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Glass transition temperatures of microphase-separated semi-interpenetrating polymer networks of polystyrene-*inter*-poly(*cross*-2-ethylhexyl methacrylate)

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The glass transition temperature of semi-interpenetrating polymer networks (semi-IPNs) of atactic polystyrene (PS) in crosslinked methacrylates was studied by systematic variation of the morphology, that is domain size, continuity and concentration in the domains. Semi-IPNs were prepared from homogeneous polymer solutions in a two-step process, of liquid–liquid demixing upon cooling followed by gelation, and subsequent ultra-violet polymerization. Semi-IPNs with very little developed phase separation could be obtained, which exhibited optical transparency and a mechanical behaviour similar to that expected for corresponding homogeneous systems. A low PS concentration inside the domains indicated that these domains consisted of only an interphase layer. Samples that were phase separated to a larger extent showed normal two-phase behaviour.

(Keywords: semi-IPNs; glass transition; phase separation)

INTRODUCTION

Ideally, interpenetrating polymer networks (IPNs) can be described as homogeneous blends of two or more components, of which at least one polymer is cross-linked. In the latter case a semi-IPN is formed. Owing to the incompatibility of most polymers, (semi-)IPN synthesis usually results in a phase-separated system. Because of topological interlocking, the domain sizes found in semi-IPNs can be considerably smaller than those obtained by blending of linear polymers. For instance, in the case of sequential IPNs, where a cross-linked polymer had been swollen in a second monomer that was subsequently crosslinked, the domain sizes are determined by the crosslink density of the first network, and can be of submicrometre size[1]. Under suitable conditions, it is possible to obtain two continuous phases, even when the volume fractions of the constituent polymers are rather different. In this case, interesting mechanical and swelling properties are observed, and the materials can be used as adhesives or noise damping materials.

Because morphology formation in the conventional synthesis of semi-IPNs depends on a number of parameters that cannot be controlled strictly, systematic studies of the mechanical behaviour (i.e. glass transition temperatures) as a function of the morphology are difficult to perform and therefore scarce[2–4]. Determination

of the glass transition temperature is an often used method to determine whether an amorphous polymer mixture is phase-separated. If the glass transition temperatures of the constituent polymers in a blend are significantly different, two T_g values will be observed in the demixed state, while a homogeneous mixture is characterized by a single T_g (ref. 5). A complementary technique is the investigation of the morphology by light and electron microscopy.

The present study was directed towards investigation of the glass transition temperatures of semi-IPNs, in correlation to a systematic variation of the morphology. Semi-IPNs were prepared via a two-step synthesis, which separated morphology formation and polymerization. Thus, domain sizes and whether a dispersed or co-continuous system was formed could be varied rather widely, without changing the overall semi-IPN composition.

Semi-IPN preparation and obtainable morphologies

In conventional semi-IPN synthesis, it is rather difficult to control the final morphology. In the study described here, semi-IPNs with well controlled morphology were prepared by a two-step process which makes use of the intersection of the liquid–liquid demixing curve of a polymer solution and the T_g–concentration curve of the plasticized polymer[6,7]. The steps include (1) (spinodal) liquid–liquid demixing upon cooling a solution of a polymer in a monomer mixture followed by physical arrest of phase separation by vitrification of the polymer-rich phase and (2) u.v. polymerization and

crosslinking of the liquid monomeric solvent below the gelation temperature. By rapid quenching of the polymer solution into the spinodal demixing region, binodal demixing could be repressed. No indication for additional phase separation due to polymerization could be observed.

In a previous paper[7], we investigated the morphology development of semi-IPNs of 4 wt% polystyrene (PS) in a methacrylate mixture with transmission electron microscopy. Depending on the viscosity of the polymer solution (polymer concentration and molecular weight) and the quench conditions (quench temperature and geometry of the sample), several morphologies could be obtained. Initially, small PS-rich domains were formed which were separated over regular distances. A co-continuous morphology associated with spinodally demixed systems only developed in a relatively late stage of demixing.

Spinodal demixing originates from concentration fluctuations of different wavelengths, of which the most dominant one will most rapidly increase in amplitude (concentration difference between the polymer-rich and the polymer-poor phase)[8]. It was suggested that the separated domains visible in the transmission electron micrographs[7] represented the high-polymer concentration segment of the most dominant concentration fluctuation ('summit'), which could pass beyond the gelation concentration. The domains were separated over a distance equal to one or several times the wavelength of spinodal demixing. Because the concentration difference between the polymer-lean and polymer-rich phases increases with time, a higher PS concentration can be expected for domains that were arrested in a later stage of demixing than for domains arrested in a very early stage. Thus, the final semi-IPN morphology can be varied systematically by arresting phase separation of a polymer solution in different stages.

