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Rheological and thermodynamic study of the miscible blend polystyrene/poly(cyclohexyl methacrylate)

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Blends of anionically prepared narrow-molecular-weight-distribution polystyrene (PS) and poly(cyclohexyl methacrylate) (PCHMA) of different molecular weights have been studied. The molecular weights of the PCHMA samples are in the range of two to three entanglement molecular weights M_e. The phase diagram was determined by turbidimetry. The critical temperature is about 245°C. Differential scanning calorimetry investigations of the blends show one glass transition temperature and a width of the glass transition that give evidence of miscibility. The viscoelastic properties of the blend components and the blends have been studied in a wide range of temperatures. The investigations of the isotherms of the storage and loss moduli of the blends show that individual relaxation of the blend components is observed to a certain degree. Nevertheless, the deviations from a master curve are small, and comparison with other miscible polymer blends supports the idea that time–temperature superposition holds approximately. Material parameters like the Newtonian viscosity η_0, the plateau modulus G_p and the terminal relaxation time λ_0 are determined from the material functions. These parameters follow a quadratic mixing rule for the logarithm of the material parameter rather than for the parameter itself. In analogy to Wu's equation, the mixing rule contains a material parameter m_{12} that accounts for the hetero contacts between dissimilar chains. In our case, this material parameter is the viscosity η_{12}, the plateau modulus G_{p12} or the terminal relaxation time λ_{012}, respectively. The values of these parameters support the concept of enthalpic interactions, which cause miscibility in the PS/PCHMA blend system. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The mixing of polymers—miscible and immiscible—is interesting for several reasons. First of all, it is an economic way to create materials with desired properties. To do so, it is helpful to know how the blend will behave knowing the properties of the neat components. This is only possible on the basis of the understanding of the processes that go on during mixing. In the second place, mixing of polymers is interesting from a theoretical point of view. One can learn something about the mutual interaction of chemically and therefore physically dissimilar chains and its influence on blend properties. A better understanding of the correlation between the structure and properties of blends is the result.

Among all the possible combinations of existing polymers, miscible blends are a rather small group[1,2]. Owing to the high molecular weights, polymers exhibit only a small entropy of mixing. Together with the weak repulsive forces between the monomer units of the polymers, these blends become immiscible. A typical representative of this group is the pair polystyrene/poly(methyl methacrylate) (PS/PMMA). If the interaction forces are attractive, miscibility is observed. Typical and well investigated miscible blends are the systems polystyrene/poly(phenylene ether) (PS/PPE)[3-5], polystyrene/poly(vinyl methyl ether) (PS/PVME)[6-14], poly(methyl methacrylate)/poly(styrene acrylonitrile) (PMMA/PSAN)[15,16] and poly(methyl methacrylate)/poly(vinylidene fluoride) (PMMA/PVDF)[17,18]. Stronger enthalpic interactions based on hydrogen bonds or charge-transfer complexes enhance miscibility further.

A lot of different methods exist[1,2] to investigate miscibility. Recently, combined techniques (rheology and luminescence[9,10] or birefringence[8,19]) have become prominent to investigate relaxation and therefore miscibility. Miscibility is commonly derived from the existence of a single glass transition temperature (T_g) on the basis of differential scanning calorimetry (d.s.c.) or dynamic mechanical analysis (d.m.a.).

In latter years, rheological techniques observing the relaxation of blends in the plateau and terminal relaxation regions have also been used. Unfortunately, in most of the mentioned miscible blends, polydisperse polymers were used and it was not possible to measure rheological material functions of their mixtures for small frequencies or long times. Only in a few papers[20-22] were the viscoelastic properties of miscible blends, namely poly(methyl methacrylate)/poly(ethylene oxide) (PMMA/PEO), 1,2-polybutadiene/1,4-polybutadiene (1,2-PB/1,4-PB) and

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1,2-polybutadiene/1,4-polyisoprene) (PB/PI), with nearly uniform chain size of blend components studied. In this way it was possible to detect material parameters like the Newtonian viscosity η_0 and the coefficient of the first normal stress difference ψ_{10} at vanishing frequencies ($G' \propto \psi_{10}\,\omega^2$, $G'' \propto \eta_0\,\omega^1$). It turned out that the flow region is especially sensitive for interchain interactions. Microheterogeneity was observed on the basis of individual relaxation of blend components.

From this point of view a polymer blend composed of the polymers polystyrene (PS) and poly(cyclohexyl methacrylate) (PCHMA), which can be obtained anionically, would be promising. As we will see, the glass transition temperatures T_g of blend components are not very far from each other. This way, it is also possible to overcome the rheological problems connected with polymers having very different glass transition temperatures—one polymer is near the glassy state and the other in the terminal region.

It is the aim of this paper to contribute to the investigation of thermodynamic and rheological properties of miscible blends. Using rheological techniques for the study of miscibility, it is important to deal with monodisperse samples. In our case the rare system PS/PCHMA was used. The properties are studied as a function of molecular weight and composition.

EXPERIMENTAL

Materials

Polystyrene (PS) was obtained from BASF. Poly(cyclohexyl methacrylate (PCHMA) was synthesized in our laboratory by anionic polymerization of cyclohexyl methacrylate in tetrahydrofuran (THF), with diphenyllithium as initiator and a small amount of lithium chloride. This method is similar to that proposed by Teyssié[23] for the synthesis of poly(methyl methacrylate). Osmometry and gel permeation chromatography (g.p.c.) were used for the determination of molecular weight and polydispersity. ^{13}C n.m.r. measurements were performed to determine the tacticity of the PDCHMAs. The density of the polymers used was determined with a Mettler scale AE-240 equipped with a Mettler ME-333690 tool for the determination of the density of solids. *Table 1* lists the characteristics of the blend components.

