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Dynamic mechanical properties of semi-interpenetrating networks based on poly(styrene-co-maleic anhydride)

2. PS-cross-P(ScoMA) semi-IPN's

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Summary:

Semi-interpenetrating networks based on linear anionic polystyrene (PS) and poly(styrene-*co*-maleic anhydride) P(ScoMA) of low MA content are prepared by crosslinking the P(ScoMA) with 4,4'-diphenylmethanediamine (DPMDA). It is demonstrated by dynamic mechanical analysis and by DSC that immiscible semi-IPN's are obtained for MA contents greater 5 wt.-%. In miscible semi-IPN's the relaxation of free PS chains is observed as a second maximum in the loss tangent at higher temperatures. The position of this maximum is shifted to higher temperatures for a polystyrene of molecular weight 500000 compared to a polystyrene of molecular weight 150000. The experimental temperature shift is in good agreement with a M^3 dependence of the terminal relaxation time. In addition the temperature of this second $\tan \delta$ maximum is shifted to higher temperatures with increasing crosslink density. Again the shift is in good agreement with the theoretical prediction of an increased terminal relaxation time of the relaxing chains with decreasing tube diameter.

Introduction

Polymeric multicomponent systems with one or two crosslinked components (semi-IPN's or IPN's) have found increasing attention due to their potential applications as materials for sound damping./1/ Most crosslinked multicomponent systems are phase separated and the morphology results from the processes occuring during polymer built up, network formation and phase separation./2-4/ Only recently semi-IPN's and IPN's based on miscible polymer pairs have found increasing attention, especially to study the influence of crosslinking on phase separation and dynamics./5-6/ We have reported the synthesis and characterization of semi-IPN's

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based on poly(vinyl methyl ether) and polystyrene./7-9/ To use a nonradical process for crosslinking we used poly(styrene-co-maleic anhydride) (P(ScoMA)) copolymers of low MA content and hexamethylenediamine as crosslinker. At low crosslink densities homogeneous semi-IPN's are obtained while phase separation occurs at higher crosslink density with the aliphatic crosslinker. The problems resulting from the HMDA crosslinker are the high reactivity of the highly basic aliphatic amino group which requires rather high dilution for homogeneous crosslinking and as a result the problem of salt formation. A considerable improvement can be obtained by using an aromatic diamine as a crosslinker. Crosslink reaction occurs at a much slower rate, and the formation of imido carboxylic acid as well as salt formation is suppressed./11-12/ In the present paper we try to attempt the following questions related to the problem of multicomponent miscible semi-IPN's: i) first we have to face the problem whether the P(ScoMA) copolymer is a good model for PS, ii) second we would like to study the influence of crosslinking on the relaxation behaviour of free chains of different chemical structure in the network. As a first step we will report preliminary results of free PS chain relaxation in the P(ScoMA) network. In a subsequent paper the results will be extended to PPEcrossP(ScoMA) semi-IPN's./13/

Experimental

Polystyrenes (PS150, PS500) were prepared by standard anionic polymerization high vacuum technique in THF using s-BuLi as initiator. To samples were prepared for the present study: PS150 (M_n = 151000) and PS500 (M_n = 490000). Both samples had narrow molecular weight distribution (PS150: M_w/M_n = 1.18, PS500: M_w/M_n = 1.2)

Poly(styrene-co-maleic anhydride) (P(ScoMA)): technical grade P(ScoMA) copolymers with different composition (4.7 - 10.4 wt.% maleic anhydride units) were used./14/ Characterization of the samples, including the results of DMA, is given in Table 1.

Table 1: Characterization of poly(styrene-co-maleic acide) copolymers

sample	MA content wt.-%	M_n a) g/mol	M_n b) g/mol	M_w/M_n	E''^{max} c)	$\tan\delta^{max}$ c)
PS-A	4.7	135000	165000	2.45	110	119
PS-B	5.8	135000	131000	1.87	117	126
PS-C	10.4	135000	145000	2.4	128	136

a) membrane osmometry
b) size exclusion chromatography (calibration using PS standards)
c) measured on 1 % crosslinked samples