Growth of the domains could be restricted by physical gelation of the PS-rich phase, and by the formation of the methacrylate network[7]. However, the question remained whether the phase composition was also retained during u.v. polymerization. This will be investigated by determination of the glass transition temperatures of such semi-IPNs in correlation to a systematic variation of the morphology. The present paper describes first the phase behaviour and morphology of PS in poly(*cross*-2-ethylhexyl methacrylate) (PS/EHMA) depending on PS concentration and quench temperature. Subsequently, a correlation between the glass transition temperature and the morphology is attempted. Semi-IPNs of PS/EHMA were chosen for two reasons: (1) both constituent components had T_g values that differ considerably (100°C and 15°C respectively), and (2) this system was expected to yield morphologies similar to those formerly obtained with PS/methacrylate mixtures[7], based on the viscosity of the PS/EHMA monomer solution[9].

Determination of miscibility of polymers

Glass transition temperatures of homopolymers depend on the molecular structure of the polymer (chain stiffness, number and bulkiness of the side groups, and the inter- and intramolecular interactions) and on the crosslink density of the polymer. Typically, a crosslinked polymer exhibits a higher and significantly
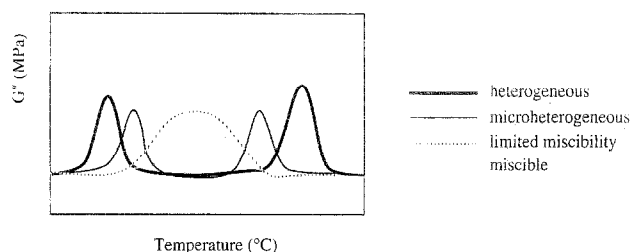
Figure 1 Generalized mechanical loss $(G''(T))$ behaviour for different types of polymer blends (50/50)

broader T_g than a linear polymer because of the different and restricted mobilities of the crosslinked chain segments[10]. Because of this 'smearing' of T_g, thermal methods (like differential scanning calorimetry) are less suitable to determine the glass transition temperature of semi-IPNs than mechanical methods. During the study reported here, mechanical loss spectra measured in shear experiments by means of a torsional pendulum were used to determine T_g.

The degree of phase separation of a polymeric sample containing two or more phases can be evaluated from the mechanical loss modulus as a function of temperature $(G''(T))$; see *Figure 1*. Two completely separated phases will show two different G'' peaks at the positions of the pure polymers. A low degree of miscibility, or microheterogeneity, induces the two peaks to shift towards each other. A very low degree of phase separation will result in one very broad T_g between the two peaks of the pure components. True miscibility is indicated by the existence of one narrow peak, which is situated between the T_g values of the pure polymers according to the concentration of both polymers. The Fox equation, $1/T_g = w_1/T_{g,1} + w_2/T_{g,2}$, with w the polymer weight fraction, can be used to describe the T_g of a homogeneous mixture[11].

Two approaches have been introduced to explain the merging of two glass transitions into one broad transition in the case of microphase-separated polymer blends[12,13]. The first states that the volume required for chain motion (50 monomer units) is not available between different regions of space with different compositions. Because of the increasing contribution of the interfacial fraction, a broadening of T_g will result. According to the second theory, local concentration fluctuations are expected to occur in the boundary or interphase region at the level of 50–100 Å. As a result, these regions will display their own T_g. Both theories indicate that in domains smaller than 10 nm, which is approximately the radius of gyration of the polymer, T_g will be broadened because these domains consist only of an interphase layer.

Studies on block copolymers with strongly incompatible blocks revealed however that phases with domain sizes of molecular dimension still showed two glass transition temperatures at the position of the homopolymers[14,15]. Mechanical studies on full IPNs, which were shown by electron microscopy to have rather large domains, yielded two separate T_g values[2-4]. 'Increased compatibility', as indicated by a smaller domain size, resulted in an inward shift of both T_g values and eventually one broad intermediate T_g was found. In the latter case, the T_g was consistent with the prediction of

the Fox equation. A comparison of semi-IPNs and full IPNs[4] showed that full IPNs are less strongly phase-separated than semi-IPNs due to faster catenation of chains during polymerization. Typically they showed a narrower G'' peak in the loss spectrum.

EXPERIMENTAL

Materials

Atactic polystyrenes were prepared anionically. Molecular weights were measured by g.p.c./l.a.l.l.s. (Waters LALLS detector Chromatix KMX-6): PS2M, $M_n = 1739\,000\,\mathrm{g\,mol^{-1}}$, $M_w/M_n = 1.19$; and PS100K, $M_n = 100\,000\,\mathrm{g\,mol^{-1}}$, $M_w/M_n = 1.23$.