Preparation of blends

All blends were prepared by solution blending in THF, which is a good solvent for both PS and PCHMA. A solution of 10 wt% of the total amount of polymer in THF was prepared and precipitated in methanol. The precipitate was dried in vacuum.

The blends were designated as B*i* or B*iX* where *i* characterizes the PCHMA ($i = 1$ corresponds to PCHMA82, 2 to PCHMA100 and 3 to PCHMA113) and X ($= w_2$) is the amount of PCHMA in weight per cent in the blend. Thus B125 is the blend composed of PS100 containing 25 wt% of polymer (= PCHMA82).

Table 1 The investigated polymers and their characteristics

Polymer	$\bar{M}_n$ (g mol^{-1})	M_w/M_n	Tacticity	Density (g cm^{-3})
PS100	91 300	1.08	atactic	1.05
PCHMA82	82 000	1.07	63% st	1.11
PCHMA100	100 000	1.09	67% st	1.11
PCHMA113	113 000	1.03	67% st	1.11

For the rheological measurements, discs of 25 mm diameter and 1 mm thickness were prepared by compression moulding.

For turbidity measurements, films of various compositions were prepared. A 20 wt% solution of polymer mixtures in THF was vaporized at room temperature.

Methods

Thermal analysis was carried out using differential scanning calorimetry (d.s.c.) on a Perkin Elmer DSC-7. The scanning rate was 10 K min^{-1} and the T_g values were determined with the inflection point method in the second heating run.

The turbidity measurements were performed on a self-made heating block. The cloud point was determined by measuring the temperature when the intensity of the incident light was attenuated significantly. For that, the films were fixed between two quartz discs and heated up in an aluminium block with an orifice to observe the cloud points. For the turbidity measurements we used polystyrene with a molecular weight of 230 kg mol^{-1} (PS230, $M_w/M_n = 1.11$) and poly(cyclohexyl methacrylate) with a molecular weight of 110 kg mol^{-1} (PCHMA10, $M_w/M_n = 1.26$). This system was chosen to lower the critical temperature and therefore the admissible demixing temperature at the edges of the phase diagram. This prevents degradation of the blend under investigation during repeated heating and cooling when measuring the cloud points.

Rheological measurements were carried out by dynamic mechanical spectroscopy on a Rheometrics RMS800. The dynamic moduli were measured by sinusoidal oscillation with a maximum rate of 100 rad s^{-1} and a minimum rate of 0.1 rad s^{-1}. The temperature ranged between 140 and 220°C. Before measuring the moduli, strain sweep tests at various frequencies were carried out to make sure that the applied deformation did not exceed the limit of linear viscoelastic behaviour.

RESULTS AND DISCUSSION

Thermal analysis: phase diagram

Figure 1 shows the phase diagram of PS/PCHMA, which exhibits lower critical solution temperature (*LCST*) behaviour. From the experimental cloud points, the Flory–Huggins parameter χ was determined as a function of temperature and composition. The χ parameters at the different temperatures were determined from the equation:

$$\chi = \frac{\ln(\phi_1'/\phi_1'') + (1 - r_1/r_2)(\Phi_2' - \Phi_2'')}{r_1(\Phi_2''^2 - \Phi_2'^2)} \tag{1}$$

resulting from the equilibrium of chemical potentials of component 1 in both phases, $\mu_1' = \mu_1''$. Prime and double prime indicate the phases one and two respectively. From the equilibrium of component 2 in both phases, i.e. $\mu_2' = \mu_2''$, results:

$$\chi = \frac{\ln(\phi_2'/\phi_2'') + (1 - r_2/r_1)(\Phi_1' - \Phi_1'')}{r_2(\Phi_1''^2 - \Phi_1'^2)} \tag{2}$$

Here Φ_i $(i = 1, 2)$ are the volume fractions of the components. The volume fractions were calculated from the weight fractions assuming a vanishing excess mixing volume. The r_i $(i = 1, 2)$ are the numbers of segments per chain, which were chosen according to the equation $r_i = P_{ni}V_i(V_1V_2)^{-1/2}$, where P_{ni} is the number-average degree of polymerization and V_i $(i = 1, 2)$ are the monomer volumes.

Both expressions for χ should yield the same result. However, they turn out to be different. This might be due to the fact that the symmetry of the experimental phase diagram is at variance with that predicted by Flory–Huggins theory. The latter predicts that the critical temperature is shifted towards the component with the lower molecular weight, which is not observed experimentally.

A plot of χ vs. $1/T$ (*Figure 2*) corresponding to the equation:

$$\chi = A + B/T \tag{3}$$

yields the parameters $A = 0.022$ and $B = -10.759$ respectively. A χ parameter of -1.76×10^{-3} at 180°C is in good agreement with the χ parameter calculated from the interaction energy density determined in the literature[16,24].

With this temperature-dependent χ parameter, we computed the phase diagrams of the systems PS100/PCHMA82 and PS100/PCHMA113 (*Figure 1*). For these computations, we adopted the well known equations from the Flory–Huggins theory[25].

Thermal analysis: glass transition temperature T_g

In *Figure 3*, the glass transition temperatures of the blends are plotted *versus* the composition. All systems show positive deviation from linear behaviour. There is no dependence of T_g on the molecular weight of the blend components and the scatter in the data represents the experimental error. For all compositions only a single T_g is obtained. This is not surprising (and tells us little about the miscibility) because the T_g values of the pure components are not very far from each other. In this case, the width of the glass transition, T_w, may be a measure for compatibility. If this value remains smaller than a certain critical value, then miscibility is assumed[2]. The dependence of T_w on composition is shown in the inset of *Figure 3*. For pure polymers one expects a T_w of about 6°C, for miscible blends of about 10 to 20°C and for immiscible blends $T_w > 30$°C[2]. The T_w values obtained for all PS/PCHMA blends are well below 20°C.