Preparation of semi-IPN's: 4,4'-diaminodiphenylmethan (DADPM) was used as crosslinker. DADPM was dissolved in $CHCl_3$ (0.48 mol/l). The polymer components were dissolved in $CHCl_3$ (1 - 1.5 g in 6 ml solvent). The calculated amount of crosslinker was added. The highly viscous solution is stirred for 5 minutes. Then films were cast on cellulose acetate film. In first experiments films were cast on glass plates but it was not possible to remove the glassy semi-IPN from the glass plate. After 10 - 15 minutes onset of gelation is observed. After solvent evaporation at room temperature the films are dried in a vacuum oven by stepwise increase of the temperature up to 190°C. During this drying process imidization of the initially formed amic acid to the imide takes place. In a control experiment PS was treated with DADPM under identical conditions. No changes in the molecular weight could be detected by DSC.

Table 2: Sample designations and compositions of PS-cross-P(ScoMA) semi-IPN's

sample	copolymer	content wt.-%	PS	content wt-%	x-link density mol%
c1-PS-A	PS-A	100			1
PS150-*c1*-PS-A(2:8)	PS-A	80	PS150	20	1
PS150-*c1*-PS-A(4:6)	PS-A	60	PS150	40	1
PS150-*c1*-*PS*-A(6:4)	PS-A	40	PS150	60	1
PS150-*c1*-PS-A(8:2)	PS-A	20	PS150	80	1
PS150-*c4*-PS-A(2:8)	PS-A	80	PS150	20	4
PS500-*c1*-PS-A(2:8)	PS-A	80	PS500	20	1
c1-PS-B	PS-B	100			1
PS150-*c0*-PS-B(4:6)	PS-B	60	PS150	40	0
PS150-*c1*-PS-B(2:8)	PS-B	80	PS150	20	1
PS150-*c1*-PS-B(4:6)	PS-B	60	PS150	40	1
PS150-*c1*-PS-B(6:4)	PS-B	40	PS150	60	1
PS150-*c1*-PS-B(8:2)	PS-B	20	PS150	80	1
c1-PS-C	PS-C	100			1
PS150-*c1*-PS-C(4:6)	PS-C	60	PS150	40	1

Measurements:

DSC experiments were performed on a Perkin Elmer DSC 7 at heating rates between 10 and 40 K/min. The first heating was neglected in the evaluation of T_g. 'Dynamic' glass transition temperatures were taken as the inflection point of the heat capacity change. 'Static' T_g's were obtained by extrapolation to heating rate 0. Reproducibility of the static glass transition temperatures is ± 1 K.

Dynamic mechanical measurements (DMA) were performed on a RHEOMETRICS

RSAII solid analyzer in the dynamic tensile mode. Strips of 32 mm length, 7 mm width and 0.2 mm thickness were cut from the original samples using a heated knive. The film geometry allows accurate measurements in the interesting range of the modulus between 10^9 and 10^6 Pa. Experiments reported here were obtained at constant frequency at 1 rad/sec. Measurements were made every 3 K. To allow for temperature equilibration a soak time of 3 minutes was chosen until temperature was constant. In some experiments where we were interested in the behaviour at high temperatures nitrogen was used as purge gas to avoid oxidative degradation. This results in slightly larger temperature fluctuation. For each series optimum experimental parameters in terms of prestrain and strain amplitude were determined to insure linear viscoelastic response at maximum stress output.

