# Controllable specific interactions and miscibility in polymer blends: 4. Effect of hydrogen bonding density in interpenetrating polymer networks

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Sequential interpenetrating polymer networks (IPNs) composed of poly(butyl acrylate) as the first network and modified polystyrene containing proton-donor hydroxyl groups [PS(OH)] as the second network are studied by d.s.c., transmission electron microscopy and dynamic mechanical analysis. The apparent miscibility between the components increases considerably as the hydroxyl content in PS(OH) increases. However, differing from the corresponding blends of the linear polymers, for which ~2 mol% hydroxyl introduced into PS(OH) leads to complete miscibility, the IPNs always show two-phase structures even when the hydroxyl content in PS(OH) is as high as 30 mol%.

**(Keywords: IPNs; hydrogen bonding; miscibility)**

## INTRODUCTION

Polymer–polymer miscibility is one of the basic factors governing morphologies and properties of multicomponent polymers. Although preparing a polymer blend with desired properties does not necessarily need complete miscibility between the components, making the miscibility and morphology controllable is certainly of great significance for realizing the molecular design of multicomponent polymers. In this respect, modification of a polymer component by copolymerization or polymer reaction to introduce certain chemical groups capable of forming intercomponent specific interactions, such as ion–ion or ion–dipole interactions[1] and hydrogen bonding, has been proved effective. In the latter case, Pearce *et al.*[2] and Jiang *et al.*[3,4] reported introducing strong proton donors into polystyrene for increasing its miscibility with poly(acrylic ester)s. Jiang *et al.* studied a series of blends composed of modified polystyrene, denoted PS(OH), which was a copolymer of styrene and hydroxyl-containing monomer *p*-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)-α-methylstyrene (HFMS) and poly(acrylic ester)s. The miscibility of the blends was found to be strongly dependent on the hydroxyl group content in PS(OH) and the consequent hydrogen bonding density between the hydroxyl in PS(OH) and the carbonyl in the poly(acrylic ester) as evidenced by d.s.c. and transmission electron microscopy (TEM). In particular, studies of non-radiative energy transfer fluorescence[5] for the blends with chromophore labels showed a continuous increase of the degree of phase mixing as the hydroxyl content in PS(OH) increased. It was found that only ~2 mol% of the hydroxyl-containing units in PS(OH) rendered the otherwise immiscible blends miscible. This miscibility enhancement in blends of non-crosslinked polymers has motivated us to extend our research to the area of interpenetrating polymer networks (IPNs).

There have been many reports in the literature relevant to IPNs with intercomponent specific interactions. Xiao *et al.*[6] studied IPNs composed of polyurethane (PU) and poly(methyl methacrylate-*co*-acrylic acid) (PMMA–AA). In the polyurethane, tertiary amine groups were incorporated for establishing ion–ion interactions with the carboxylic acid groups in MMA-*co*-AA. IPNs with only one glass transition were obtained when the PMMA-AA contained 9–20 mol% AA units. However, the blends showed a phase-separated structure by scanning electron microscopy (SEM) observations. Nishi and Kotaka[7] studied IPNs composed of the complex-forming polymer pair of polyoxyethylene (POE) and poly(acrylic acid) (PAA). It was found that only IPNs with a low crosslink density exhibited a single phase structure. As the crosslink density increased, POE-rich and PAA-rich phases appeared in coexistence with the complex phase and finally existed exclusively, which implied that complexation was no longer possible between the highly crosslinked POE and PAA networks. This disadvantageous effect of crosslinking on the miscibility was also reported by Bauer *et al.*[8] for systems of polystyrene (PS) and poly(vinyl ether). However, Frisch[9] obtained single-phase IPNs not only from miscible polymer pairs, e.g. PS and poly(2,6-dimethyl-1,4-phenylene oxide), but also from immiscible polymer pairs such as PS and PMMA. It is noteworthy that all the blends studied by Frisch were simultaneous polymer networks

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rather than the usual sequential IPNs. A different preparation procedure might be one of the reasons for the difference in the effect of crosslinking on the miscibility. For a semi-IPN system, composed of a miscible pair, i.e. phenol–formaldehyde resin and an ethylene–vinyl acetate (EVA) copolymer[10,11], the variation of the fraction of hydrogen-bonded carbonyl groups in EVA was monitored by i.r. spectroscopy during heating cycles. It was found that on heating the phenolic resin undergoes reaction leading to an increase in molecular weight, degree of branching and crosslinking. Kim *et al.*[12] studied another IPN system derived from the miscible pair of phenol–formaldehyde resin and PMMA. It was observed that at high crosslinking temperature, the dissociation of hydrogen bonding was extensive and only a small fraction of the original hydrogen bonding was recovered in the semi-IPNs on cooling. This implies that crosslinking hinders the attainment of equilibrium segmental interactions.

