Colloid & Polymer Science Colloid Polym Sci 272:261–269 (1994)

Dynamic mechanical properties of semi-interpenetrating networks based on poly(styrene-co-maleic anhydride): 3. Poly(2,6-dimethyl-1,4-phenylene ether)-cross-poly(styrene-co-maleic anhydride)

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Abstract: Semi-IPN's based on linear poly(2,6-dimethyl-1,4-phenylene ether) (PPE) and diamine crosslinked poly(styrene-co-maleic anhydride) (PScoMA) copolymers containing small amounts of maleic anhydride (PSA = 4.7 wt.-% MA, PSB = 5.8 wt-% MA) are studied with respect to the influence of crosslinking on the phase behavior. Temperature-dependent dynamic mechanical analysis (DMA) and DSC show that the semi-IPN's prepared from concentrated solution show weak crystallinity of the PPE phase. After heating above the PPE melting transition the semi-IPN's remain amorphous and the relaxation in the glass transition region as well as the terminal relaxation of the free PPE chains in the network is studied as a function of PPE concentration and network density.

Key words: PPO/PS-Semi – IPN's – dynamic mechanical analysis

Introduction

Semi-interpenetrating and interpenetrating polymer networks (IPN's and semi-IPN's) have found increasing attention owing to the possibility to taylor the morphology in immiscible polymer multicomponent systems via chemical crosslinking. The final morphology results from complex processes occurring during polymer build-up, network formation and phase separation [1–3]. However, the present state of knowledge clearly demonstrates that the picture of two molecular interwined networks (Fig. 1) is generally not correct. Such a situation may only be realized if the two polymeric components are thermodynamically miscible. Such systems offer the opportunity to study the influence of crosslinking on phase separation [4, 5]. Other interesting features of miscible semi-IPN's based on poly(vinyl methyl ether) (PVME) and polystyrene (PS) are the dynamic mechanical behavior in the glass transition region [4, 6], the dynamics of phase separation [5], and the possibility to prepare novel microfoam materials [7] with some potential for membrane application [8]. To avoid network build-up by a radical crosslinking polymerization process [4, 5] poly(styrene-co-maleic anhydride) (P(ScoMA)) copolymers of low MA content may be used as the starting styrenic component [6–9]. The copolymer was crosslinked in the presence of the linear (fractionated) PVME by aliphatic or aromatic diamines [9]. If hexamethylene diamine (HMDA) is used as crosslinker the high reactivity of the strongly basic aliphatic amino group requires rather high dilution to obtain homogeneous networks. Reaction rate is strongly influenced by the type of amine. In addition, the aliphatic amines have a higher tendency towards salt formation between the amide acid and the amine. Salt formation will result in some network heterogeneity and induce phase separation [9]. A considerable improvement can be obtained by using

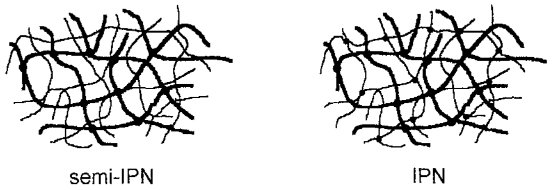


Fig. 1. Schematic representation of semi-interpenetrating and interpenetrating polymer networks

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 [10, 11].

In the present paper the same synthetic route is applied to semi-IPN's of linear PPE in PS networks. PPE/PS is one of the most intensively studied miscible polymer blend systems [12–16]. However, besides the paper of Frisch [15], only blends have been considered. By crosslinking of copolymers of styrene containing small amounts of maleic anhydride using aromatic diamines in the presence of fractionated, endcapped PPE, PPE-*cross*-P(S-co-MA) semi-IPN's are prepared. Crosslinking efficiency in pure P(S-co-MA) networks is checked by swelling and mechanical analysis.