Results and Discussion

The glass transition in PS-cross-P(ScoMA) semi-IPN's

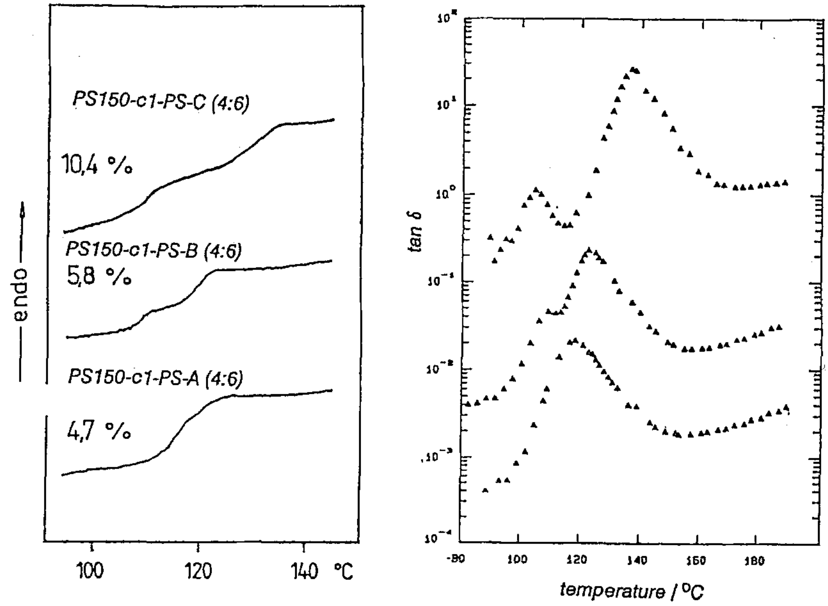

Fig. 1: DSC traces (20 K/min) (left) and tan δ (1 rad/s) (right) of PS150-c1-PS-A (4:6), PS150-c1-PS-B (4:6), PS150-c1-PS-C (4:6)

To attack the problem whether P(ScoMA) copolymers of low MA content are a easily crosslinkable substitute for PS in semi-IPN's, we prepared semi-IPN's varying in the maleic anhydride content of the P(ScoMA) copolymer, composition and crosslink density. All samples were prepared at the same polymer volume fraction during crosslinking. Sample designations and compositions which are used in the present work are listed in Table 2. In a first set of experiments semi-IPN's of constant composition (60 wt.-% copolymer) and crosslink density but different maleic anhydride content in the copolymer were studied.

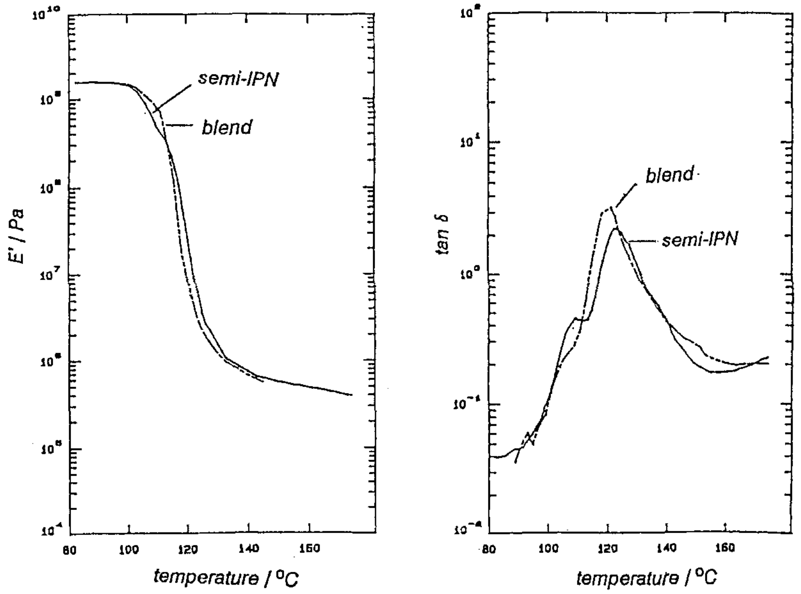

Fig. 2: E' (left) and tan δ (right) of blend (a) and semi-IPN (b) of PS150 and P(ScoMA) copolymer PS-B, composition PS150:PS-B = 4:6

Fig. 1 shows the DSC traces and the *tan δ* curves for these samples. For PS-C and PS-B two glass transitions are clearly identified by DSC and DMA, while both methods only show a single transition for PS-A. Apparently 5 % of comonomer units are sufficient to induce immiscibility. This is known for other homopolymer/copolymer pairs./15/ As has been shown for PVME-cross-P(ScoMA) semi-IPN's crosslinking has a considerable influence on the phase behaviour. Fig. 2 shows *E'* and *tan δ* for an uncrosslinked and crosslinked (1%) mixture of PS150 and copolymer PS-B. In the uncrosslinked blend there is only a slight shoulder on the low temperature side of the *tan δ* maximum which is rather pronounced in the crosslinked sample. The differences are also obvious in the storage modulus data. Apparently phase separation is more pronounced in the semi-IPN. The differences are also observed in the location of the *tan δ* maximum, which is located at 121°C for the blend, at 123°C for the semi-IPN and at 126°C in the case of the pure network *c1*-PS-B.