The composition dependence of the glass temperature

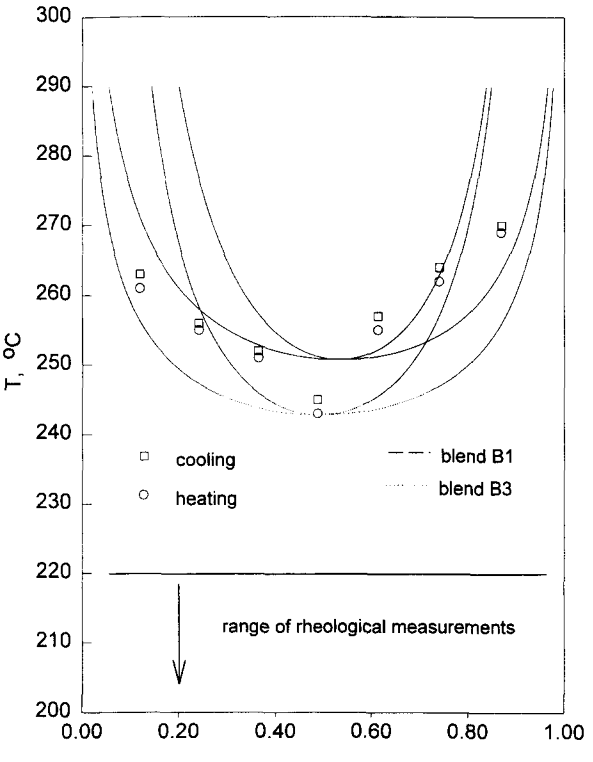

Figure 1 Composition dependence of the cloud points (open circles and squares). The dashed lines and dotted lines represent the binodals and spinodals as calculated for the Flory–Huggins theory. The arrow marks the range where the rheological measurements were performed

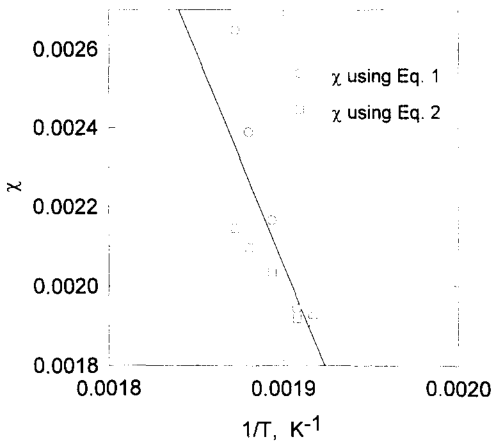

Figure 2 Temperature dependence of the interaction parameter χ

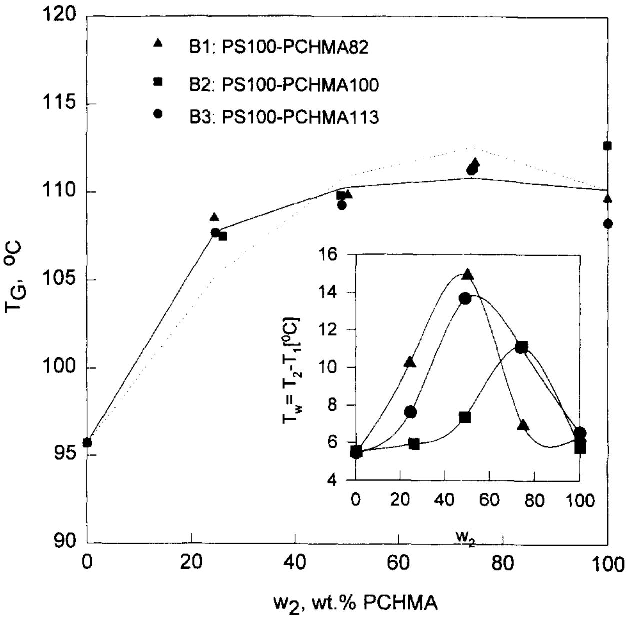

Figure 3 Composition dependence of the glass transition temperature T_g. The points correspond to the measurements and the lines to equations describing this dependence: dotted line, Gordon–Taylor–Kwei equation with $K = T_{g1}/T_{g2}$; full line, the same equation without any restriction. The inset represents the width of the glass transition, T_w, as a function of the composition