Experimental

Sample preparation

Poly(oxy-2,6-dimethyl-1,4-phenylene) (PPE) was obtained by phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenole according to the method developed by Percec et al. [17]. Tetrabutylammoniumhydrogensulphate (TBAH) was used as phase transfer agent, air was bubbled through the reacting solution as oxygen supply. After a reaction time of 28 h the raw product of $M_n = 74\,000$ and $M_w/M_n = 3.3$ was obtained. To avoid the redistribution reaction, characteristic for PPE [18], the terminal OH groups were blocked with dimethyl sulfate via phase transfer catalysis [19, 20]. After several reprecipitations to remove the low molar mass fractions a polymer with $M_n = 95\,000$, $M_w/M_n = 2.6$ was obtained. Further fractionation (toluene as solvent, methanol as nonsolvent) yielded a main fraction with $M_n = 108\,000$, $M_w/M_n = 1.6$. This polymer was used in the study of the terminal relaxation behavior.

Poly(styrene-co-maleic anhydride) (P(ScoMA)): technical grade P(ScoMA) copolymers with different composition (PSA = 4.7 wt% and PSB = 5.8 wt% maleic anhydride units) have been used. Characterization of the samples is given in Table 1.

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 min. Then films were cast on cellulose acetate film. In first experiments

Table 1. Characterization of crosslinked P(ScoMA) networks

Sample	Degree of crosslinking	Degree of swelling[a])	M_C^{exp}	$M_C^{Theoretical}$	T_g/°C[b])	E''_{max}	$\tan_{max}$	M_C(DMA)[c])
PSA	0				107	109.5	118.5	
c1-PSA	1	6.0	12500	10300	108	110.5	120.5	21200
c2-PSA	2	4.8	7100	5150	108	112.5	122.5	10000
c3-PSA	3	3.9	4700	3400		113.5	124.0	8200
c4-PSA	4	3.4	3600	2575	109	115.0	127.5	7800
PSB	0				111			
c1-PSB	1	5.7	11000	10300	114	117.5	126.5	14100
c2-PSB	2	4.4	6200	5150	115			
c3-PSB	3	3.6	3900	3400				
c4-PSB	4	3.1	2700	2575	116			

[a]) Degree of swelling $q = 1/2$; 2 = volume fraction of polymer in the swollen gel

[b]) DSC, after extrapolation to heating rate zero

[c]) Calculated according to $M_C = 3\,RT/E$, if the phantom model is taken as the basis, the values are just half as high, in reasonable agreement with the swelling data; E was taken as E' at 200 °C at 1 rad/s

films were cast on glass plates, but it was not possible to remove the glassy semi-IPN from the glass plate. After 10–15 min 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 cyclic imide takes place.

Measurements

Swelling measurements: Equilibrium swelling experiments were performed in toluene at 25 °C. The data were obtained as average values taken from three samples. Degree of swelling was determined gravimetrically. Analysis of the swelling data was attempted according to the Flory–Rehner equation [21] corrected for dangling chain ends [22] using a χ-Parameter of 0.44 [23].

DSC experiments were performed on a Perkin Elmer DSC 7 at heating rates between 10 and 40 K/min. The instrument was calibrated using standard procedures. 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 was obtained by extrapolation to heat rate 0. Reproducibility of the static glass transition temperature 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 knife. The film geometry allows accurate measurements in the interesting modulus range between 10^9 and 10^6 Pa. Experiments reported here were obtained at constant frequency at 1 rad/s. In general, measurements were made every 3 K. To allow for temperature equilibrium a soak time of 3 min was chosen after the heating chamber had reached the temperature. In some experiments where we were interested in the behavior at high temperatures nitrogen was used to avoid oxidative degradation. This results in a slightly higher 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

Characterization of P(ScoMA) copolymers and PPE

Table 1 includes the DMA results obtained for the uncrosslinked P(ScoMA) copolymers. The loss modulus maxima measured at 1 rad/s and the midpoint of the glass transition as observed by DSC at 10 K/min are located at the same temperatures. The main transition of the PPE strongly depends on the sample history. A film cast from $CHCl_3$ and subsequently dried at 190 °C is partially crystalline. The peak maximum of the melt transition (DSC) is located at 255 °C, which is in excellent agreement with the values reported by Wunderlich [24]. No glass transition is detected by DSC in the first heating cycle. In the mechanical spectrum the loss modulus maximum is located at 235 °C. This again is in excellent agreement with the literature value of the glass transition in partially crystalline PPE [24]. In a second experiment the solution cast sample was heated to 260 °C for 20 s. After cooling no crystallinity could be detected anymore. The glass transition determined from both, DSC and DMA ($E^{\circ\circ}_{\max}$), is located at 220 °C.

