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Interpenetrating polymer networks with controllable intermolecular hydrogen bonding

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Summary

The effect of introducing simultaneously crosslinking and intermolecular hydrogen bonding into blends of poly(styrene) and poly(butyl acrylate) on miscibility was studied by DSC, TEM and IR. Incorporation of strong proton-donor groups into PS apparently promotes its miscibility with PBA due to hydrogen bonding. Single phase IPN can be prepared but much higher content of the proton-donor is needed in comparison with the corresponding blend without crosslinking. The interlocking structure of the networks appears unfavourable to forming real miscible IPNs.

Introduction

The existing techniques to improve compatibility or miscibility in polymer blends can be broadly classified into two catagories - physical and chemical. In the former, preparing interpenetrating polymer networks (IPN) has proved interesting and fruitful (1). A basic and important conclusion in IPN studies is that the crosslinking structure in one or both of the component polymers is advantageous to compatibility as indicated by phase size, specific phase surface area etc. As for the chemical approach, a great progress has been made in recent years. By introducing ions or polar groups capable of establishing specific interactions (ion-ion, hydrogen bonding, complexation between electron-donor and electron-acceptor etc.) between the polymer components into a otherwise immiscible blend, the miscibility can be considerably enhanced. For example, incorporation of the units carrying strong proton donor groups $(CF_3)_2(OH)C-$ into PS, even the amount is as small as about 2 mol%, would make PS miscible with a series of carbonyl-containing polymers (2-4). A remarkable advantage of this approach is that by adjusting the conditions of polymerization, one can control hydrogen bonding between the hydroxyl and carbonyl groups, which are connected to the two components respectively, and hence the morphology and properties of the blends. In this study, we concentrate on combining the two major approachs by introducing intermolecular hydrogen bonding into IPN. Meanwhile, we adress the following questions: Are the respective effects caused by crosslinking and hydrogen bonding synergestic. simply additive or subtractive? Is it possible to produce a genuine single phase IPN by introducing hydrogen bonding into otherwise immiscble polymer networks ?

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Experimental

materials Hydroxyl-containing monomer p-(1,1,1,3,3,3,-hexafluoro-2-hydroxypropyl)-α-methyl styrene (HFMS) was prepared as described previously (2). Styrene (Shanghai Gaoqiao Chemical Co.), butyl acrylate (BA, Beijing Dongfang Chemical Factory), acrylic anhydride (AA, Aldrich) and divinylbenzene (DB, E.Merck) were purified before use.

Preperation of PBA networks and IPN PBA networks with different degree of crosslinking were prepared by free-radical bulk polymerization. In a dry nitrogen atomosphere, purified BA was mixed with 0.5 wt% initiator AIBN and a desired amount of crosslinking agent AA. The mixture was kept in a sealed polymerization mold formed by rectangular glass plates at 60°C for 24 hrs and then at 90°C and 100°C for 2 hrs successively. The PBA network films were then dried under vacuum for at least 72 hrs. All full IPN's of PBA and PS(OH) (Copolymer of styrene and HFMS) with different degrees of crosslinking of PBA networks and contents of the hydroxyl groups in PS(OH) networks were prepared by a sequential procedure. First, PBA network was swollen with a mixture of desired amount of styrene, 1 wt% initiator BPO, 1 mol % crosslinking agent DB and prescribed amount of HFMS. The swollen film was allowed to reach uniformity in composition via diffusion for 24 hrs in a sealed cell. Copolymerization of styrene and HFMS and drying of the resultant IPNs were performed using the same temperature programme as that for PBA networks. The samples' codes and compositions are listed in Table 1. In series A, the samples have the same crosslinking density in PBA networks but different hydroxyl contents as indicated by the numeral following the code A. Series B, in which the hydroxyl content is almost identical, has different contents of AA units in PBA networks as indicated by the numeral after code B.