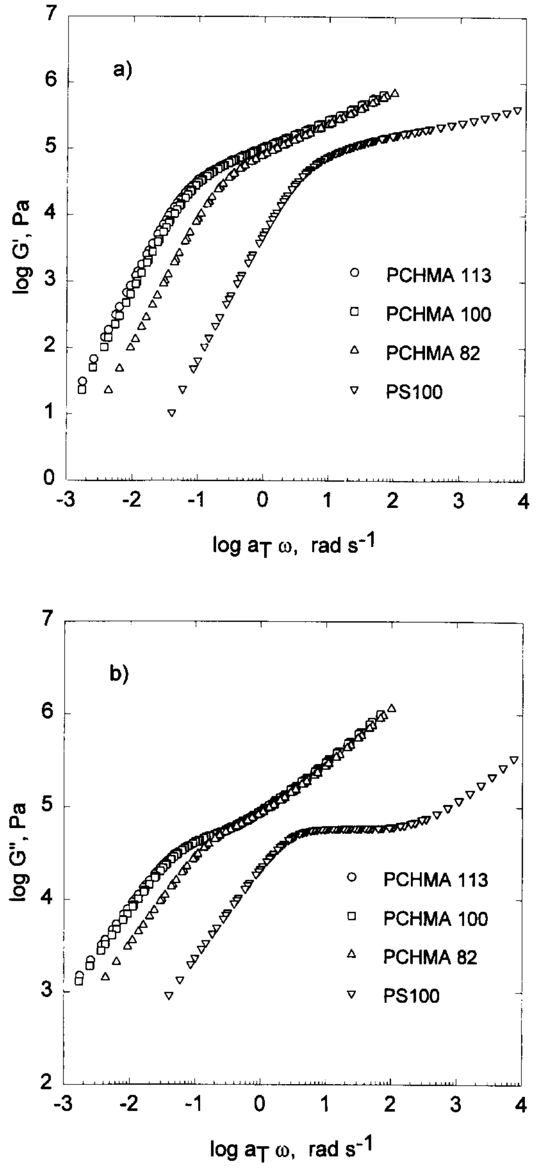

Figure 4 Dependence of (a) the storage modulus G' and (b) the loss modulus G'' on the reduced frequency $a_T\omega$ for the blend components

can be described by different equations. These results are also depicted in *Figure 3*. The Gordon–Taylor–Kwei[2] equation:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2 \qquad (4)$$

represents the experimental results best. Using the approximate relation $k = T_{g1}/T_{g2}$, q was obtained as 33.8 K. This value is a strong indication for enthalpic interactions in the blend[26]. This dependence is shown in *Figure 3* by the dotted line. A better fit is obtained using k as a free parameter: $k = 9.23$ and $q = 5.98$ K.

Rheological analysis

In *Figures 4a* and *4b* the dynamical material functions G' and G'' are shown for the blend components. These data display Rouse-like behaviour, with a slope of 1/2 for G' and G'' at high frequencies and a slope of 2 and 1 for G' and G'', respectively, for the smallest frequencies. It can also be seen that these polymers show the first attributes of a plateau.

Comparing our data qualitatively with those of PMMA above the entanglement threshold (see Ferry[27]), we see that the PCHMAs behave like polymer melts slightly above the entanglement molecular weight M_e. The plateau modulus G_p and the corresponding entanglement molecular weight of this polymer are not known from the literature, and we have to estimate these values on the basis of our data. To determine this characteristic molecular weight we use the following equation:

$$M_e = \rho RT/G_p \qquad (5)$$

In this equation, ρ and G_p are the density and the plateau modulus of PCHMA respectively (see *Table 1*), R the gas constant and T the temperature. In our case, G_p was determined from the storage modulus G' at the minimum of $\tan\delta$ of the different PCHMA. These moduli are given in *Table 2*. We are not sure whether the change in our data is systematic or corresponds to experimental scatter. Thus, we use the average value of the plateau modulus ($G_p^{\text{PCHMA100}} = 95\,000$ Pa) to determine the entanglement molecular weight to be about 40 kg mol^{-1}. This is only a rough estimate because the accessible molecular weight range is too small to judge about the molecular-weight independence of G_p. A comparison of our M_e value with values of a series of different methacrylates given by Ferry[27] may be helpful. On the basis of the entanglement molecular weights for poly(2-ethylbutyl methacrylate) ($M_e^{\text{PEBMA}} = 21.4$ kg mol^{-1}), poly(n-hexyl methacrylate) ($M_e^{\text{PNHMA}} = 34$ kg mol^{-1}) and poly(n-octyl methacrylate) ($M_e^{\text{PNOMA}} = 87$ kg mol^{-1}) a value of about 40 kg mol^{-1} for PCHMA is reasonable. Nevertheless, a more detailed investigation concerning the determination of M_e of PCHMA has to be done in future.

It is well accepted that for homopolymers time–temperature superposition (TTS) works. The horizontal shift factors, a_T, are given in *Figure 5* for the PCHMAs

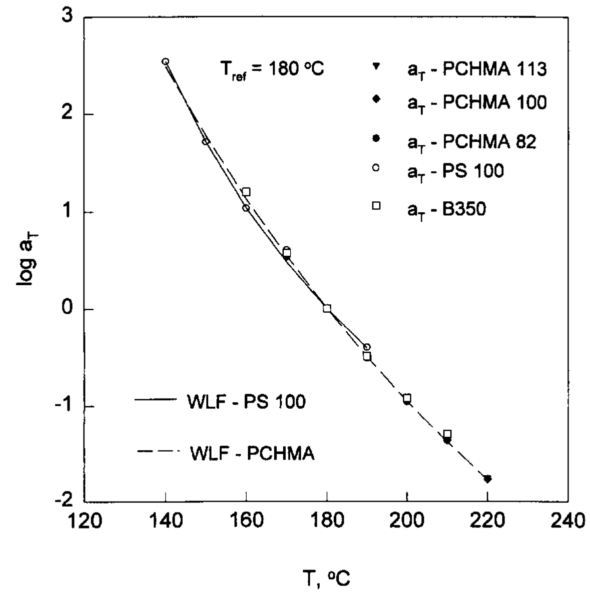

Figure 5 Dependence of the horizontal shift factor a_T from the temperature. The full line represents the WLF relation for the PS and the dashed line for the different PCHMAs. The open squares are for the blend B350