Monomer 2-ethylhexyl methacrylate (EHMA) was crosslinked with 8 mol% ethylene glycol dimethacrylate (EGDMA).

Phase diagrams

Cloud-point curves were visually determined by turbidity measurements at a cooling rate of $0.2°C\,\mathrm{min^{-1}}$. The temperature at which opalescence was observed was assumed to be the demixing temperature T_D ($\pm 1°C$). The low polydispersity of the polymers ensured that the measured cloud-point curve resembled the binodal curve quite accurately. Gelation temperatures (T_{gel}) of low concentrated solutions were determined by slowly cooling the solutions in test tubes, until elastic behaviour was qualitatively observed, and the solution could be removed in one piece. Glass transition temperatures of highly concentrated solutions were measured by d.s.c. (Perkin Elmer DSC7) and extrapolated to $1\,\mathrm{K\,min^{-1}}$ heating rate ($\pm 2°C$).

Semi-IPN preparation

Homogeneous solutions of polystyrene in EHMA with 8% EGDMA (crosslinker) and benzoin methyl ether (u.v. initiator) were rapidly quenched to a temperature below the gelation temperature. Films were prepared by filling moulds at room temperature with the polymer solution and bringing them subsequently into contact with the cooling block, while a smaller precooled aluminium block was simultaneously pressed on top of the film. Cooling rates of 60 to $140°C\,\mathrm{s^{-1}}$ could be obtained by quenching to $-60°C$ and $-100°C$ respectively[7]. U.v. polymerization was initiated below T_{gel} with two 4 W u.v. lamps (366 nm) and the samples were irradiated at low temperature for 10 h to ensure high conversion of the methacrylate monomer. Post-curing was performed by u.v. irradiation at room temperature (15 W), and by a heat treatment of 20 min at 100°C without noticeable changes in the morphology.

Transmission electron microscopy

A JEOL 200 CX transmission electron microscope (200 kV) was used to study the morphology. Samples for transmission electron microscopy were cut out of the middle of the films on a LKB 2188 Ultratome Nova. Sections of 70–90 nm thickness were transferred to copper grids and stained with RuO_4 vapour to enhance contrast[16]. In the TEM micrographs, polystyrene is visible as the dark phase.

Mechanical behaviour

A Myrenne torsional pendulum was used at a frequency of approximately 1 Hz. Samples of 12 mm length, 8 mm width and 1 mm thickness were monitored at a heating rate of $1.5°C\,\mathrm{min^{-1}}$. The glass transition temperature (T_g) was identified as the temperature where the loss modulus G'' had a maximum.

RESULTS

Phase behaviour

The phase diagrams of PS100K (M_n $100\,000\,\mathrm{g\,mol^{-1}}$) and PS2M ($M_n$ $1739\,000\,\mathrm{g\,mol^{-1}}$) in EHMA/8% EGDMA are shown in *Figure 2*. PS2M solutions showed a critical temperature (maximum of the demixing curve) of $-20°C$ at 4 wt% polystyrene and a T_{gel} of $-31°C$. The PS concentration at the intersection point of the demixing curve and the T_g-concentration line, the gelation concentration, was approximately 55–60 wt%. PS100K solutions showed a critical temperature of $-34°C$ at 15 wt% and a T_{gel} of $-44°C$. Because of the lower demixing temperatures, and therefore lower intersection temperature of the demixing curve with the T_g-concentration line, the PS concentration at gelation was found to be approximately 10 wt% lower for PS100K compared to PS2M (at about 45 wt%).

Morphology

Solutions of 4 wt% PS2M in EHMA/8% EGDMA were quenched to different temperatures, thereby inducing different rates of cooling. As a result, demixing was arrested at different stages and different domain structures were obtained. This was a much more dominant effect than the variations in domain size because of the dependence of the concentration fluctuations on the quench depth[7,17].

Figure 3a shows a sample of 4 wt% PS2M in EHMA/ 8% EGDMA that had been quenched to $-80°C$. The polystyrene-rich phase appears black in the TEM micrographs due to preferential staining with RuO_4. Small, dark domains of 60–200 nm thickness are dispersed in the methacrylate matrix. The lack of methacrylate