With respect to the effect of crosslink structure on miscibility in IPNs with strong intercomponent interactions and the possibility of preparing single-phase IPNs by introducing hydrogen bonds, the results mentioned above do not lead to a concordant conclusion. In most systems studied each segment within the components has its own group capable of forming a specific interaction, so the density of intercomponent interactions cannot be simply adjusted. In this paper, we concentrate on IPNs based on polyacrylate and PS(OH) with controllable hydrogen bonding. In the study, we enjoyed the flexibility of both the intercomponent interaction and intracomponent crosslinking being independently controllable. Therefore, we were able to study the effects of hydrogen bonding at different levels of crosslink density and the effects of crosslinking at different levels of hydrogen bonding on morphology, miscibility and properties. This and the next paper of this series[13] deal with hydrogen bonding density and crosslink density, respectively.

## EXPERIMENTAL

### *Materials*

Styrene (Shanghai Gaoqiao Chem. Co.), butyl acrylate (BA, Beijing Dongfeng Chem. Co.), acrylic anhydride (AA Aldrich), divinyl benzene (DVB, E. Merck) were purified before use. HFMS was prepared from *p*-chloro-α-methyl styrene (Aldrich) as described previously[3].

### *Synthesis of poly(butyl acrylate) (PBA) networks*

PBA networks with different crosslink densities were prepared by free-radical polymerization as follows. Purified BA was mixed with 0.5% initiator (azobisisobutyronitrile, AIBN) and a desired amount of crosslink agent (AA) under a dry nitrogen atmosphere. The reactant mixture was kept in a sealed polymerization mould constructed of rectangular glass plates at 60°C for 24 h and then at 90°C and 100°C for 2 h successively.

### *Synthesis of full IPNs*

All full IPNs of PBA and PS(OH) were prepared by a sequential procedure. First, a PBA network film was swollen with a mixture, which was purged with nitrogen, containing desired amounts of styrene, HFMS, 1 wt% initiator (benzoyl peroxide) and 1 mol% crosslink agent (DVB). The swollen film was kept for 24 h under a dry nitrogen atmosphere in a sealed container to reach composition uniformity. Copolymerizations of styrene and HFMS were performed using the same temperature programme as that for PBA networks. Finally, the IPNs obtained were heated in a vacuum oven to remove the monomer residue ($<1$–2% weight loss was found).

### *Characterization*

The number-average molecular weights between crosslinks ($M_c$) of PBA networks were calculated based on equilibrium swelling measurements in toluene, methyl ethyl ketone (MEK) and tetrahydrofuran (THF) according to the Flory–Rehner equation[14]. In this paper, we concentrate on the effect of hydroxyl content in PS(OH) on miscibility, morphology and properties. The samples had five levels of hydroxyl group contents, i.e. 0, 1, 5, 30 and 50%, while the crosslink density of PBA networks denoted B2 ($M_c=9700$, MEK) and compositions (50/50) were about the same.

In *Table 1* the sample code B2 represents the first network PBA2 and S1 and S7 denote the amount of crosslink agent in PS(OH) networks, 1 and 7%, respectively. The numerals in the middle of the code refer to the molar percentage of HFMS in PS(OH).

Thermal analysis of the IPN samples was performed with a Dupont 1090 B differential scanning calorimeter over a temperature range of −80 to 150°C at a heating rate of 20°C min$^{-1}$. The samples were pretreated at 100°C for 25 min followed by slowly cooling to room temperature.

Due to the absence of unsaturated bonds in both components of the IPNs, the routine staining agent $OsO_4$ is not effective. Instead, ruthenium tetroxide was used for selective staining of PS(OH)[3]. The ultrathin sections used for the electron microscopy observations were produced by ultratoming the IPN films followed by staining with the vapour of aqueous $RuO_4$ solution. The observations were conducted using a Hitachi H500H electron microscope.