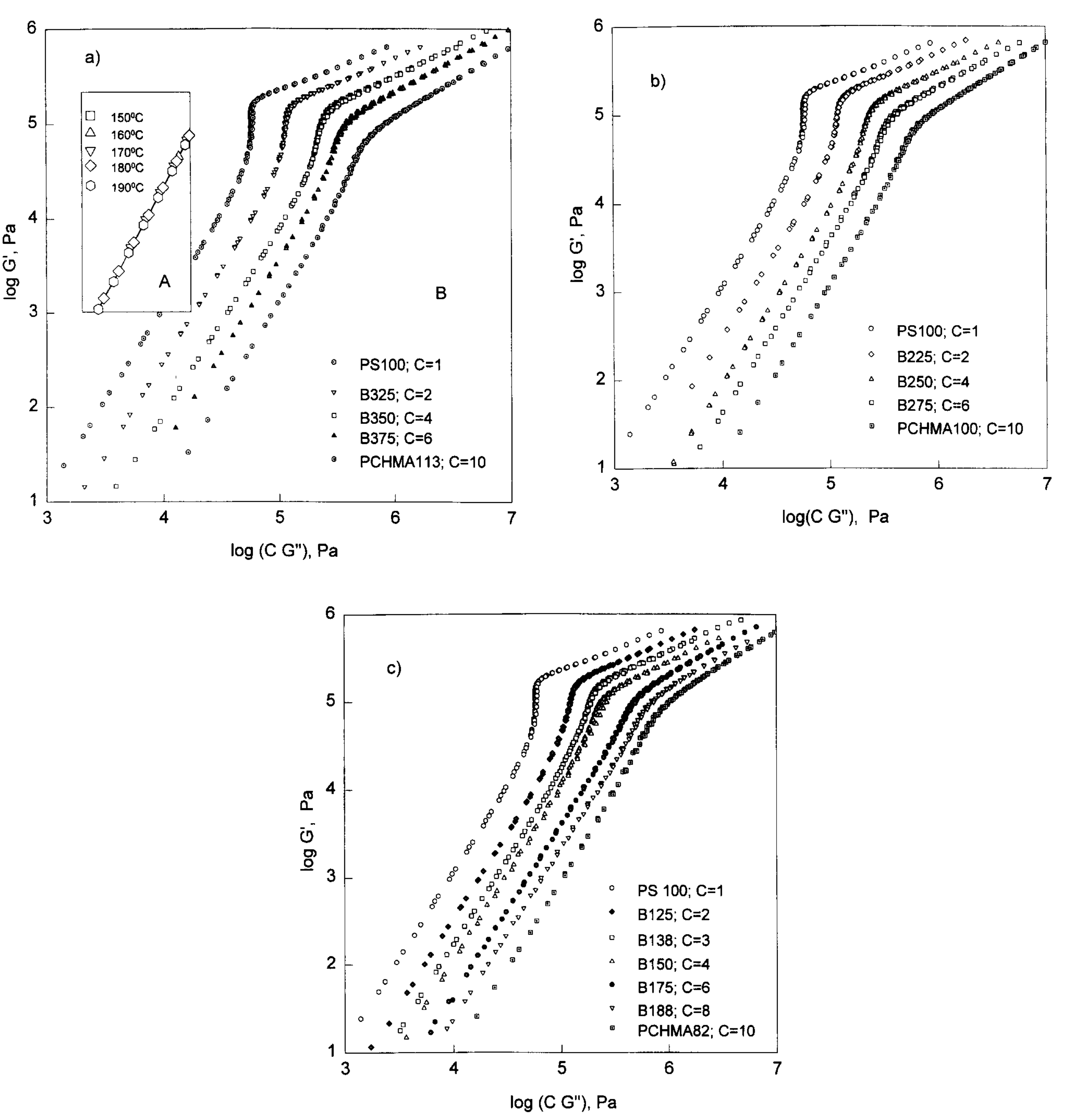

Figure 6 Plots of log G' *versus* log G'' for the different isotherms of the blends (a) B3 (PS100/PCHMA113), (b) B2 (PS100/PCHMA100) and (c) B1 (PS100/PCHMA82). The inset A in (a) indicates the points of the different temperatures for the PS blend component

and the PS. The expected WLF (Williams–Landel–Ferry) behaviour was found. The C_1 and C_2 values are located in the range known from linear homopolymers: $C_1^{PS} = 5.7$, $C_2^{PS} = 129.4$ K, $C_1^{PCHMA} = 12.5$ and $C_2^{PCHMA} = 241.1$ K. The values for PCHMA are molecular-weight-independent and the given values represent averages of the three molecular weights.

To check the validity of TTS for the blends, the dynamic moduli were plotted according to Han[28] (*Figure 6*). This kind of plot employs raw data that are not shifted. If the data points of the different isotherms fall on a common line in a log G' *versus* log G'' presentation and if the scatter in the data or the linewidth is not too broad, time–temperature superposition should be valid and miscibility is assumed[28]. To be sure that individual relaxation processes stemming from the blend components either do not occur or are not significant, we took the Han plot with the worst coincidence, i.e. B150, and analysed the isotherms. *Figure 7* shows a linear plot of G'' data over a logarithmic frequency scale. The different curves were shifted ($T_{ref} = 180°C$) to obtain coincidence between them at the smallest frequencies. From this figure it is seen that for $a_T\omega > 1$ rad s^{-1}, a small but systematic deviation from a common curve appears. This systematic deviation supports the idea of individual relaxation of each blend component in a miscible blend as proposed by Colby[20]. Nevertheless, the strength of the deviation, which depends for a given polymer pair on the molecular weights and the distance to the glass transition temperatures of the blend components, is not large in our