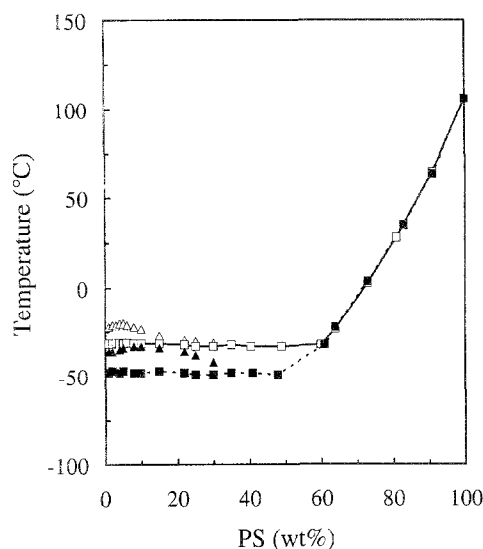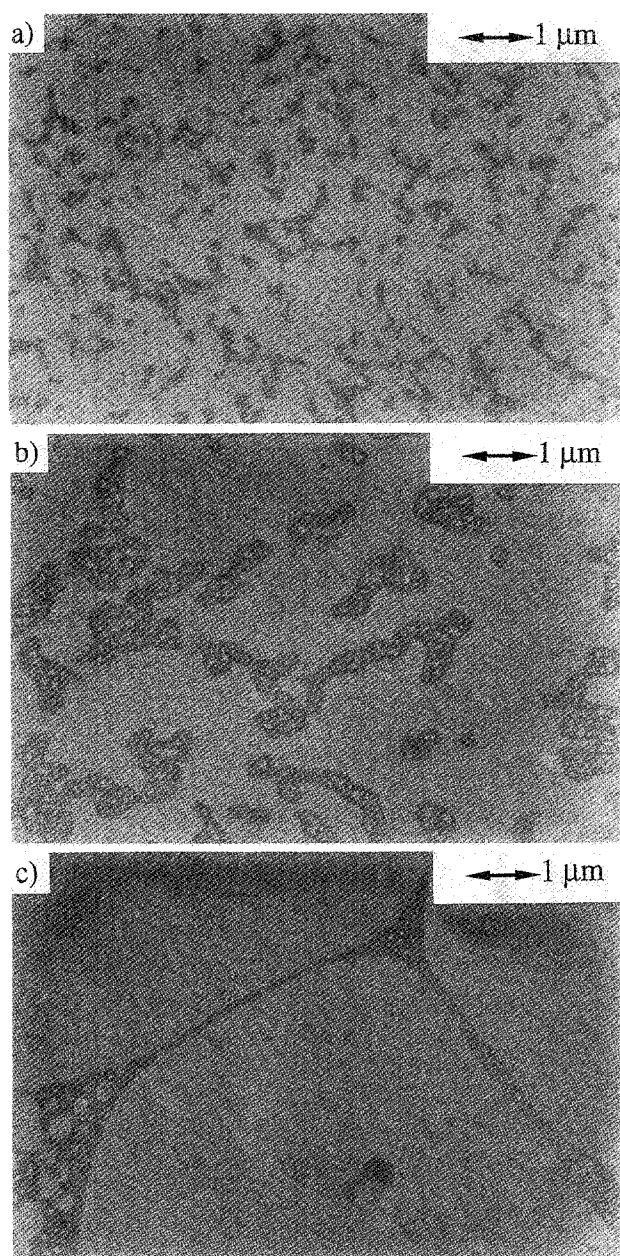**Figure 2** Phase diagram of PS2M and PS100K in EHMA/8 wt% EGDMA, showing the demixing curves and the T_g-concentration lines: ($\triangle$) T_{demix} PS2M; ($\square$) T_g PS2M (full line); ($\blacktriangle$) T_{demix} PS100K; ($\blacksquare$) T_g PS100K (dotted line)
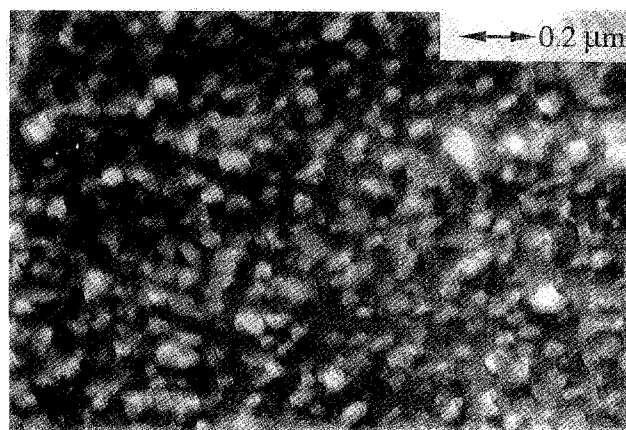
Figure 4. TEM micrograph of film sample of 35wt% PS2M in EHMA/8% EGDMA quenched to −60°C

Figure 3 TEM micrographs of film samples of 4wt% PS2M in EHMA/8% EGDMA: (a) quenched to −80°C; (b) quenched to −30°C; (c) polymerized at room temperature

inclusions within the PS domains indicates that a rather early stage of demixing was arrested, which is prior to the formation of a co-continuous system[7]. *Figure 3b* shows a sample that was quenched to −30°C (approximately T_{gel}) where the domains had grown larger (350–500 nm) and had more inclusions. At this stage, the bicontinuous network had broken up again.