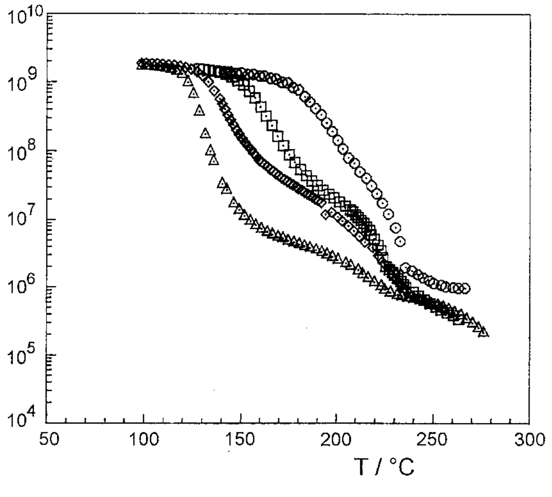
Characterization of pure P(ScoMA) networks

To obtain information about the crosslinking reaction of P(ScoMA) with aromatic diamines two series of networks were prepared where crosslinking was varied between 0 and 4%. These networks were characterized by swelling, DSC and partially by DMA. The results are collected in Table 1. The experimental M_c values calculated on the basis of the Flory–Rehner theory are slightly higher than the theoretical values. However, for PSB (5.8 mol% maleic anhydride groups) a rather reasonable agreement is observed. Crosslinking only slightly increases the glass transition. Within experimental error no change in the heat capacity change at T_g was observed with crosslinking. The glass transition region slightly broadens. However, the area below the loss modulus, which can be taken as a measure of the relaxation strength in the glass transition region according to Sperling [25], does not change with crosslinking. From the level of the rubbery plateau a mechanically effective molecular weight between crosslinks can be estimated. The data are also collected in Table 1. The M_c values for PSA networks are considerably higher than the expected values, indicating either incomplete crosslinking or the influence of cyclization. In the case of PSB only the network with the lowest degree of cross-linking has been tested by DMA. Again the experimental value for M_c for *c*1-PSB taken from E' at 200 °C is in reasonable agreement with the expected value calculated from stoichiometry. Thus, we conclude that crosslinking of PSB results in networks of reasonable defined structure.

Thermomechanical properties of PPE-cross-P(ScoMA) semi-IPN's

As we have shown in the preceding section P(ScoMA) copolymers can be easily crosslinked by diamines in concentrated solution (up to 30 wt.-%, upper limit determined by the solution viscosity) resulting in homogeneous networks of controllable crosslink density. If this crosslinking reaction is made in the presence of PPE, semi-IPN's without radically initiated crosslink reaction are available. Sample preparation was performed as described for the homo-PS-networks. The films were dried at 190 °C. All samples were transparent and tougher than the corresponding PS/PPE blends, in agreement with data reported by Frisch [15]. No experiments on the ultimate tensile properties were made up to now.