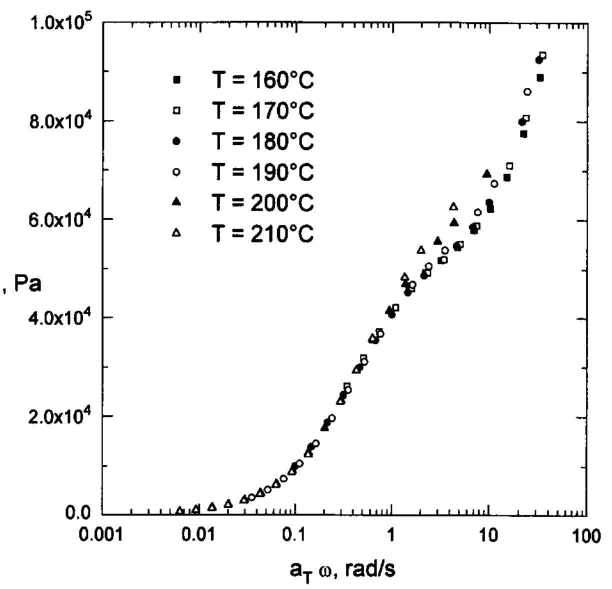

Figure 7 Plot of the loss modulus G'' *versus* the reduced frequency for the blend B150 (50 wt% PS100 and 50 wt% PCHMA82). The different points indicate the different isotherms

case. For other blends (PMMA/PEO^{20}, PB/PI^{21} and 1,4-PB/1,2-PB^{22}), which were stated to be miscible, the deviations are much stronger. Moreover, the Han plots of the mentioned PMMA/PEO^{28} and PS/PVME^{8,28} blends show a much bigger scatter.

Different pairs of polymers show deviations from the TTS in different degrees. To judge about miscibility by rheological measurements, the situation is similar to that if we use the d.s.c. technique to measure the glass transition temperature: we have a broadening of the transition, indicating the appearance of small microheterogeneities. Its scale cannot be quantified from that experiment. In rheology, small deviations from TTS give a hint of the occurrence of microheterogeneities. An estimate of the relative importance of this effect can be given following Colby's procedure^{20} by comparing the tube diameters of the constituent polymers of the blend with the characteristic length scale of the concentration fluctuations. The tube diameters of our polymers are taken from data given by He and Porter^{29}, and the length scale of the concentration fluctuations was calculated using the random-phase approximation^{30} and the interaction parameter given earlier. In Colby's blend, the fluctuations have a length of about 50 Å and the tube diameters are about 40 Å for both polymers. In the view of that author, this corresponds to a situation where the polymers are in a heterogeneous environment. In our case, the tube diameters are 40 Å for PS and about 60 Å for PCHMA and the length of concentration fluctuations is about 40 Å. This corresponds to a more homogeneous situation in comparison to the PMMA/PEO blend and explains the very moderate deviation from TTS.

From all that, we concluded that the TTS is approximately valid for our blend system, and consequently, all blends were shifted to a common reference temperature of 180°C. The shift factors for most blends are nearly the same as that of pure PCHMA. As an example, the shift parameters for the blend B350 are given in *Figure 5* as open squares.

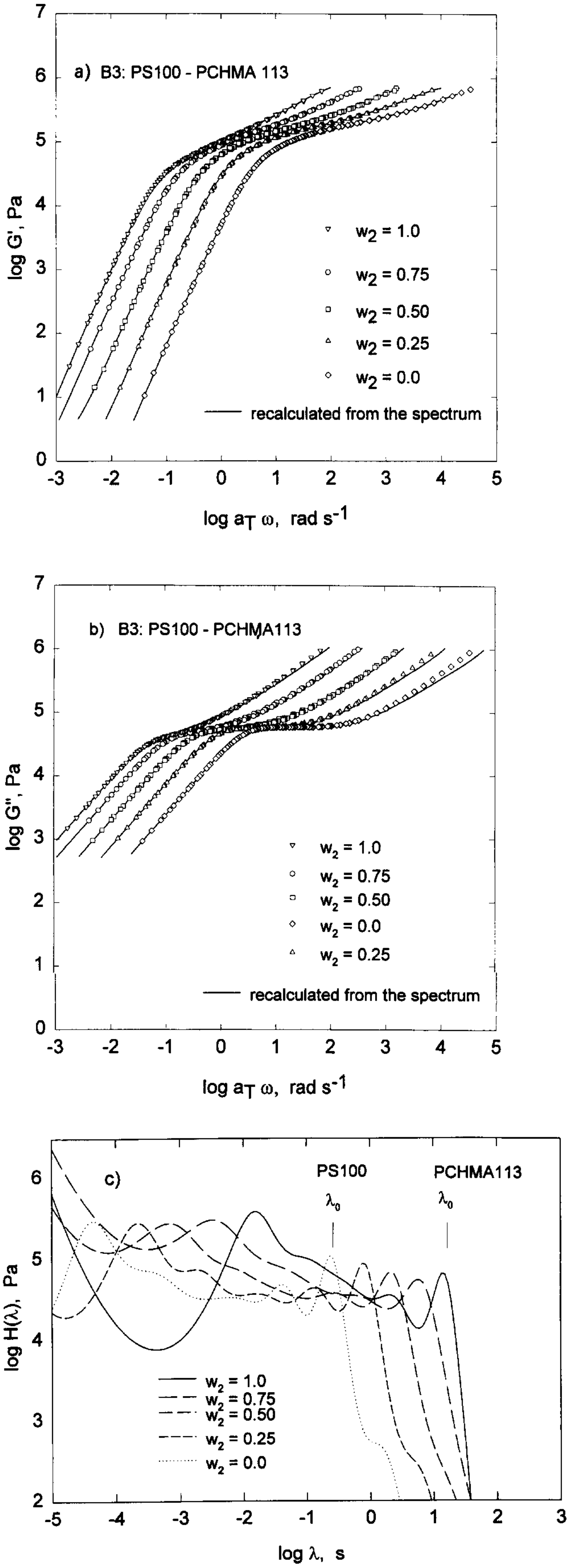

Figure 8 Plots of (a) log G' and (b) log G'' *versus* the reduced frequency for the blend B3 (PS100/PCHMA113). The points are the data and the lines represent these material functions as recalculated from the relaxation-time spectrum H