A sample that was prepared by irradiation of the homogeneous PS–EHMA/8% EGDMA solution at room temperature is shown in *Figure 3c*. A cellular structure is visible, with cell sizes of 20–50 μm, and cell walls of 50 nm thickness. This cellular structure remained upon increasing the polymer concentration from 4wt% to 6wt% and 10wt%. However, because of the higher initial viscosity, and thus lower rate of demixing, the cell size decreased by a factor of 2.

When a sample containing 35wt% PS2M was quenched

to −60°C, a continuous PS phase with domains of 40–50 nm size resulted (*Figure 4*). Considering the volume fractions of polystyrene and methacrylate (1:2), the methacrylate phase is also expected to be continuous. For comparison, a 5:95 blend of PS2M and linear poly-EHMA cast from one homogeneous solution of both polymers in chloroform showed a poly-EHMA matrix with spherical and pear-shaped PS domains of 1–4 mm size.

Generally, the influence of polymer concentration and quench conditions on the morphology of PS100K solutions was similar to that of PS2M solutions, i.e. an increase in concentration and a lower quench temperature resulted in smaller domains. However, the lower viscosity and corresponding higher rate of demixing made it impossible to arrest very early stages of demixing in PS100K solutions and the effect of quench temperature was not so pronounced.

Figures 5a–c show the effect of polymer concentration on samples quenched to −60°C. At low polymer concentrations, 5 and 10 wt% (*Figures 5a* and *5b*), separated or slightly connected domains were visible. These were 150–500 nm, which was much larger than predicted from the most dominant domain size[7,17]. They are therefore considered to represent a rather late stage of demixing. The methacrylate inclusions usually found in the PS2M samples do not appear in these pictures.

The 40wt% sample in *Figure 5c*, on the other hand, shows a bicontinuous morphology in which the methacrylate inclusions were only 15–30 nm in size. The thickness of the PS-rich domains was 10–15 nm, which was in the order of the radius of gyration of PS100K (10.4 nm)[7]. Although the sample was more than 1 mm thick and contained 40wt% of an incompatible second polymer, it was completely transparent to the eye.

From the TEM photographs, only the occurrence of a PS-rich phase can be deduced. It is very difficult to estimate the PS concentration *within* the phase. Only in the case of low concentrated solutions could this be done by comparing volume fractions. However, from the phase diagram it is known that the gelation concentration is approximately 55wt% (PS2M) and 45wt% (PS100K). It is therefore expected that samples that were arrested in an early stage had a PS concentration in the PS-rich phase of at most 55–60 wt%. In the course of
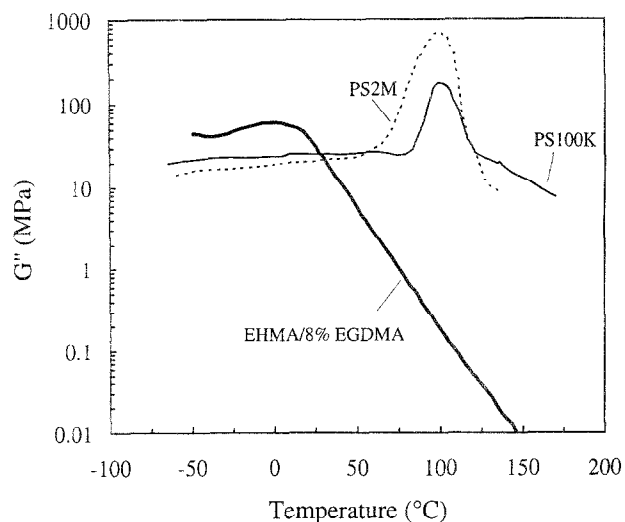
a)   ◄──►1 μm