The measurements of dynamic mechanical analysis (d.m.a.) were carried out with a rheometrics mechanical spectrometer RMS 800. The dynamic storage modulus ($E'$), loss modulus ($E''$) and loss factor ($\tan\delta$) were measured at a constant angular frequency $\omega=10$ rad s$^{-1}$ of sinusoidal tensile deformation. The film samples (~20 μm thick and 30 mm long) were deformed using special fixtures for film extension. The measurements were conducted under a nitrogen atmosphere over a temperature range of −70 to 160°C (accuracy ±0.5°C).

**Table 1** Characterization data of IPNs

| Sample code | PS(OH)/PBA | OH content in PS(OH) (mol%) | Crosslink agent content in PS(OH) (wt%) |
|---|---|---|---|
| B2-0-S1 | 48/52 | 0 | 1 |
| B2-1-S1 | 49/51 | 1 | 1 |
| B2-5-S1 | 49/51 | 5 | 1 |
| B2-30-S1 | 46/54 | 30 | 1 |
| B2-50-S1 | 46/54 | 50 | 1 |
| B2-1-S7 | 49/51 | 1 | 7 |
| B2-5-S7 | 48/52 | 5 | 7 |

The deformation amplitude was varied within the range 0.01–0.1% remaining always well within a linear viscoelastic range of the sample as tested by appropriate amplitude sweeps.

Turbidity was measured with a 1001DP turbidimeter for the IPN films that were 3 mm thick.

## RESULTS AND DISCUSSION

The turbidity $\tau$ of a blend sample has been used as one of the simplest and most intuitive criteria for miscibility. It can be calculated through the Beer–Lambert extinction law:

$$\tau = -\ln(I/I_0)/L$$

where $I/I_0$ is the transmittance of the sample with thickness $L$. Turbidity is related to the relative light attenuation caused by the scattering of light. The scattering intensity depends on the difference in the refractive indices of the scattering particles and matrix, and on the size and volume fraction of the dispersed phase. Since in the present system the refractive index and volume fraction do not substantially change, the turbidity can be used as an indication of the relative heterogeneity of the samples. Usually, for a sample with a thickness of 3–4 mm, it is totally opaque when $\tau > 1.0$ and becomes dim if $\tau > 0.4$ and finally becomes completely transparent when $\tau < 0.15$[15]. The turbidity of the IPN samples as a function of hydroxyl content of PS(OH) is shown in *Figure 1*. A large decrease of turbidity is observed when the hydroxyl content increases from 0 to 5 mol%, implying a drastic increase in the degree of phase mixing. The curve levels off at $\tau = 0.05$ when the hydroxyl content increases further. The further possible variation, if any, of the turbidity caused by a further decrease of the phase size cannot be detected by this simple measurement. However, the total transparency of the films at least implies the fine phase structure and high extent of mixing. i.e. phase size must be much smaller than the wavelength of light used.

D.s.c. analysis, which is sensitive on a scale as small as ~10 nm, presents more information about phase structure. It was found that ~2 mol% hydroxyl content in PS(OH) results in complete miscibility with PMMA in the linear polymer blends. However, as shown in *Table 2*, all the IPN samples covering hydroxyl contents in PS(OH) from 0 to 50 mol% show two glass transitions. In *Table 2*, the data for pure PBA and PS(OH) with different hydroxyl content networks are listed for reference. An interesting feature of the results is that the low $T_g$ of the IPNs is quite close to that of pure PBA and the high $T_g$ is much lower than that of PS(OH). Using the well-known 'random copolymerization equation'[15] for the glass transitions of miscible blends, $T_g = T_{g1}W_1 + T_{g2}W_2$, the approximate compositions of the coexisting phases are calculated (*Table 2*). From the results, we may designate the low and high $T_g$ phases as a pure PBA phase and a 'mixed phase' or PS(OH)-rich phase, respectively. In the PS(OH)-rich phase, the PBA content increases significantly as the OH content in PS(OH) increases from 0 to 5 mol% and then increases slowly when the OH content increases further. When the OH content in PS(OH) is >30 mol%, the PBA content in the PS(OH)-rich phase reaches 42%. This means that most of the component polymers (~86%) exist in the 'mixed phase' while only 14% of the polymer, which is almost pure PBA composes the low $T_g$ phase. In short, the d.s.c. study indicates a clear trend of miscibility enhancement with increasing OH content and hence the density of hydrogen bonds. This general trend is in accordance with that for ordinary blends without crosslink structure[3]. However the effectiveness of the miscibility increase in the IPNs is much lower than that in the corresponding non-crosslinked blends, which will be discussed in detail later.