Characterization Thermal analysis of IPN samples was performed with a Dupont 1090B differential scanning calorimeter over a temperature range from -80°C to 150°C at a scanning rate of 20°C/min. Before the measurements, the samples were annealed at 100°C for 20 minutes followed by slowly cooling to room temperature. A Perkin-Elmer 938 G infrared spectroscope was used to measure IR spectra. The specimens used were thin sections produced by cutting the IPN films with a Arkon microtome. The hydroxyl contents in IPNs were determined by fluorine analysis. Morphological observation was carried out with a Hitachi H500 electron microscope. Ultrathin sections of the IPN's were made by ultratoming the films followed by selective staining of PS(OH) with vapour of dilute solution of RuO_4 in water (2).

The average molecular weights between crosslinks $\overline{M}c$ of PBA networks were calculated from swelling measurements in methyl ethyl ketone according to Flory-Rehner equation (5) . The solvent-polymer interaction parameter for the present case is 0.358 (5). The $\overline{M}c$ and Tg values for PBA networks obtained are listed in Table 2. As expected, $\overline{M}c$ decreases as the content of the crosslinking egent increases accompanied by a small but clear increase of Tg.

Table 1. The compositions of PBA/PS(OH) IPN's

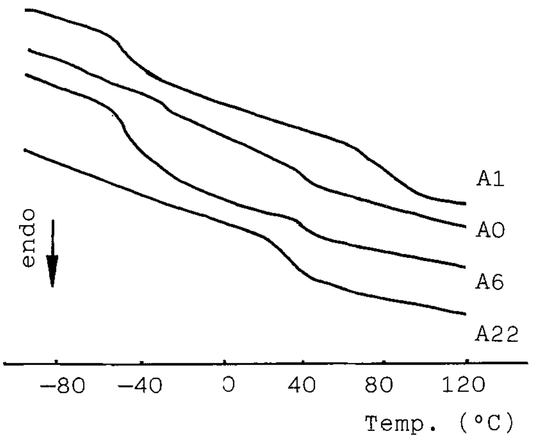
sample code	composition PS(OH)/PBA	AA content in PBA wt %	OH content in PS(OH), mol%
A0	53/47	1.0	0
A1	53/47	1.0	1.0
A6	52/48	1.0	6.4
A22 (B1)	50/50	1.0	22.3
B2	50/50	2.0	23.4
B3	51/49	3.0	24.1
B5	51/49	5.0	22.9

Table 2 Characterization Data of PBA networks

Sample	AA content wt%	$\overline{M}c$ (g/mol)	Tg (°C)
PBA1	1.0	7430	-40.7
PBA2	2.0	3050	-41.6
PBA3	3.0	1840	-39.3
PBA5	5.0	1550	-37.1

Results and Discussion

The DSC results of series A, in which PBA is lightly crosslinked with $\overline{M}c$ = 7430 g/mol, are shown in Fig.1 and Table 3. IPN A0 clearly presents two glass transitions. The lower one is close to that for pure PBA and the higher one (84.7 °C) is somewhat lower than pure PS. However, incorporation of hydroxyl into PS apparently changes the phase behaviour as seen in the DSC traces for A1 and A6. Although the two transitions still exist, the higher one apparentely shifts to much lower temperatures (41.2°C and 40.2°C) so there seems no reason to attribute this transition to the so-called "polystyrene-rich" phase. However, it is relatively close to the Tgs (30°C and 34°C) of the blends composed of linear PBA and PS(OH) (40/60 wt) with respective hydroxyl contents 1.9 and 9.7 mol % (2). Therefore, we are inclined to say that IPN's A1 and A6 are multiphase systems comprising a PBA phase and a phase composed of comparable amounts of PBA and PS, called a "`mixed phase"' below. Differing from all the others in Fig.1, IPN A22 shows the thermal behaviour of a homogeneous, miscible blend, i.e., there is only one, relatively narrow glass transition. Therefore, the minimum value of the hydroxyl content needed to make the IPNs miscible should be between 6.4 to 22.3 mol %. By comparing with the results for the blends of linear polymers (2), in which only about 2 mol% of the introduced hydroxyl renders the blends miscible, it is very clear that for the IPN systems, true miscible, homogeneous state can be realized but much higher hydroxyl content is needed.