b)   ◄──►1 μm

c)   ◄──►0.1 μm
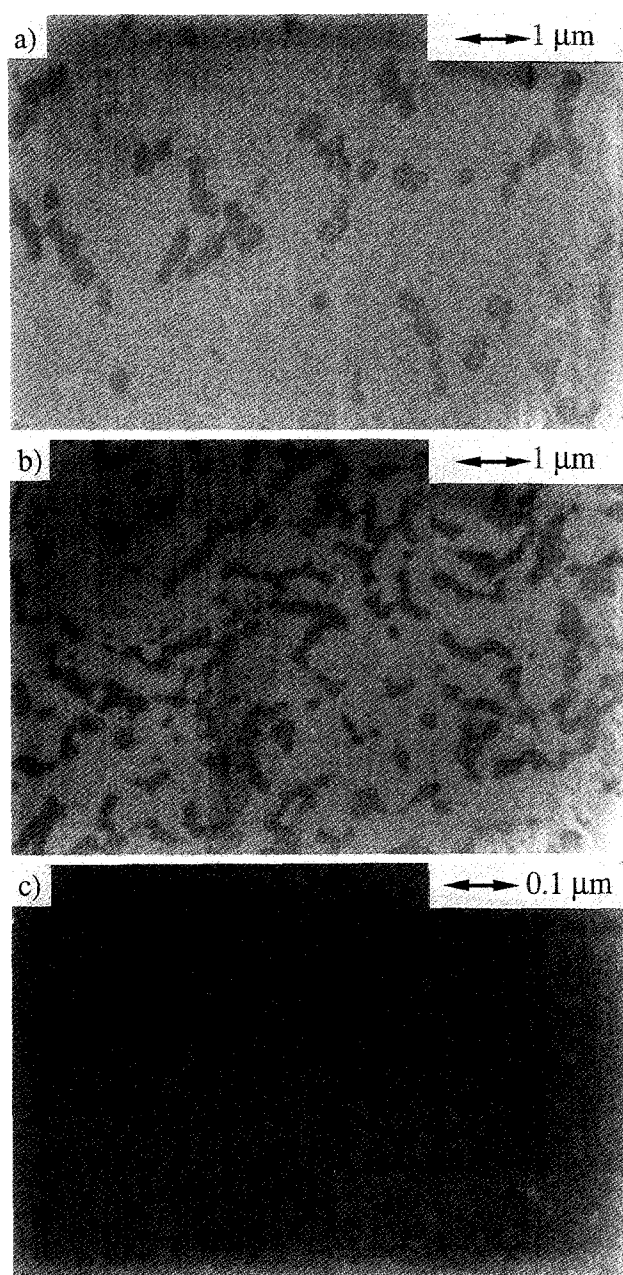
Figure 5   TEM micrographs of samples of PS100K in EHMA/8% EGDMA quenched to 60°C: (a) 5 wt% PS; (b) 10 wt% PS; (c) 40 wt% PS

Figure 6   Mechanical loss $(G''(T))$ spectra of pure PS2M, PS100K and EHMA/8% EGDMA

maximum in G''. The G'' spectra *versus* temperature of pure crosslinked 2-ethylhexyl methacrylate, PS2M and PS100K are shown in *Figure 6*. Poly(*cross*-EHMA) showed a broad T_g at 15°C, while the polystyrene T_g values were 102 and 100°C respectively. In all spectra, the thick solid line represents the $G''(T)$ spectrum of EHMA/8% EGDMA.

The mechanical behaviour of 4 wt% PS2M in EHMA/ 8% EGDMA with different morphologies is shown in *Figure 7*. No glass transition of polystyrene could be detected in samples with small domains, which were prepared by fast quenching to a low temperature (−80°C, *Figure 3a*). A broad loss peak with low intensity at 85–105°C indicated the formation of a polystyrene phase when the polymer/monomer solution had been quenched to −30°C prior to polymerization (*Figure 3b*). Room-temperature polymerization of the methacrylate resulted in a large cellular morphology (*Figure 3c*), and PS could clearly be observed as a second phase. Repeated heating did not change the position and intensity of the maxima of G'', indicating no further demixing.

demixing, even after vitrification, the concentrations of polymer-rich and polymer-lean phase will tend to grow towards the binodal concentrations associated with the quench temperature. At −60°C the concentration of the PS-rich phase can be extrapolated to approximately 70 wt%. As the PS chains are practically immobilized, this phase enrichment must be the result of monomer diffusion out of the PS-rich phase.
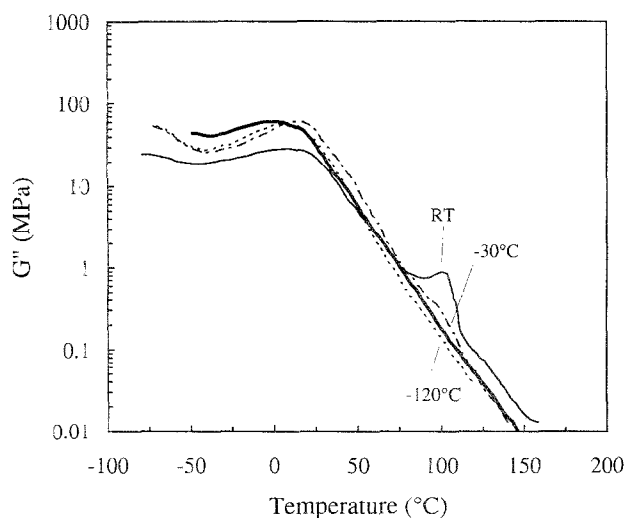
Glass transitions