In morphological studies, selective staining with $RuO_4$ of the PS(OH)-rich phase has been proved effective and results in enough contrast. The micrographs shown in *Figure 2* present a clear and intuitive feature of the effect of hydroxyl content on miscibility. *Figure 2a*, for IPNs without any hydrogen bonding introduced, clearly shows a two-phase structure on a scale of ~0.1–0.5 μm. As in ordinary IPNs there is no clear phase boundary as a result of interlock of the phases caused by the crosslinks. Besides, the bright and dark areas are about the same, as expected from the total composition. Incorporating hydroxyl-containing units into PS, even as little as 1%,

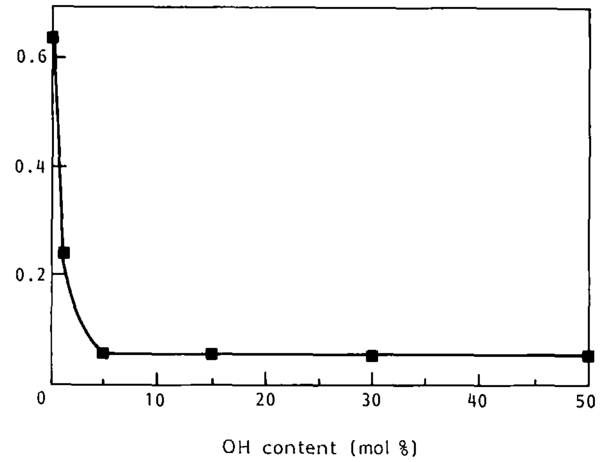

**Figure 1** Turbidity of PBA/PS(OH) IPNs plotted against OH content in PS(OH). Samples have the same crosslink density ($M_c = 9700$) of PBA networks and the same crosslink agent content (1%) in PS(OH)

**Table 2** Glass transition temperature of PBA and PS(OH) with different hydroxyl contents and their IPNs and the calculated phase compositions of the IPNs based on d.s.c. measurements

| | | | Composition (wt%) | |
|---|---|---|---|---|
| Sample code | $T_g$ (°C) | | PS(OH) in PBA-rich phase | PBA in PS(OH)-rich phase |
| B2-0-S1 | −46 | 70 | 0 | 0.22 |
| B2-1-S1 | −46 | 48 | 0 | 0.27 |
| B2-5-S1 | −48 | 58 | 0 | 0.36 |
| B2-30-S1 | −48 | 56 | 0 | 0.42 |
| B2-50-S1 | −48 | 60 | 0 | 0.42 |
| | OH content (mol%) | | | $T_g$ (°C) |
| PBA2 | – | | | −46 |
| PS(OH)-0 | 0 | | | 100 |
| PS(OH)-1 | 1 | | | 82 |
| PS(OH)-5 | 5 | | | 116 |
| PS(OH)-30 | 30 | | | 131 |
| PS(OH)-50 | 50 | | | 137 |