The master curves of G' and G'' for the blend system B3 are given in *Figures 8a* and *8b*. What we observe is the usual behaviour of polymeric melts: the plateau region and the flow region (region of terminal relaxation). In this double-logarithmic plot no relaxation of individual chains or species is observed. In *Figure 8c* the corresponding relaxation-time spectra are given. These spectra are calculated using a regularization method[31–33] for the inversion of the well known integral relations. In accordance with the observations cited above, the relaxation-time spectra show only one terminal relaxation time, λ_0.

From the master curves, it is possible to determine the zero-shear-rate viscosity η_0 using the relation:

$$\eta_0 = \lim_{\omega \to 0} (G''/\omega) \tag{6}$$

where G'' is the loss modulus and ω the frequency. *Figure 9* shows the plot of η_0 vs. the weight fraction of PCHMA in the blend, w_2, for the three blend systems. All systems show positive deviation from logarithmic additivity.

We fitted these data and those of the other material parameters to a quadratic mixing rule for the logarithm of the material parameter, m, as follows:

$$\log m = w_1^2 \log m_1 + w_2^2 \log m_2 + 2w_1 w_2 \log m_{12} \tag{7}$$

where w_2 is the weight fraction of PCHMA. Now, $m \equiv \eta_0$, $m_1 = \eta_{01}$ and $m_2 = \eta_{02}$. The viscosities η_{01} and η_{02} are the zero-shear-rate viscosities of PS100 and PCHMA respectively. The only free fitting parameter is the parameter m_{12}, which takes into account the interaction between dissimilar chains. This parameter is given in *Table 2* for the different cases considered here. The reason why we used this type of relation is that, among all known mixing rules, equation (7) gives the most accurate representation of experimental data. This type of equation was also used successfully for the description of 'mixing behaviour' of binary mixtures of monodisperse PMMA melts[30].

In *Figure 10*, the plateau moduli for all three systems are plotted against composition. As before, a positive deviation from linearity is found. The fit of equation (7) to the plateau moduli (now, $m \equiv G_p$, $m_1 = G_{p1}$, $m_2 = G_{p2}$ where G_{p1} and G_{p2} are the plateau moduli of the pure components in this case) yields a value for a plateau modulus, G_{p12}, corresponding to entanglements between dissimilar chains[15,17] which is given in *Table 2*. We determined only one curve for the composition dependence of the plateau moduli of the blends. This value is based on the assumption that the different PCHMAs exceed M_e.

On the basis of this value, Wu calculated an entanglement molecular weight, M_{e12}, according to a

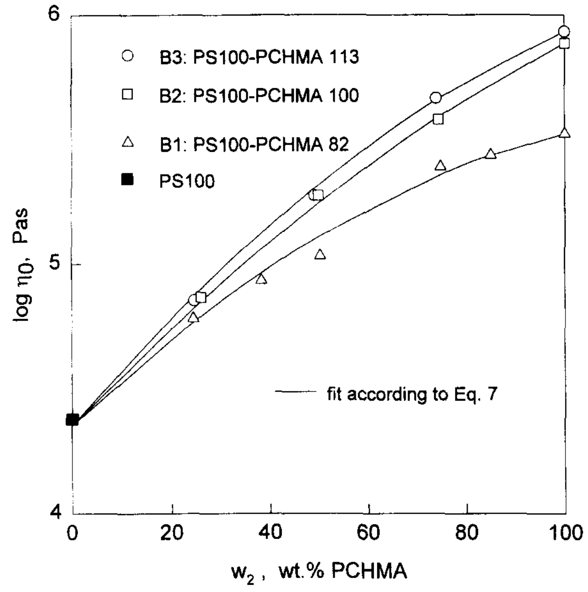

Figure 9 Composition dependence of the Newtonian viscosity η_0 of the blends. The lines correspond to a data fit according to equation (7)

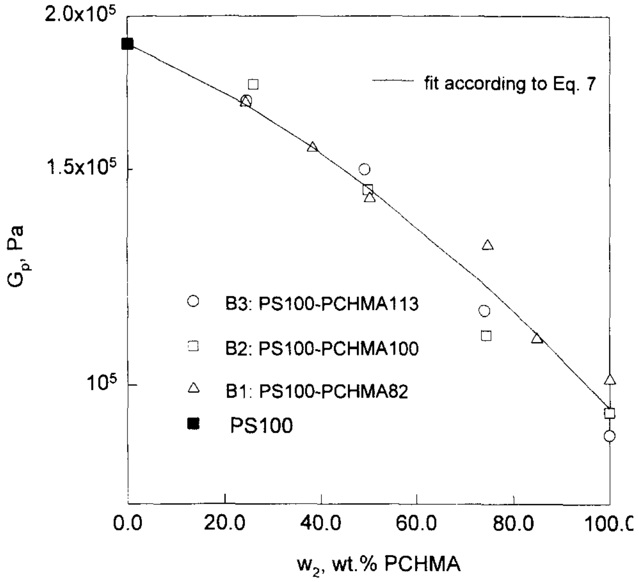

Figure 10 Composition dependence of the plateau modulus of the blends. The lines correspond to a data fit according to equation (7)