The relation between sample morphology and mechanical behaviour was investigated using a torsional pendulum. The glass transition was identified as the peak in the mechanical loss (G'') temperature instead of the peak in the loss tangent $(\tan \delta = G''/G'$, where G' is the storage modulus). In the case of poly(*cross*-EHMA), the maximum of $\tan \delta$ lies up to 50°C higher than the

Figure 7   Mechanical loss spectra of 4 wt% PS2M in EHMA/8% EGDMA, showing the influence of quench temperature
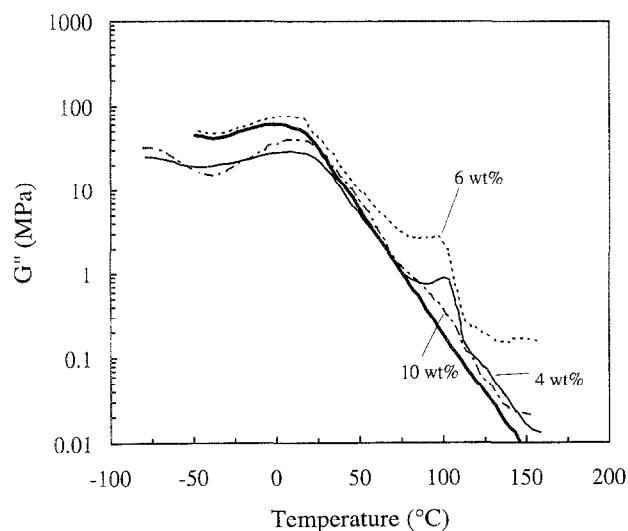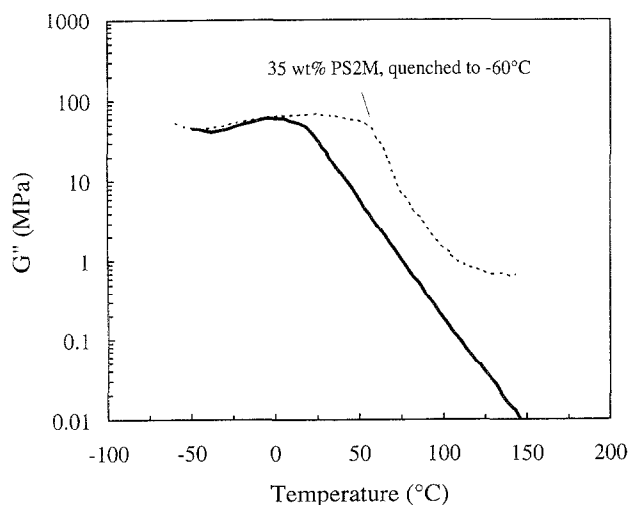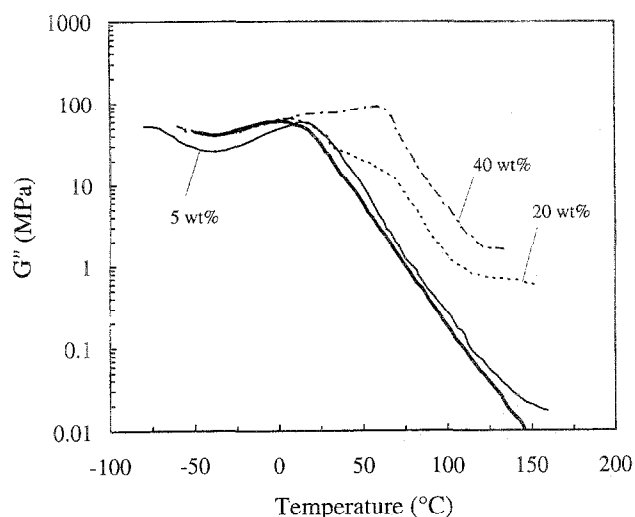
Figure 8 Mechanical loss spectra of PS2M in EHMA/8% EGDMA polymerized at room temperature, showing the influence of polymer concentration

For samples that were cured at room temperature, a broadening and an inward shift of the T_g of PS was observed when the overall PS concentration was increased starting from an initial concentration of 4–10 wt% (*Figure 8*). The higher viscosity of the solution retarded the rate of phase separation compared to the rate of polymerization, resulting in smaller cellular structures and incomplete demixing already for the 10 wt% sample.