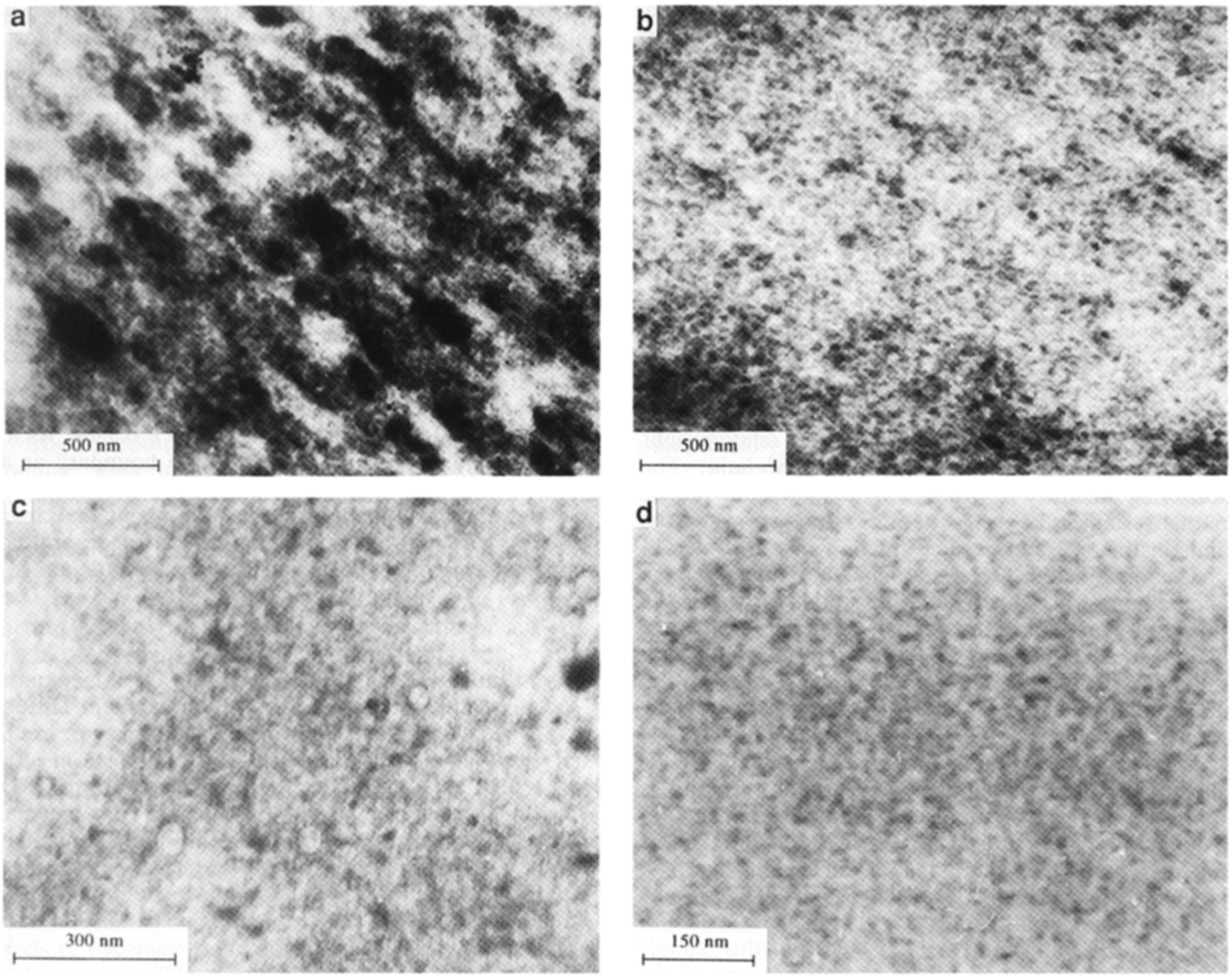

**Figure 2** Transmission electron micrographs of PBA/PS(OH) IPNs showing the effect of hydroxyl content in PS(OH) on morphologies: (a) B2-0-S1; (b) B2-1-S1; (c) B2-5-S1; (d) B2-30-S1

