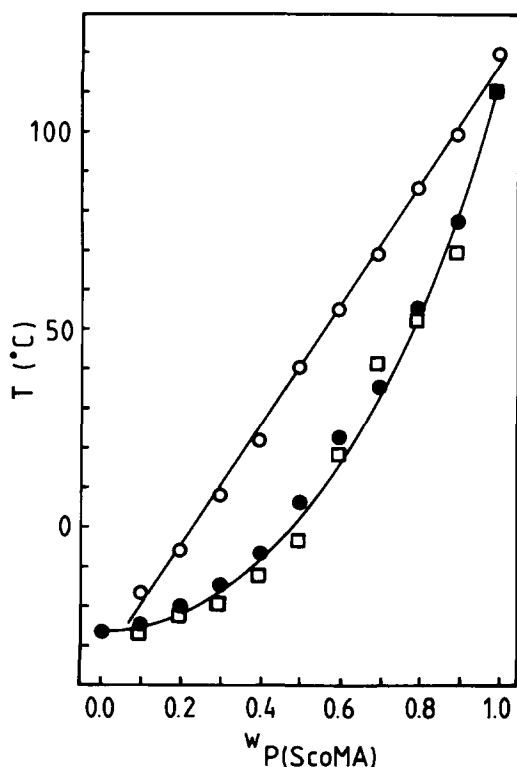


Figure 9 Glass transition temperature  $T_g$  (●), maximum of the loss modulus  $E''$  (□) and maximum of the  $\tan \delta$  (○) as a function of composition in PVME-c-P(ScoMA) semi-IPNs

behaviour and that different experimental techniques must be combined to get a deeper understanding of the details of the glass transition.

## DISCUSSION

One description of the glass transition is based on free volume considerations. According to the free volume concept, the fraction of free volume  $\phi_f$  at  $T_g$  is about the same for all amorphous polymer systems. The actual experimental values for  $\phi_f$  range between 0.013 and 0.035 (ref. 15). According to the theory of Kanig, the glass transition temperature is not given by an iso free volume state, but by a state where 'hole' free volume and 'vibration' free volume have a distinct ratio<sup>7</sup>.

The iso free-volume concept is supported by dilatometry and the analysis of the temperature dependence of the viscoelastic properties in the temperature regime above  $T_g$ , described by the WLF equation<sup>17</sup>:

$$\log a_T = -\frac{c_1(T - T_0)}{c_2 + T - T_0}$$

The constants  $c_1$  and  $c_2$  of the WLF equation are related to the free volume at  $T_0$  (reference temperature) and the expansion coefficient of the free volume. They are similar for many polymers if  $T_g$  is chosen as the reference temperature.

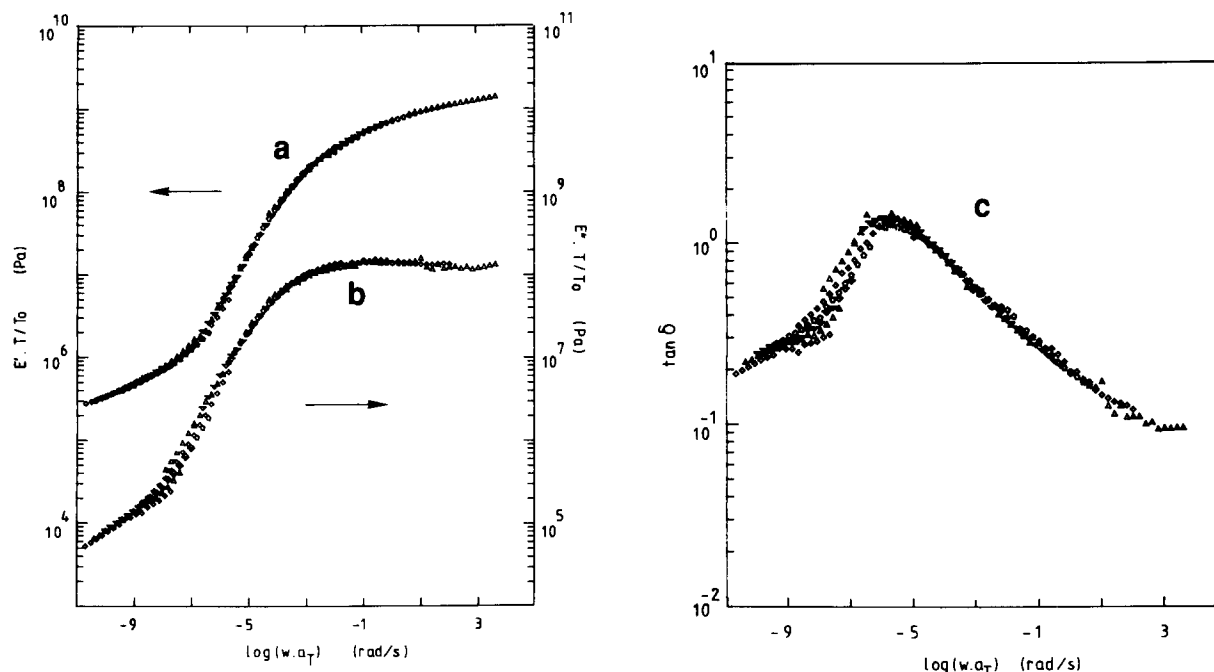
The applicability of the time-temperature superposition principle is restricted to systems which are thermorheologically simple, i.e. where all molecular relaxation processes with different characteristic relaxation times have the same temperature dependence.