When the monomer contained a high concentration of polystyrene, a morphology with very small domains was obtained (as shown in *Figure 4*). In this case, the mechanical loss spectrum in *Figure 9* exhibited one rather broad T_g at 55°C as would be typical for a homogeneous system. The temperature corresponds approximately to that calculated by the Fox equation for $w_{PS} = 55$ wt%, i.e. the PS concentration of the PS-rich phase at gelation. This indicates phase separation at a very small scale, i.e. at molecular level. It was thus demonstrated that phase separation was effectively

Figure 9 Mechanical loss spectrum of 35 wt% PS2M in EHMA/8% EGDMA quenched to −60°C

Figure 10 Mechanical loss spectra of PS100K in EHMA/8% EGDMA quenched to −60°C, showing the influence of polymer concentration

arrested by vitrification of the polymer-rich phase. Apparently no additional phase separation occurred during polymerization and the PS concentration did not increase, owing to the very high viscosity of the system.

A corresponding influence of the initial concentration was observed when mixtures with PS100K were quenched to −60°C (*Figure 10*). A very weak glass transition of the PS-rich phase was observed at 5 wt% PS. Increasing the initial PS concentration to 10 wt% shifted both T_g values by 20°C towards each other. In the 40 wt% PS sample, one broad T_g was observed at 65°C. According to the Fox equation the T_g value would correspond with $w_{PS} = 65$ wt%, which is substantially higher than the binodal concentration at gelation. The value approximately equals the binodal concentration at the quench temperature, indicating that some additional phase enrichment had taken place after vitrification.

DISCUSSION AND CONCLUSIONS

By arrest of demixing of PS/EHMA solutions and subsequent polymerization/crosslinking of the methacrylate resin, morphologies with different sizes were obtained, while simultaneously the concentrations inside of the PS-rich domains were varied. For polystyrene-polybutadiene (tri-)block copolymers it had been found that even domains of 20 nm diameter clearly yielded separate glass transitions in the mechanical loss spectrum[14,15]. Owing to the incompatibility of the blocks, no, or only a very thin, interface layer was formed, and the domains consisted of the pure compound. An estimation of the thickness of the interface layer (d) under equilibrium conditions could be made from the Flory–Huggins parameter (χ), by $d \sim \chi^{-1/2}$ (ref. 18), and for two incompatible polymers $(\chi \gg 0.5)$ the interphase layer will indeed be smaller than 1–2 nm.

In the case of the semi-IPN samples described in this paper, the concentration of the polystyrene-rich phase varied with the extent of liquid–liquid phase separation. The applied quench procedure resulted in vitrification of a fraction of material already at a PS concentration of 60 wt%. By further phase enrichment

the PS concentration could reach the binodal concentration at the quench temperature (approximately 65–70 wt%).

In samples quenched to −80°C, not only was the domain size very small (60–200 nm), but also the PS concentration was low (maximum 70 wt%). The early stage of the demixing process results eventually in an inhomogeneous composition across the domain diameter. Different parts of the domains can be assumed to have different compositions below 70 wt%, and therefore different T_g values. The T_g of the PS-rich phase was shifted and broadened to such an extent that it was not visible any more. In addition, an upward shift of $T_{g,poly-EHMA}$ of 5°C was observed.

In the sample quenched to −30°C, the PS domains were larger (300–500 nm), yielding a broad PS glass transition temperature, slightly shifted downward. Also, an upward shift of the T_g of poly-EHMA (3°C) was observed. The position of the T_g of PS indicated PS domains of approximately 80–95 wt% concentration. Samples with a low initial PS concentration that were polymerized at room temperature yielded phase separation into two pure phases due to the upward shift of the demixing curve during polymerization, and the subsequent increase in the binodal PS concentration. This was shown very clearly in the mechanical behaviour.

In conclusion, it can be stated that the two-step preparation route of semi-IPNs allows one to control the morphology and to combine two incompatible polymers with smaller domain size than the conventional (semi-)IPNs. The morphologies of samples with the same overall composition were found to differ distinctly, ranging from dispersed domains to co-continuous phases. The semi-IPN with 40 wt% PS was an example of how two incompatible polymers can, via an alternative route be brought into a (non-equilibrium) state where optical and mechanical behaviour indicative of a homogeneous semi-IPN is obtained.

Quenched samples that were phase-separated to a low extent showed a decrease in $T_{g,PS}$ indicative of a low PS concentration inside the domains, even after repeated heating. Thus, not only is the growth of the domains

efficiently restricted, but also decomposition itself is limited to concentrations near to those of the binodal before curing. Samples that were phase-separated to a larger extent showed normal two-phase behaviour.

It may be concluded that the PS concentration inside the domains has a larger influence on the mechanical behaviour than the absolute domain size as measured from the electron micrographs.

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