Figure 2a)–c) shows the dynamic mechanical data (E', E'', tan δ) obtained for networks of constant crosslink density but with varying composition. At first glance the results were rather surprising. PS and PPE are known to form miscible blends in the whole composition range [12–16], but the DMA results indicate the presence of a two-phase structure. However, the data are not consistent with a simple phase separation between P(ScoMA) and PPE. The E″ maximum shifts to higher temperature with increasing PPE content, but this shift is lower than expected from corresponding amorphous miscible blends. Using the Gordon–Taylor equation, which describes the composition dependence of the glass transition of PS/PPE blends adequately [16], the composition



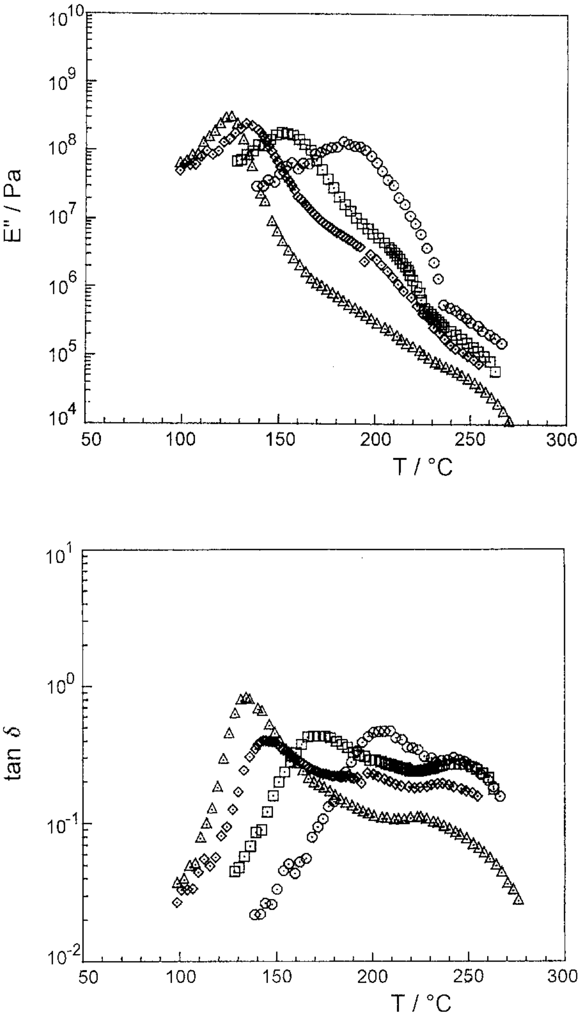


Fig. 2. Storage modulus (a), loss modulus (b) and tan δ (c) as a function of the temperature for semi-IPN's of PSB (crosslink density = 1%) and partially crystalline PPE: (△) 80/20, (◇) 60/40, (□) 40/60, (○) 20/80

of the mixed phase, accounting for the E'' maximum can be estimated. These data are collected in Table 2. It is evident that this "mixed" phase contains a larger fraction of the P(ScoMA) than expected from the overall composition.

In addition, the second relaxation process of the phase separated system has its main transition at a temperature higher than the glass transition of amorphous PPE. Figures 3 and 4 show the DSC traces of the same set of semi-IPN's in the first and second heating cycle. In the first heating cycle the glass transition is lower than expected for the mixture and a small endothermic peak is observed at about 250 °C, characteristic for partially crystalline PPE. This melting had disappeared in the second heating cycle which was recorded immediately after cooling. The degree of crystallinity is very small, only a small part of the PPE crystallizes, and no crystallites could be detected by transmission electron microscopy. Apparently, these crystallites are so small that the semi-IPN becomes completely homogeneous during the first DSC heating cycle.

Table 2. Composition of the amorphous part in the semicrystalline semi-IPN's calculated from T_g according to the Gordon–Taylor equation with $T_{g1} = 117\,°C$, $T_{g1} = 220\,°C$, $K = 0.8$

Composition PS/PPE	T_g (°C)	Calculated composition PS/PPE
80/20	123	93/7
60/40	133	81/19
40/60	152	60/40
20/80	186	28/72

