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polymer communications

Phase behaviour and interfacial tension of polysiloxane blends

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The cloud point curve for blends of poly(dimethyisiloxane) (PDMS, $M_w = 2.5\,\mathrm{kg\,mol^{-1}}$) and poly(hexylmethylsiloxane) (PHMS, $M_w = 113\,\mathrm{kg\,mol^{-1}}$] was determined turbidimetrically. The system demixes upon cooling and the UCST amounts to 36°C. The interfacial tension γ was determined at the critical composition for three temperatures by means of a spinning drop tensiometer. The dependence of γ on the reduced critical temperature can be described within experimental error by both the mean field theory and the Ising-3D theory. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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Introduction

While interfacial tensions are known for many *highly incompatible* polymer pairs[1], data in the critical region have to our knowledge only been measured for oligomers[2–4]. Due to experimental difficulties resulting from high viscosities and slow phase separation reliable values for truly high molecular weight blends are difficult to obtain. It is therefore still unclear which of the theoretical approaches used to describe the critical behaviour of polymer mixtures is correct.

We therefore wanted to measure interfacial tensions γ for systems where the molar mass of both components is as large as possible. For that purpose we choose mixtures of different poly(siloxane)s since these substances have very low glass transition temperatures. Phase diagrams are known for oligo(dimethylsiloxane)/oilgo(methylphenylsiloxane)[5] and for poly(dimethylsiloxane)/poly(ethylmethylsiloxane)[6,7]. Unfortunately the latter system is, however, unsuited for the envisaged study since the densities of the components are too similar for reliable γ measurements. As a solution the ethyl group of the second component of the latter system was replaced by a hexyl group; although the miscibility decreases markedly by this change, it is still possible to measure phase diagrams and interfacial tensions for these blends.

Experimental

Poly(dimethylsiloxane) PDMS 2.5 (the numbers of the abbreviations give the weight average molar mass in kg mol^{-1}) and poly(hexylmethylsiloxane) PHMS 113 were commercial samples supplied by Wacker (PDMS) and Petrach (PHMS), respectively. Both polymers are terminated by trimethylsilyl groups according to the suppliers. Molecular weight of the PDMS and polydispersities of both polymers were determined by means of GPC in toluene (using the universal calibration for PDMS) while the molecular weight of PHMS was measured by light scattering in toluene. Details are given in *Table 1*.

Blends were prepared by stirring the mixtures at approximately 15–20°C above the phase separation temperature for 12 h. The clear coexisting phases required for interfacial tension measurements were obtained by keeping the blend for 1 week in a thermostat and separating the macroscopically coexisting phases with a syringe.

Turbidities were measured at a fixed cooling rate of 0.1°C min^{-1} by passing a laser beam of intensity I_0 through the mixtures leaving it with the intensity I. From the linear part of the plots of I/I_0 *versus* T in the region of phase separation two characteristic temperatures can be obtained: by its intercept with $I/I_0 = 1$ the upper limit T_U of the demixing temperature and with $I/I_0 = 0$ the corresponding lower limit T_L.

The critical point was obtained in the following manner. The phase volume ratios r were measured for different constant temperatures as a function of the volume fraction φ_{PHMS} by slowly cooling from the homogeneous state to the equilibrium temperature using graduated 10 mL cuvettes. The separation of two clear macroscopic phases typically takes 10 days. Knowing $r(\varphi_{PHMS})$ the composition with $r = 1$ was determined and plotted in the phase diagram; the intersection of the extrapolation of the thus obtained curve with the cloud point curve yields the critical data.

Interfacial tensions between the coexisting phases were determined with a commercial spinning drop tensiometer (Krüss Germany). Densities (given in g cm^{-3}) of the pure polymers and of the coexisting phase were measured with 1 mL pycnometers as a function of temperature t (in °C) yielding $\rho_{PDMS} = 0.9538 - 0.0007t$ and $\rho_{PHMS} = 0.9346 - 0.0006t$.

The viscometric information stems from measurements on a Carri-Med CSL 500 instrument using a cone and plate geometry.

Results and discussion

In the range of $\rho_{PHMS} = 0.2$ to 0.4 the temperature dependence of the turbidity resembles that of polymer solutions. The difference between T_U and T_L, the two extrapolated characteristic temperatures, is less than 1°C in this region. A typical example is given in *Figure 1*(a).