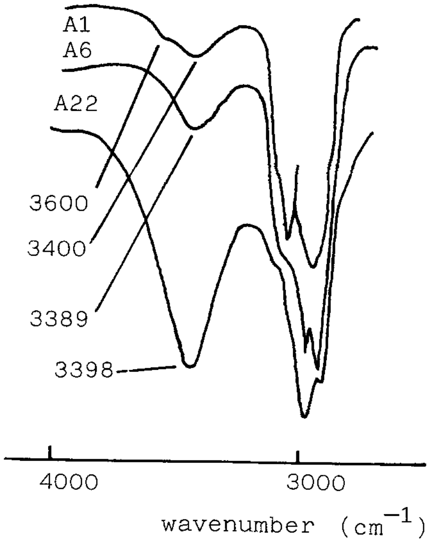


Fig.1 DSC results of IPN series A

Fig.2 IR spectra of series A , part associated with OH stretching is shown

Table 3. The glass temperature Tgs of IPN A and B series

Sample code	Tg (°C)		Sample Code	Tg (°C)	
A0	-43.8	84.7	B1	39.7	
A1	-40.6	41.2	B2	-45.4	38.1
A6	-43.5	40.2	B3	-44.1	27.1
A22	39.7		B5	-42.4	38.1

As that observed in the blends without crosslinking (2), the stretching band of hydroxyl in the IR spectra of IPNs A (Fig.2) shifts to lower frequency by as much as about 200 cm^{-1} reaching 3400 cm^{-1} due to H-bonding. However, for A1, a small band at 3600 cm^{-1}, characteristic of free hydroxyl stretching, can still be detected but disappears in the spectra of A6 and A22. Slightly differing from the case of blends of linear polymers where the frequency shift is independent of the hydroxyl content, the shift in the presnet case varies over a range of 10 cm^{-1} depending on the hydroxyl content. A general trend of the miscibility increasing with the hydroxyl content can be seen more clearly by examining the related electron micrographs. Fig.3a for A0, in which no hydroxyl was incorporated, presents a multiphase morphology but without distinct phase boundary, this is believed to be caused by the presence of crosslinking. It is noted from Fig.3b and 3c that the morphology apparently changes when hydroxyl is introduced into PS(OH) networks. Now the size of the dark area comprising PS(OH) component turns smaller and smaller and the coexisting two phases show higher and higher level of interconnectivity. IPN A22 is the only sample transparent showing no structure under electron microscope, so both morphological study and DSC measurement lead to the conclusion of its complete miscibility.

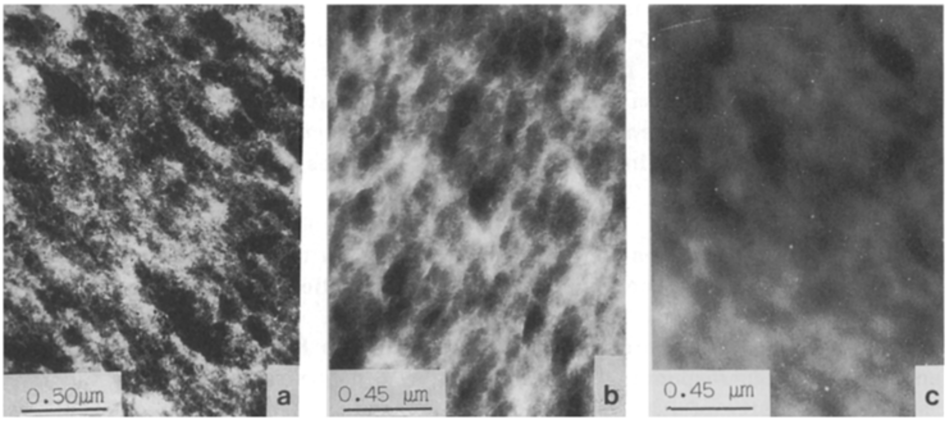


Fig.3 Electron micrographs of A0 (a), A1 (b) and A6(c)