In miscible multicomponent polymer systems several questions are still unanswered, for example, whether the viscoelastic behaviour still obeys the conditions of

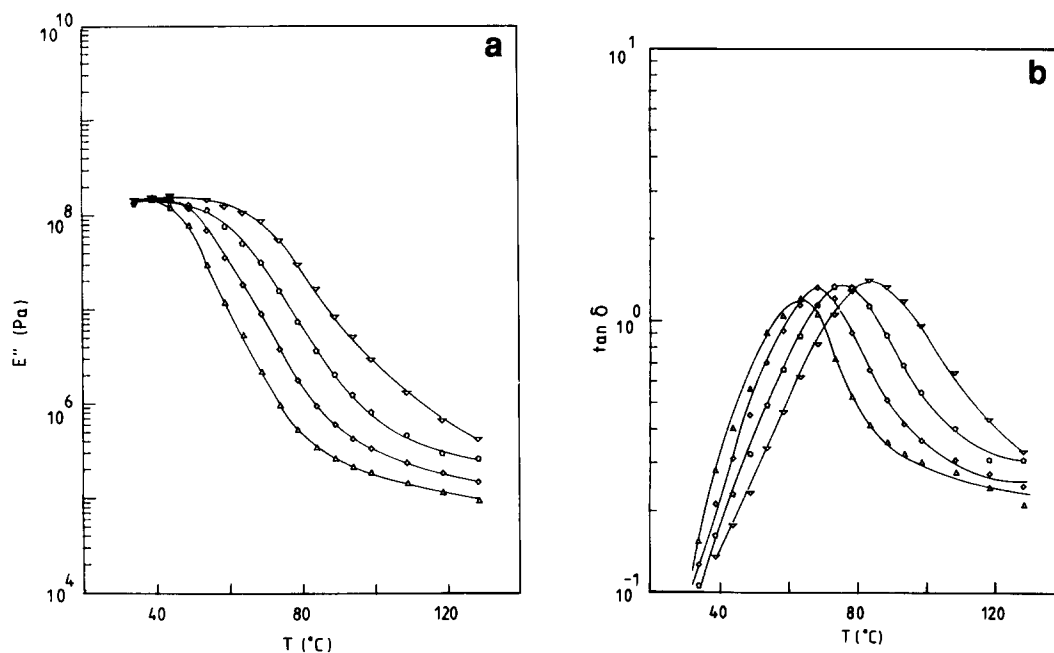
thermorheological simplicity or whether such materials are thermorheologically complex because the two components have a different temperature dependence of their molecular relaxations. Though this might be generally true, it has been demonstrated by several authors that the WLF equation also can be used to describe the viscoelastic behaviour of miscible polymer blends in the terminal region<sup>16-19</sup>. In most of the systems reported, the investigated materials had broad molecular weight distribution. As a consequence the relaxation spectrum is extremely broad, and deviations from thermorheological simplicity might be smeared out. In the case of PS/PPE blends we have prepared narrow distributed materials and analysed the viscoelastic properties of PS with PPE of various molecular weights<sup>20</sup>. The temperature dependence of PS-PPE blends of various compositions and with various PPE chains lengths obeys the conditions of thermorheological simplicity<sup>20-22</sup>. According to Colby<sup>23</sup>, direct experimental evidence for testing the conditions of thermorheological simplicity can be made by analysing the viscoelastic response of binary mixtures, where two separate relaxation processes are observed in the experimental frequency range at one temperature. By temperature variation the relative positions of the two maxima along the frequency axis must be constant for thermorheological simplicity. Colby has shown for PMMA/PEO blends that this is not the case. For PS/PPE the similar test still remains to be done.

The varying distance between the  $E''$  and the  $\tan \delta$  maxima in the PVME-c-PS-semi-IPNs is an indication that the relaxations related to the glass transition are more complex than in a system consisting of only one component. The lack of thermorheological simplicity in the glass transition regime of this miscible system can be demonstrated by frequency dependent measurements. In Figure 10a-c the frequency dependence of the viscoelastic response in the glass transition region of a 30:70 PVME-c-P(ScoMA) semi-IPN is shown. The storage modulus isotherms have been used as basis to construct a master curve by horizontal shifting of the reduced data. The corresponding master curves for  $G''$  and  $\tan \delta$  obtained by using the same shift factors  $\log a_T$  are shown in Figure 10b and c. It is evident that the data for  $G''$  and thus  $\tan \delta$  cannot be shifted to a master curve applying the same shift factors. This complication shows up at the low frequency side of the glass transition region. At lower or higher frequencies the data for  $G'$  and  $G''$  can be superposed to a master curve. Similarly a master curve can be obtained on the basis of the  $G''$  data. In that case the  $G'$  data show a scatter beyond the experimental error. Due to the width of the glass relaxation this thermorheological complex behaviour is largely smeared out. The WLF constants determined for this specific mixture are in reasonable agreement with those reported in the literature<sup>24</sup>.