leads to a considerable change in the phase structure as shown in *Figure 2b*. First, the phase size becomes much smaller ($< \sim 50\,\mu$m), and second, the rough area ratio of dark to bright becomes much higher indicating that the PS(OH)-rich phase becomes dominant. Of course, this variation is in agreement with the composition analysis based on d.s.c. measurements mentioned above, i.e. more PBA component enters into the PS(OH)-rich phase when the OH content goes up. Further morphological change, i.e. phase size getting finer ($\leqslant \sim 10$ nm) can be seen from a comparison of *Figures 2b, c* and *d*. This general trend of miscibility enhancement by increasing hydroxyl content is further confirmed by the results shown in *Figure 3* for IPNs in which the crosslink density of the PS(OH) networks is higher than those shown in *Figure 2*. At this higher crosslink level of PS(OH) networks, a similar and apparent decrease of phase size is also observed when the hydroxyl content in PS(OH) increases from 1 to 5 mol%. In fact, in the case of B2-5-S7, the phase structure is so fine and the phases are so tightly interpenetrating that it is almost impossible to give a definite phase size at the present resolution of TEM used. From the above discussion, it is very clear that the study of glass transition temperature ($T_g$) and morphological observation of the IPNs lead to the same conclusions with respect to both the trend and limitation of miscibility enhancement via introducing hydrogen bonding. However, with respect to the effectiveness of hydrogen bonding on miscibility, an apparent discrepancy exists between the IPNs and the corresponding blends of the linear polymers. For blends of PS(OH) and the poly(acrylic ester)s, i.e. PMMA, poly(ethyl methacrylate) (PEMA), poly(butyl methacrylate) (PBMA) and PBA, reported by Pearce *et al.*[2] and Cao *et al.*[3], it is found that only $\sim 2$ mol% hydroxyl in PS(OH) makes the blends miscible as judged by d.s.c. and TEM. However, in the IPNs, the two-phase structure is maintained even when the hydroxyl content in PS(OH) is as high as 30–50 mol%, and although the film looks transparent, the phase structure is extremely fine and the composition of the dominant phase is close to the total composition. This substantial difference, of course, can be attributed to the role of crosslinking. The argument dealing with the role of intracomponent crosslinking in retarding the intimate interaction between the components finds additional support from the following results. In the blends of linear PS(OH) and PMMA, a macromolecular complex due to hydrogen bonding may form both in bulk and

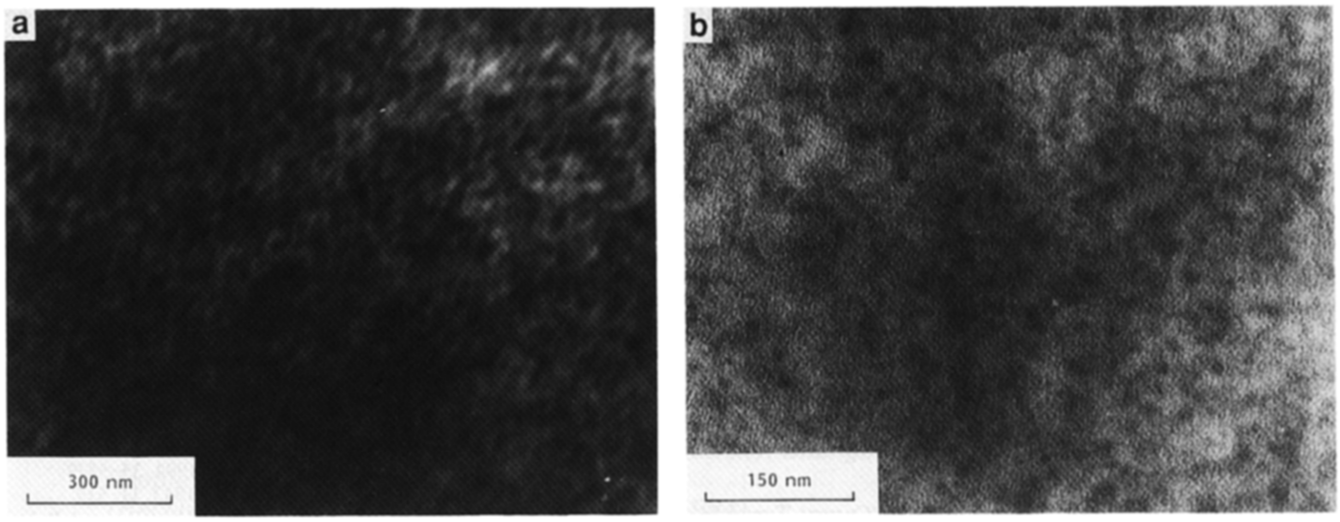

**Figure 3** Transmission electron micrographs of PBA/PS(OH) IPNs with high crosslink density of PS(OH) network showing the effect of hydroxyl content in PS(OH) on morphologies: (a) B2-1-S7; (b) B2-5-S7