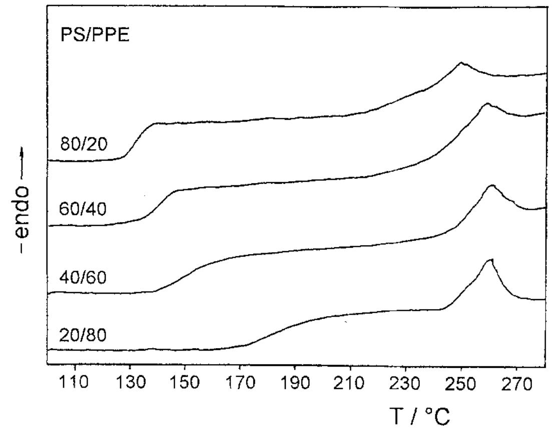


Fig. 3. DSC diagram of the first heating cycle of the semi-IPN's of PSB/PPE for various compositions; crosslink density = 1%, heating rate = 30 K·min^{-1}

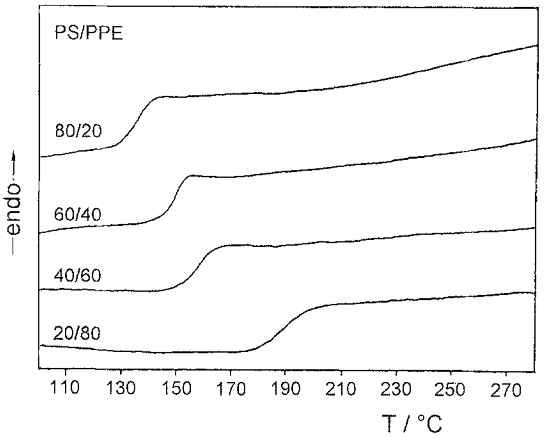


Fig. 4. DSC diagram of the second heating cycle of the semi-IPN's of PSB/PPE for various compositions; crosslink density = 1%; heating rate = 30 K·min^{-1}

To check this result, samples for DMA measurements were heated for 15 s under nitrogen to 260 °C. After rapid quenching the mechanical spectra were recorded. The results are shown in Figs. 5a)–c). Now, a rather sharp glass transition is observed in E' and E''. There is no indication for a phase separated (semicrystalline) morphology in the semi-IPN's. The glass transition temperatures obtained from E''_{max} are again in good agreement with the values expected for a homogeneous semi-IPN having the same concentration dependence of the T_g as the blends.

In E', E″ and also tan δ a weak transition is observed at higher temperatures. This transition is related to the terminal relaxation of the free PPE chains within the PS network. The temperature of this second tan δ maximum is designated as T_d for disengagement temperature (at the experimental frequency of 1 rad/s) in analogy to the disengagement time τ_d [26]. The intensity of this relaxation increases with increasing PPE content. The modulus in the rubbery plateau at temperatures $T_g < T < T_d$ is considerably higher than the corresponding plateau modulus of semi-IPN's of P(ScoMA) with linear polystyrene [27]. The origin of the higher plateau modulus in the PPE-*c*-P(ScoMA) semi-IPN's compared to PS-*c*-P(ScoMA) is the lower entanglement molecular weight M_e of PPE (about 2500 [28, 29] as