The conclusion that semi-IPNs exhibit thermorheologically complex behaviour, can also be drawn from Figure 11a and b where  $E''$  and  $\tan \delta$  are plotted as a function of temperature for four frequencies. If the frequency is changed from 0.1 to 100 rad/s the  $E''$  maximum shifts for about 10 degrees, while the  $\tan \delta$  maximum shifts for 25-30 degrees. This clearly proves the occurrence of molecular relaxations with different rate constants that have a different temperature dependence, classifying the relaxation behaviour in the glass transition region as thermorheologically complex.



**Figure 10** Mechanical properties of a PVME-c-P(ScoMA) (30 wt% of PVME) semi-IPN as a function of frequency in the glass transition regime;  $T_{ref} = 40^\circ\text{C}$ ; (a)  $E'$ , (b)  $E''$ , (c)  $\tan \delta$ ; WLF constants to describe the temperature dependence:  $C_1 = 18.8$ ,  $C_2 = 69.7$



**Figure 11** Mechanical properties of a PVME-c-P(ScoMA) (30 wt% of PVME) semi-IPN as a function of temperature for various frequencies:  $\Delta$ , 0.1;  $\diamond$ , 1;  $\circ$ , 10;  $\nabla$ , 100 rad/s (a)  $E''$ , (b)  $\tan \delta$

Fluorescence studies on the dynamic behaviour of PS-PVME blends at a certain temperature above  $T_g$  show that the two components have different mobility<sup>24,25</sup>. The results presented in this paper give strong support that this different mobility is responsible for the observed dynamic-mechanical results. The strong frequency dependence of the  $\tan \delta$  maximum indicates that the relaxation rates of PVME and P(ScoMA) are different in the glass transition region, despite the fact that the system is miscible according to small angle light scattering and d.s.c.

According to Kanig's idea of the glass transition<sup>7</sup>,  $T_g$  is the temperature where the thermal energy is sufficient

to generate holes by the separation of polymer-polymer contacts. Below  $T_g$  the number of holes is constant. In binary copolymers and miscible polymer blends three different free energies  $A_{ij}$  of hole formation have to be distinguished:  $A_{AA}$ ,  $A_{AB}$ ,  $A_{BB}$ . These free energies can be obtained from the analysis of the glass transition. As discussed recently, the energy to separate A-B contacts in PS-PPE blends is given by the arithmetic mean for PS-PS and PS-PPE contacts. As a consequence the  $T_g$  composition curve can be described by the Gordon-Taylor equation<sup>4</sup>. Similarly, for PS/PVME, the energy for separation of PS-PVME contacts and generation of free volume is considerably larger than the arithmetic

mean. Thus, the generation of free volume at  $T_g$  might be dominated by separating PVME–PVME contacts. Using this argument it is reasonable that the glass transition observed by dilatometry and d.s.c. is dominated by the onset of molecular motions associated with the PVME. Consequently a lower mobility has to be attributed to the polystyrene segments at, or just above the d.s.c. glass transition. The main gain of segmental mobility of the PS segments occurs at slightly higher temperatures and thus gives rise to the strong shift of the  $\tan \delta$  maximum as compared to the  $E''$  maximum. As a consequence of this, the different frequency dependence of  $\tan \delta$  and  $E''$ , giving rise to the observed thermorheological complex behaviour, can be explained as well. Just above  $T_g$  (d.s.c.), the more 'rigid' PS chains have a higher activation energy for the local flow processes. As a consequence their response is much more frequency dependent. These arguments easily explain the observed strong shift of the  $\tan \delta$  maximum as compared to the  $E''$  maximum, as well as the relatively high modulus  $E'$  of the material just above  $T_g$ . The maximum in  $\tan \delta$  changes linearly with composition at a frequency of 1 rad/s (Figure 9). Further studies are necessary to test, to which extent this is influenced by the frequency of the measurement.

## CONCLUSIONS

We have shown in the preceding section that detailed information about the glass transition region in miscible polymer blends can be obtained from combined d.s.c. and dynamic mechanical analysis. The detailed thermomechanical analysis of the transition from the glassy state into the rubbery plateau has been made possible by weak crosslinking of one of the components. This crosslinking has negligible effects on the glass transition temperature as measured by d.s.c. The major point of this work is that the glass transition region in the miscible PVME-c-P(ScoMA) semi-IPNs is characterized by a thermorheological complex behaviour. This only can be explained by a different mobility of the components just above the glass transition, supporting the results of the fluorescence measurements<sup>25</sup>. Other polymer blends which show similar strong deviations from linear  $T_g$  composition curves might behave in a similar way and the different mobility of the components at  $T_g$  could account for the observed behaviour, which cannot be satisfactorily explained by many of the mixing rules.

## ACKNOWLEDGEMENTS

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