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Table 1 Characterization of the polymer samples with toluene as solvent

Polymer	M_w (kg mol^{-1})	M_w/M_n	dn/dc (mL g^{-1})	A_2 (mL*mol g^{-2})
PDMS	2.5 (GPC)	1.28 (GPC)	—	—
PHMS	113 (LS)	3.73 (GPC)	0.0559, $T = 30$°C	2.82*10^{-4}, $T = 30$°C

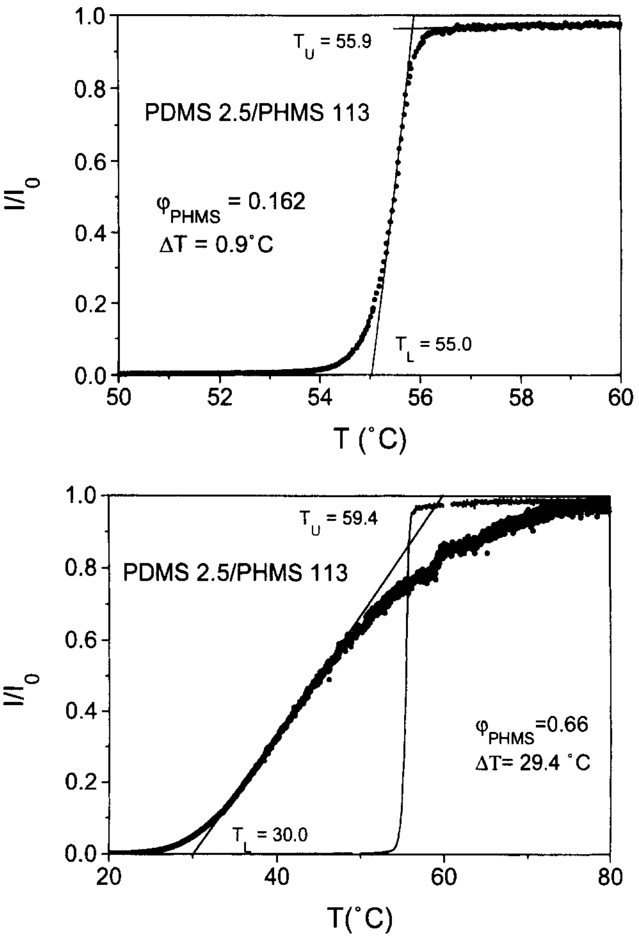

Figure 1 Transmittance as a function of temperature for blends of PDMS 2.5 and PHMS 113 at the indicated volume fractions of PHMS. (a) Example for the development of turbidity within a comparatively small temperature interval; and (b) for a rather smeared out behaviour [for comparison the curve of part (a) is again reproduced in this graph]

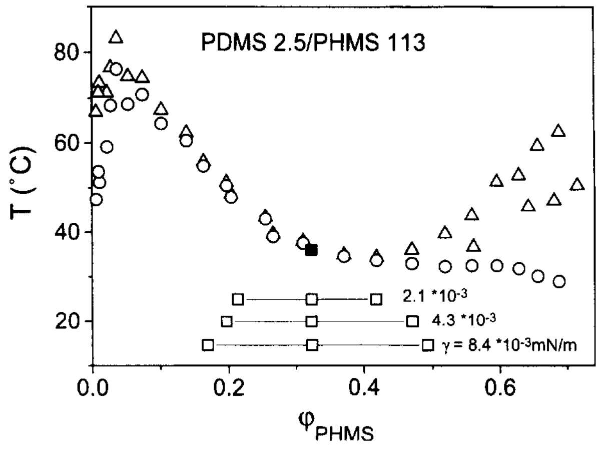

Figure 2 Cloud point curve for the system PDMS 2.5/PHMS 113. The open triangles give the upper limit of the demixing temperature (T_U) and the open circles the lower limit (T_L): the critical point is indicated by a full square. Also shown are some tie lines (the compositions of the coexisting phases are represented by squares) for a critical overall composition and the corresponding interfacial tensions 2.1 × 10^{-3} mN m^{-1} at 25°C, 4.3 × 10^{-3} mN m^{-1} at 20°C and 8.4 × 10^{-3} mN m^{-1} at 14.6°C

For compositions closer to the pure components the difference between the two temperatures increases significantly until only the first characteristic temperature can be obtained for high contents of PHMS. An example for a broad transition range is shown in *Figure 1*(b). The errors in T_U and T_L may become rather large for these compositions due to the comparatively short linear part of the curves.

The phase diagram constructed from the measured T_U and T_L data is given in *Figure 2*, and it shows a pronounced minimum for the first characteristic temperature and a shoulder for the second characteristic temperature, respectively. The occurrence of a bimodal cloud point curve or a shoulder, respectively, has been observed for other polymer blends e.g. polystyrene/polyisoprene[8] where this phenomenon appears to be very sensitive to molecular weights and their distributions.

It is obvious that the actual phase diagram remains rather uncertain, particularly on the PHMS side. The experimentally determined critical point at 36 ± 1°C is not located in the maximum ($\varphi_{PHMS} \cong 0.05$ and $T \cong$ 80°C), but shifted significantly from the maximum of the cloud point curve towards higher contents of PHMS, the component of larger polydispersity, as expected from theoretical considerations[9].