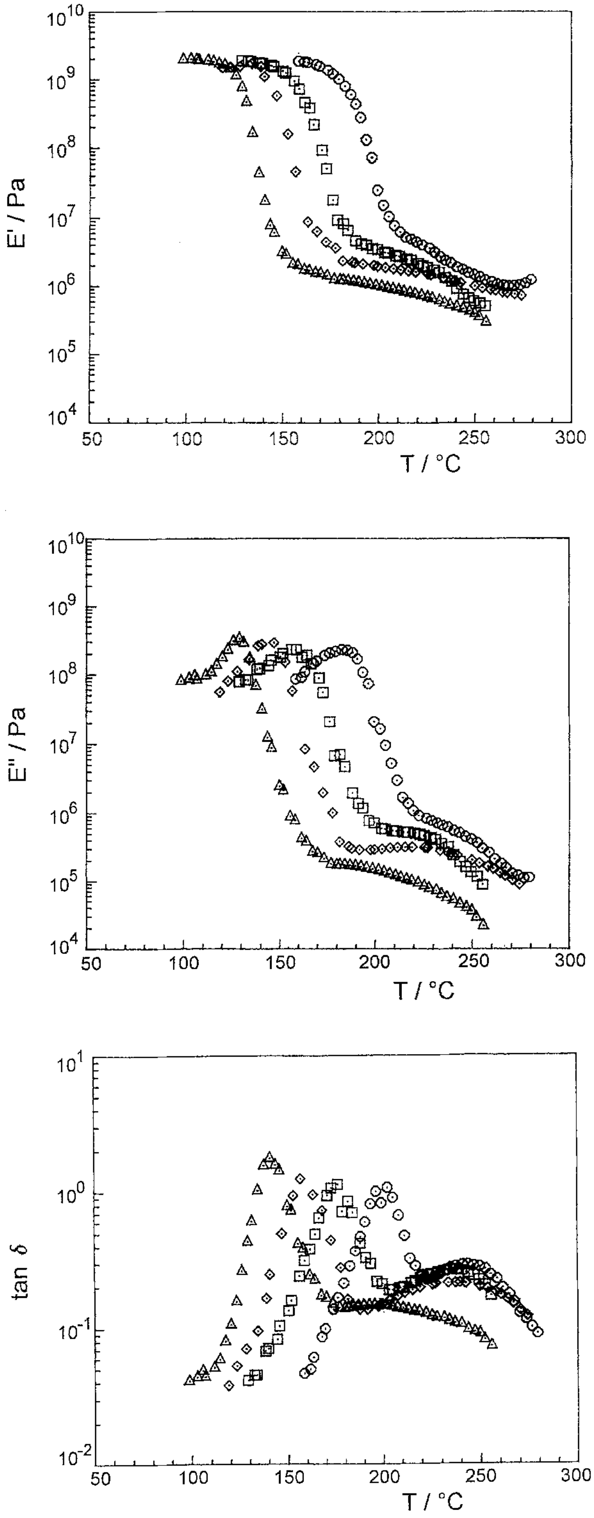


Fig. 5. Storage modulus (a), loss modulus (b) and tan δ (c) as a function of the temperature for semi-IPN's of PSB (crosslink density = 1%) and amorphous PPE: (△) 80/20, (◇) 60/40, (□) 40/60, (○) 20/80

compared to PS (about 18 000 [30]). According to different authors [12, 31–34] the entanglement molecular weight of a homogeneous blend is expected to be intermediate between the components. Several mixing rules have been proposed.

$$M_e = \phi_1 M_{e1} + \phi_2 M_{e2} \quad (1)$$

$$1/M_e = \phi_1/M_{e1} + \phi_2/M_{e2} \quad (2)$$

Additional modifications may include factors which account for specific interactions [31, 32]. For PPE/PS blends we have shown [33] that Eq. (2) gives the best description of the data. In the case of semi-IPN's an increase of the modulus in the rubbery regime can be expected as long as the free PPE chains are not relaxed ($T_g < T < T_d$) and as long as the molecular weight between chemical crosslinks of the c-P(ScoMA) network is larger than M_{ePPE}.

From Fig. 5a the plateau modulus of the unrelaxed mixture is taken at the minimum of tan δ inflection point [31, 32], though there might be some error introduced by this simple attempt [29]. As can be seen in Fig. 6a, the reduced Young's modulus $E^* T_0/T$ increases linearly with PPE content in the temperature region where the PPE is still elastically active. As for the polymer blends the effective network molecular weights calculated from these data are in good agreement with the theoretical values estimated using Eq. (2) (Fig. 6b).