Fig. 3 shows the influence of composition on the shape of the *tan δ* curve in the PS150-*c1*-PS-B series. Even at a copolymer content of 80% (upper curve) a shoulder, related to a practically pure PS phase is observed at 106°C. The maximum of the *tan δ* is located at 124°C, only slightly below the value of the pure PS-B network (Table 1). At 60% copolymer content the two glass transitions are clearly resolved as already has been discussed before. For higher PS contents the glass transition of the copolymer is not resolved anymore. The *tan δ* curve only shows a pronounced broadening at higher temperatures. At 40 % copolymer content the glass transition is located at 113°C where it would have been expected for a homogeneous mixture on the basis of linear mixing rules.

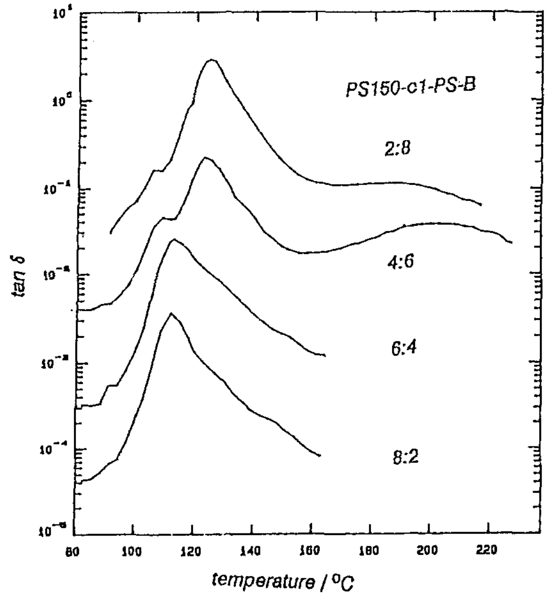

Fig. 3:
tan δ (1 rad /s) for PS150-c1-PS-B - semi-IPN's of various compositions; from top: 2:8; 4:6; 6:4; 8:2; curves are shifted for one decade

Relaxation of free chains in PS-cross-P(ScoMA) semi-IPN's.

The two upper curves in Fig. 3 show a second relaxation maximum located at temperatures above T_g. This maximum is related to the terminal relaxation process of the free PS chains. Antonietti et al /16/ have studied the dynamics of free chains in a network by means of forced Rayleigh Scattering. Such investigations are important tests for theories of viscoelasticity. According to the tube model /17/ the tube diameter should be altered by increasing the crosslink density of the network. As a consequence the terminal relaxation time of the free chains should by enhanced. In the present paper we will restrict the discussion to isochronous measurements.

To study the relaxation of the free chains in the network semi-IPN's based on PS-A were prepared, which are not phase separated. According to reptation theory τ_d should be proportional to the third power of the molecular weight M^3. An increase of the molecular weight of the linear chains should show up in isochronous measurements as a considerable shift along the temperature axis. To probe the relaxation of free chains we used a volume fraction of 20 % linear chains. As can be seen in Fig. 4 a pronounced second maximum is observed in the loss tangent curves. The maximum shifts from 195°C for PS150 to 240°C for PS500. Using the WLF equation /18/ and the constants given for PS we can estimate the frequency/time difference which corresponds to the temperature difference of 45°C. Using C_1 = 8.86 and C_2 = 101.6 at $T_{ref} = T_g + 50$ a frequency difference of 1.86 decades is calculated. From the increase in the molecular weight the increase is expected to be 1.78 decades which is an excellent agreement in view of the ramifications made above.