In order to know whether the region in the phase diagram between the two characteristic temperatures corresponds to a homogeneous state or to a two phase equilibrium, a sample with $\varphi_{PHMS} = 0.6$ was kept at 40°C for several days. The sample was opaque but did not show any indication of macroscopic phase separation, even when subjected to a centrifugal field 700 times larger than that of the earth for 6 h. A further indication that the system does not phase separate under these conditions was obtained from viscosity measurements as a function of temperature. In the entire range between 90 and 15°C one does not observe any indication for the segregation of a second phase, in contrast to the situation observed in the critical region. It is presently still unclear why this is so; one simple explanation could be that the viscosity of the coexisting phases is nearly identical.

A possible explanation of the strange cloud point curve on the PHMS side of the phase diagram could lie in the formation of clusters by the hexyl side chains of this polymer. Such a intersegmental association would end up with some sort of microphase separation, i.e. larger local differences in composition, which might cause the opaqueness of the sample. This behaviour would be analogous to the formation of a thermoreversible gel in a theta solvent, observed for poly(n-butyl methacrylate)[10]; with the present polymer blend, PDMS could be considered to take the place of the theta solvent in the case of the solution. However, more research, e.g. detailed dynamic mechanical measurements, would be necessary to clarify this situation.

Figure 2 also gives the tie lines and interfacial tensions for three temperatures and the critical overall composition; the compositions of the coexisting phases were determined by measuring their refractive indices n, assuming a linear concentration dependence. We refrained from the experiments concerning $n(\varphi)$ or the application of more sophisticated equations in view of the inevitable and much larger

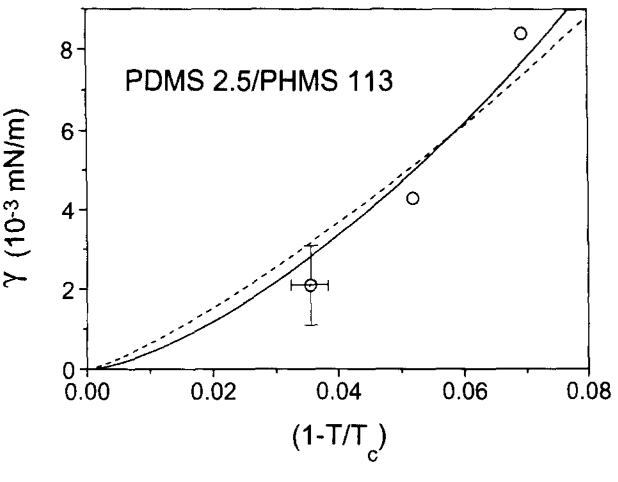

Figure 3 Interfacial tension γ for a mixture of PDMS 2.5 and PHMS 113 of critical composition as a function of the reduced distance to the critical temperature; the corresponding dependence calculated from the mean field theory is shown as a full line and that resulting from the Ising-3D model as a broken line. The error bars indicated for the lowest interfacial tension become only slightly smaller as the reduced temperature is increased

experimental uncertainties in the determination of the interfacial tension. As indicated in *Figure 2*, γ results extremely small as compared to the values of incompatible blends, in accordance with the theoretical expectation. It is now investigated whether the temperature dependence of γ can be described by scaling laws. In terms of the reduced critical temperature $\tau = (1 - T/T_c)$ the scaling law for the interfacial tension reads[11]

$$\gamma = \gamma_\tau \cdot \tau^\mu \tag{1}$$

with μ being the critical exponent.

According to mean-field theory the value of μ amounts to 1.5; it is 1.26 for the Ising-3D theory. The measured interfacial tensions together with the theoretical predictions are shown in *Figure 3*. The resulting prefactors γ_τ = 0.422 mN m^{-1} (mean field) and 0.213 mN m^{-1} (Ising-3D) are considerably smaller than those typical for polymer solutions[11].

All data points are situated closer to the theoretical curve calculated on the basis of the mean field theory than to that resulting for the Ising-3D model; this observation, however, does not justify the statement that the former theory describes reality better than the latter in view of the low number of measurements and the experimental uncertainties plus any unknown effects of the rather broad molecular weight distribution. It is worthwhile to note in this context that the errors with the present, rather difficult measurements mainly result from the very small differences in the density of the coexisting phases and from the uncertainties in the determination of the critical temperature. Nose *et al.*[2] have found for oligo(styrene)/oligo(dimethylsiloxane) a critical exponent of 1.27 indicating Ising-3D behaviour. However, due to the lack of experimental data it remains unclear which behaviour is true for high molecular weight polymers. It is therefore presently impossible to decide which of the theoretical approaches is better for the description of truly high molecular weight blends.

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