Another feature of the homogeneous PPE-c-P(ScoMA) semi-IPN's becomes evident from the tan δ curve given in Fig. 5c. With increasing PPE content both the glass transition and the secondary maximum associated to T_d are shifted to higher temperatures. However, the shift of T_g is much stronger and, as a result, the temperature distance between the two maxima decreases. As we have pointed out in an earlier paper the temperature dependence of the viscoelastic properties of PPE/PS blends can be described independent of the blend composition and PPE molecular weight if an iso free volume state is taken as reference [29]. Though the expansion coefficients of the free volume are different for PS and PPE, we assume as a 0th order approximation that we may describe all samples by a unique time-temperature dependence. Under this assumption the difference $T_g - T_d$ may be transformed into a frequency difference and the variation of the terminal relaxation

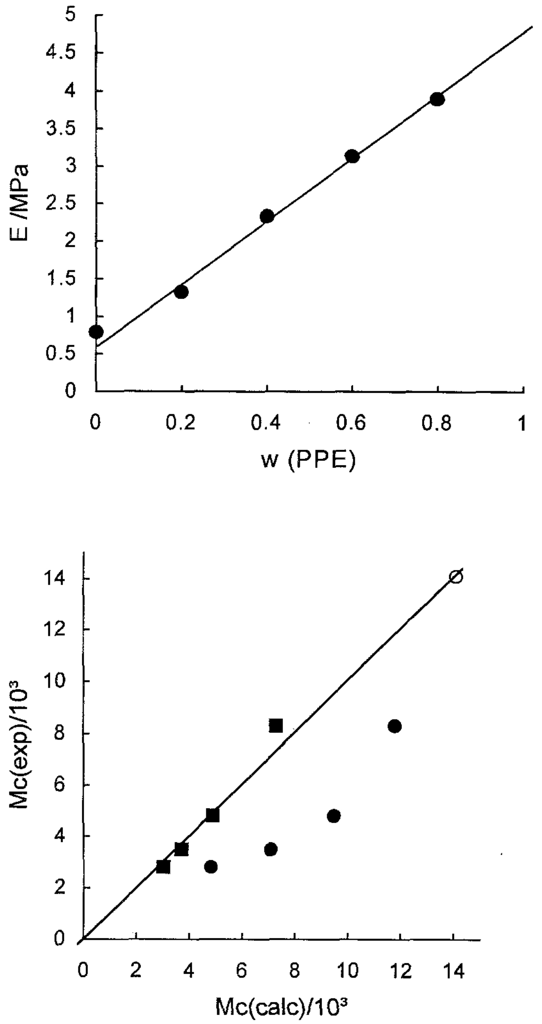


Fig. 6. a) Reduced Young's modulus as a function of the PPE weight fraction; b) comparison of experimental and calculated molecular weights of the network chains, ● Eq. (1), ■ Eq. (2), the straight line corresponds to a 1:1 agreement between experimental and calculated values

Table 3. Distance between the α- and the terminal relaxation

Composition (wt % PS)	T_g(°C)*)	$T_d - T_g$(°C)	$\log a_T$
80	129.0	75	-8.30
60	147.0	70	-8.05
40	157.5	60	-7.49
20	182.5	50	-6.80

*) From $E''_{\max}$

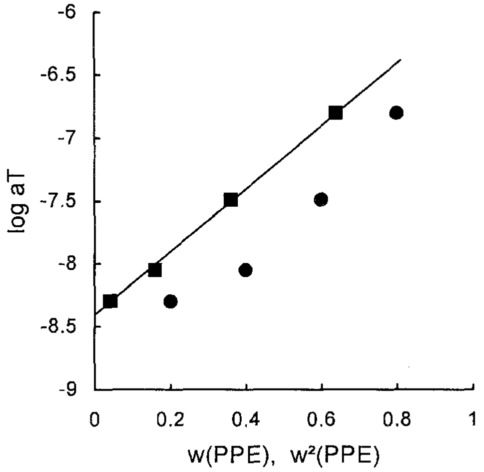


Fig. 7. log a_T versus w (●) and w^2 (■)

of the free PPE chains in the network can be estimated. The calculations show that the difference between the frequency of α-relaxation (glass transition) and the terminal relaxation of the free PPE chains decreases with increasing PPE content. The data are collected in Table 3. A plot of $\log(\tau[T_d]/[\tau T_g]) = \log(a_T[T_d - T_g])$ versus w and w^2 is shown in Fig. 7. In the latter case a linear dependence is observed. According to this analysis the PPE chain relaxation occurs at a considerable higher rate if the fraction of PPE is increased. The dependence of the PPE relaxation time on the square of the concentration would indicate that constraint release processes play a dominant role in the overall relaxation of the PPE chains in the network. However, if the analysis is not made under the assumption of unique time-temperature dependence for all samples, quite different results may be obtained. Frequency dependent experiments in the temperature range of the PPE chain relaxation could be performed to check the basic assumptions.