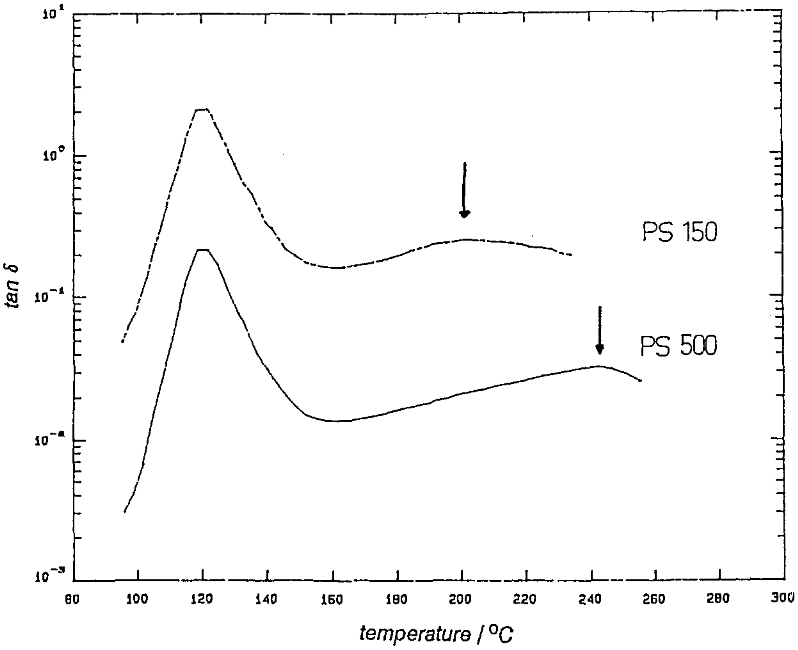

Fig. 4:

Loss tangent (tan δ) as a function of temperature (1 rad/s) for semi-IPN's PS150-c1-PS-A (2:8) and PS500-c1-PS-A (2:8), arrows indicate second tan δ maximum related to the terminal chain relaxation, the two curves are shifted for 1 decade to avoid overlapp

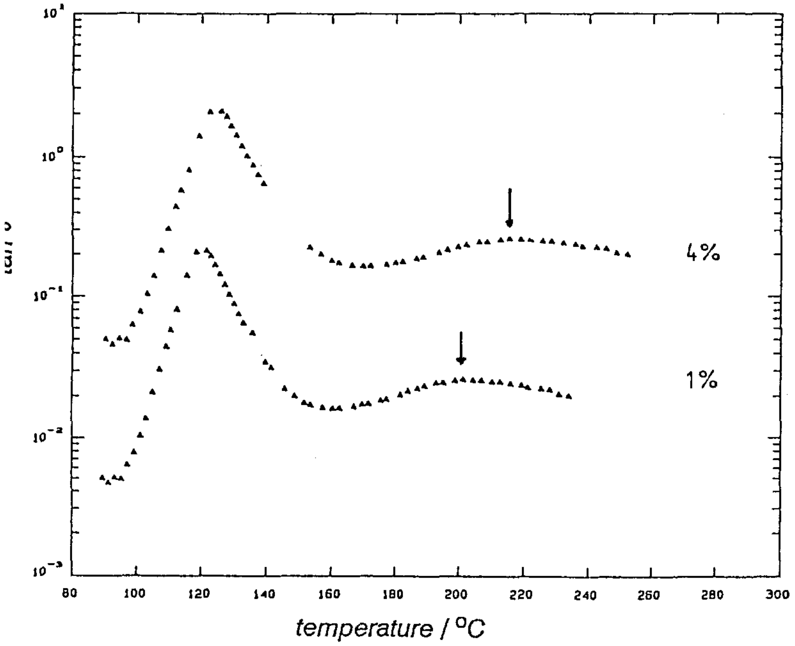

Fig. 5:

Loss tangent (tan δ) as a function of temperature (1 rad/s) for semi-IPN's PS150-c1-PS-A (2:8) and PS150-c4-PS-A (2:8), arrows indicate second tan δ maximum related to the terminal chain relaxation, the two curves are shifted for 1 decade to avoid overlapp

Fig. 5 shows the *tan δ / T* curves for two semi-IPN's differing in their crosslink density: PS150-*c1*-PS-A (2:8) and PS150-*c4*-PS-A (2:8). According to the reptation theory the disengagement time τ_d is inversely proportional to the tube diameter and thus to the molecular weight between crosslinks M_c. In agreement with the general expectation the secondary *tan δ* maximum shifts to higher temperatures when the amount of crosslinker is increased. The observed shift from 203 to 215 K again can be transformed in a frequency shift which is 0.63 decades. An increase of the crosslink density by a factor of 4 would cause a change in τ_d of 0.6 decades which again is in excellent agreement with the experimental estimate. These preliminary experiments clearly show that semi-IPN's based on P(ScoMA) copolymers at low maleic anhydride content are suited to test viscoelasticity models. However, careful choice of the comonomer content is essential.

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