Table 2 Material parameters like the Newtonian viscosity η_0, the plateau modulus G_p and the terminal relaxation time λ_0 for the blend components and the characteristic values for the 1–2 interaction between dissimilar chains of these parameters according to equation (7) at $T = 180°C$

	Material parameters of the pure polymers			Fit parameters of the blends with PS100		
Polymer	$\eta_0 \times 10^{-4}$ (Pa s)	$G_p \times 10^{-4}$ (Pa)	λ_0 (s)	$\eta_{012} \times 10^{-4}$ (Pa s)	$G_{p12} \times 10^{-4}$ (Pa)	λ_{012} (s)
PS100	2.4	19	0.25	–	–	–
PCHMA82	33.4	10.1	4.6	16.6	15.5	3.6
PCHMA100	76.9	9.5	12.3	24.6	15.5	3.5
PCHMA113	85.8	9.1	15.4	27.7	15.5	3.3

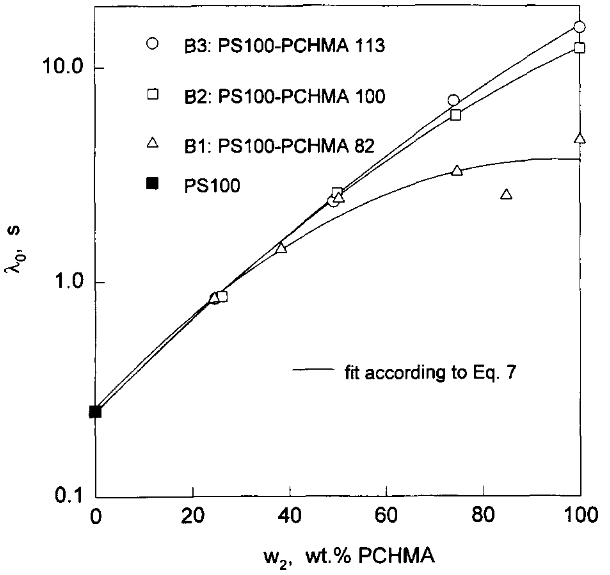

Figure 11 Composition dependence of the terminal relaxation time λ_0 of the blends. The lines correspond to a data fit according to equation (7)

modified equation (5):

$$M_{e12} = (\rho_1\rho_2)^{1/2}RT/G_{p12} \qquad (8)$$

Defining the case $G_{p12} = (G_{p1}G_{p2})^{1/2}$ as a reference state that corresponds to an unchanged entanglement molecular weight in the blend in comparison to those in the homopolymers, he was able to account for the altered entanglement density. Our case corresponds to G_{p12} greater than $(G_{p1}G_{p2})^{1/2}$ and implies a smaller entanglement molecular weight and therefore an enhanced interaction. In other words, the chains are getting more flexible. This picture is consistent with Wu's picture of cooperative relaxation and chain motion. The interaction viscosity for which a similar calculation can be performed also supports this idea. These values are also given in *Table 2*.

Finally we would like to discuss the composition dependence of the terminal relaxation time λ_0 (*Figure 11*). This value was determined as the characteristic time labelling the last maximum in the relaxation-time spectrum (see *Figure 8c*). Again, the dependence of the terminal relaxation time on composition is similar to that of the viscosity. This is not surprising because for linear monodisperse polymers it is known that this time is given by the ratio of Newtonian viscosity and plateau modulus. Owing to the slight composition dependence of the plateau modulus (see *Figure 10*) the relaxation time has nearly the same dependence as the viscosity.

The fit of equation (7) to the terminal relaxation time ($m \equiv \lambda_0$ in this case) yields values for this time which are given in *Table 2*. In this case, the following notations are used in equation (7): $\lambda_{01} = m1$, $\lambda_{02} = m_2$, where λ_{01} and λ_{02} are the relaxation times of the pure components. All three values are nearly the same and significantly lower than those of the pure PCHMAs.

SUMMARY AND CONCLUSIONS

The blend system PS/PCHMA shows *LCST* behaviour with a lower critical solution temperature of about 245°C. D.s.c. measurements reveal only one glass transition. The width of this transition is small enough to conclude on miscibility. Additionally, the q parameter in the Gordon–Taylor–Kwei equation is in the range typical for miscible blends. Time–temperature superposition is observed approximately for the systems under consideration. The shift factors follow WLF behaviour. Comparing the validity of TTS of our blends with that of other blend systems, we found that our data follow this principle best.

From the master curves the relaxation-time spectrum was determined, and from them the terminal relaxation time λ_0. The existence of a single terminal relaxation time whose value is between those of the pure components gives evidence of enhanced interactions.

Such rheological material parameters like zero-shear-rate viscosity η_0 and plateau modulus G_p are derived directly from the master curves and analysed together with the terminal relaxation time as a function of composition. The logarithm of the material parameters follows a quadratic mixing rule with parameters η_{012}, G_{p12} and λ_{012} that account for the interaction between dissimilar chains. We found, contrary to Wu[15,17], that there is no stiffening of the chains stemming from interchain interactions. The mobility for the PCHMA molecules in the system PS/PCHMA is greater than in pure PCHMA and therefore we found a positive deviation of G_p. This means that entanglement between dissimilar chains is improved. The interaction viscosity shows the same tendency.

We conclude that the enthalpic interactions have a pronounced influence on the viscoelastic behaviour of the investigated blends. This raises the hope that a rheological method for the determination of the interaction parameter χ should be possible.

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