In another set of experiments the influence of the chemical crosslink density on T_d has been studied. For this purpose semi-IPN's containing 20 and 30 wt.-% of PPE (crosslink density 1 and 4 mol%, semi-IPN's based on PSB) were compared. Figure 8 shows the $\tan\delta$ curves for semi-IPN's containing the 30 wt % PPE. The α-relaxation at about 140 °C is practically independent from crosslink density. The weak secondary maximum, related to the relaxation of the free PPE chains is marginally shifted to higher temperatures. For similar PS-*cross*-P(ScoMA) semi-IPN's the influence of increasing crosslink density

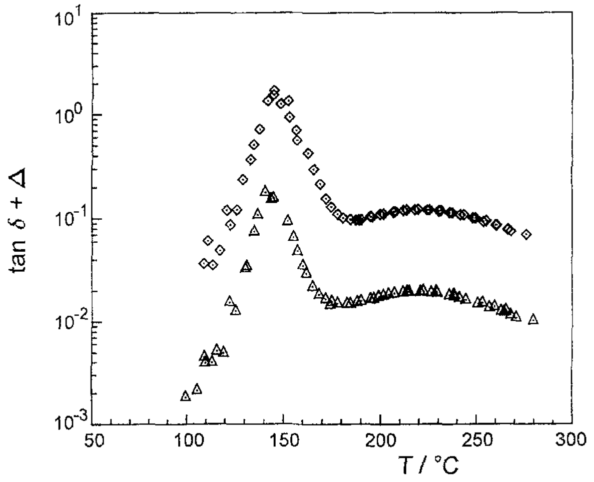


Fig. 8. tan δ as function of the temperature for PPE-cross-P(ScoMA) semi-IPN's (30/70 wt%) with 1 (△) and 4% (◇) crosslinking density

on the terminal relaxation of the free PS chains is much more pronounced [27]. Also, no change in T_d with crosslinking density was observed for the semi-IPN containing 20 wt % of PPE. At first glance, these results are rather surprising because the chemical crosslink density of the P(ScoMA) network has been changed by a factor 4. On the other hand, PPE has a much smaller (a factor of eight) entanglement molecular weight than P(ScoMA). Even the network with crosslink density 4% shows a molecular weight between crosslinks larger than the entanglement molecular weight of the PPE. Apparently, the relaxation of the PPE chains is dominated by their own entanglements network, at least for low degrees of crosslinking.

Conclusions

In the present study we have shown that homogeneous amorphous semi-IPN's based on crosslinked polystyrene and linear poly(2,6-dimethyl-1,4-phenylene ether) (PPE) can be prepared at various crosslink densities. The terminal relaxation of the linear PPE chains in the crosslinked matrix demonstrate that constraint release processes play an important role in the overall relaxation behavior. This is in contrast to the behavior of free chains dispersed in the network of the same chemical structure. It could be the result of the very low entanglement molecular weight of the PPE chains. Owing to this fact, the effective tube is created mainly by the PPE, though the PS network might be present in large excess.

The overall analysis in this system is complicated by the strong variation of the glass transition in the mixtures. These difficulties can be overcome by additional frequency dependent measurements.

Acknowledgements

Financial support from Deutsche Forschungsgemeinschaft through Sonderforschungsbereich 262 (Glaszustand und Glasübergang nichtmetallischer amorpher Materialien) and Deutscher Akademischer Austauschdienst (DAAD) (fellowship for L.F.) are gratefully acknowledged.

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Received April 1, 1993;
accepted June 28, 1993

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