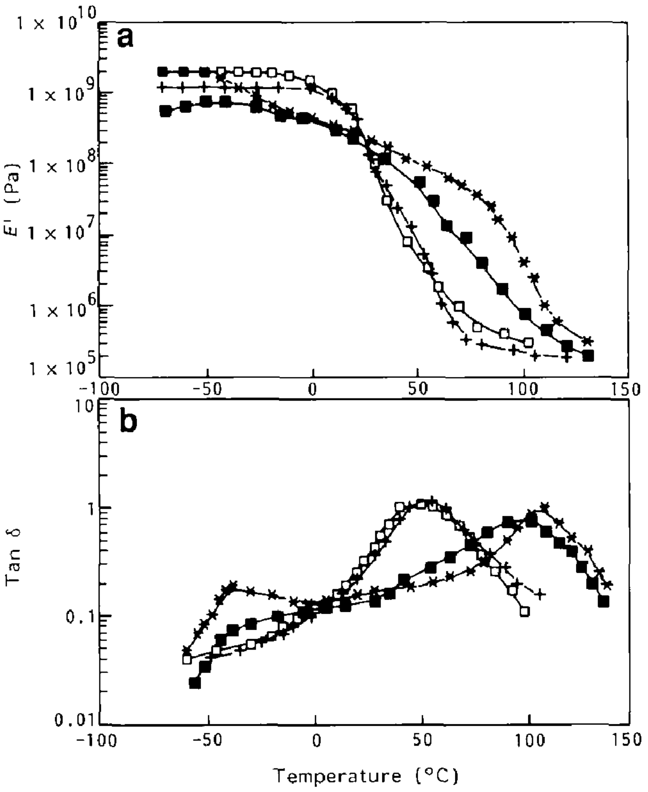

**Figure 4** (a) Storage modulus $E'$ and (b) tan $\delta$ of PBA/PS(OH) IPNs plotted against temperature showing the effect of OH content in PS(OH): (*)B2-0-S1; (■) B2-1-S1; (□) B2-5-S1; (+) B2-30-S1

solution[16] when the hydroxyl content in PS(OH) reaches ~5–10 mol%. The complex is no longer soluble in toluene although both the components are readily soluble. In some complementary experiments, a semi-2 IPN composed of a PBA network and linear PS(OH) with 50 mol% hydroxyl content was prepared. It was found that the PS(OH) in the semi-2 IPN could be quantitatively extracted by toluene. In addition, after chemically destroying the crosslink structure of PBA in the semi-2 IPN, the two components were totally dissolved in toluene. Therefore, both the experiments proved that crosslinking in the IPNs apparently retarded the intimate interaction and complexation for the cases with high hydroxyl content in PS(OH).

*Figures 4a* and *b* show the dynamic mechanical spectra, i.e. $E'$ and tan $\delta$ as a function of temperature, respectively, for IPNs with a total composition around 50/50. What is of interest here is how the glass transitions change with hydroxyl content. For IPNs without hydrogen bonding, there are two clear transitions shown in both the $E'$ and tan $\delta$ plots. From the peak positions, the high and low $T_g$ are found to be 110°C and −40°C, respectively, both are higher than those from d.s.c. measurements. Only 1 mol% hydroxyl incorporated results in a considerable change in the spectra, i.e. the peak of the low $T_g$ turns into a shoulder while the higher one shifts to a lower temperature and becomes much broader. This indicates that miscibility increases by introducing intercomponent hydrogen bonding. A more pronounced change is observed when the hydroxyl in PS(OH) increases to 5 and 30 mol%. In these cases, the low temperature transition unexpectedly disappears and only one relatively sharp transition associated with the 'mixed phase' is observed around 50°C. This dynamic mechanical behaviour seems to correspond to a homogeneous system without phase separation. Obviously, the general trend of miscibility enhancement caused by introducing hydroxyl and then hydrogen bonding in the IPNs examined by d.m.a. is in agreement with that obtained from d.s.c. and TEM studies. However, for the important question whether higher hydroxyl content ($>5$ mol%) can lead to a 'real' miscible IPN or not, the answer from d.m.a. is different from those based on d.s.c. and TEM. The reason for this apparent discrepancy will be discussed in the next paper of this series[13].

It is noteworthy that the IPNs with lower (0 and 1 mol%) hydroxyl content in PS(OH) show a quite different $E'$-temperature behaviour from that of the IPNs with higher (5 and 30 mol%) hydroxyl contents. Over the temperature range from −30 to 30°C, due to the former having a lower glass transition, the modulus is apparently lower than that of the latter. However, for the latter, because the main glass transition of the dominate phase occurs over a temperature range from 30 to 70°C, which is much lower than that of the former, the modulus at ~50°C of the IPNs with higher OH contents becomes two orders of magnitude lower than those with lower OH contents.

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