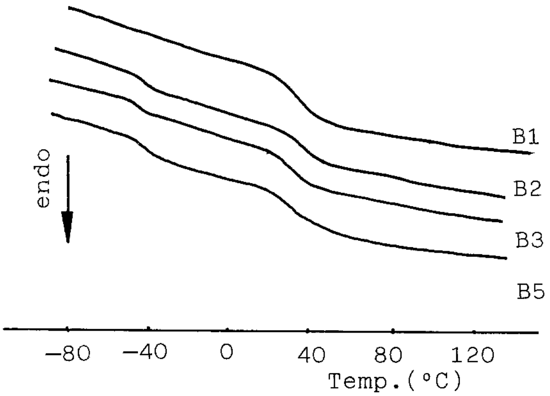


Fig.4 DSC results of IPN series B

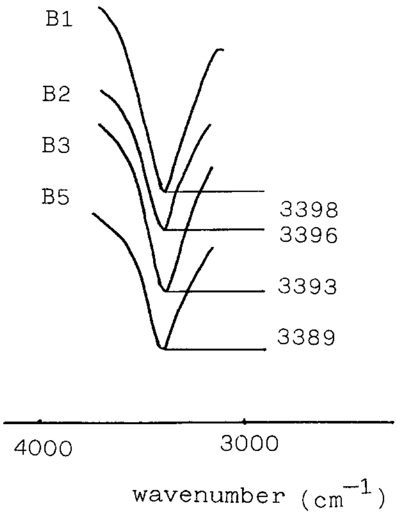


Fig.5 IR spectra of series B, only part associated with OH stretching is shown

The parallel study on B series, in which the crosslinking density of PBA networks varies but hydroxyl content in PS(OH) is around 22%, clearly reveals the effect of crosslinking on the miscibility. Fig.4 and Tab.3 show that except B1 (A22) with the least crosslinking density, all the samples are multiphase systems. Based on the Tg data (Tab.3) it is not difficult to conclude that the two phases existing are PBA phase and a phase composed of PBA and PS(OH) in comparable proportions. It is interesting that in this series, although the crosslinking density changes considerably, there is no apparent change of the higher Tg value, which suggests that the composition of the mixed phase is almost independent of the crosslinking. The multiphase character of B5 is confirmed by microscopic observation showing very fine interpenetrating phase structure. However, The IR spectra, in which the band at 3600 cm^{-1} disppears, indicate that all hydroxyl groups are involved in H-bonding even the phase separation occurs. Besides, the spectra show that the H-bonding intensity slightly increases as the crosslinking density increases.

There are only a few cases in litereture dealing with IPN system having intermolecular hydrogen bonding. Nishi et al.(6) studied poly(oxyethylene)/ poly(acrylic acid) systems. They found that only in the IPNs with light crosslinking, the components form complex leading to homogeneity, as in the blends of the corresponding non-crosslinked polymers. However, as the crosslinking density of POE increases, the blends turn to a multi-phase system. This result clearly shows the unfavourable effect of crosslinking on the H-bond formation. Recently, Coleman et al.(7) reported that even for the strongly interacting systems (EVA/phenolic resin), phase separation occurred on crosslinking. A similar conclusion can be found in a recent communication of Kim et al.(8). As just mentioned, in our experiment, we did find the unfavourable role of crosslinking on miscibility, however, in our case, because the introduced hydroxyl-containing units only existed in a minor part of PS(OH) chains, almost all of them were still able to form H-bonds due to the existance of much higher amount of carbonyl groups, even though phase separation occurred. Now we may ask why crosslinking appears to play opposite roles as regard miscibility in IPNs composed of immiscible pairs and strongly interacting pairs. For the former case, intuitively, the interlocking network structure reduces the molecular mobility necessary for phase separation and aggregation. Therefore, the denser the crosslinking of polymer networks, the smaller the phase domains will be. However, as far as we know, there has not been any case reproted that a entirely homogeneous structure can be reached from a typical immiscible polymer pair only by introducing crosslinks. Even for the case of IPN composed of poly(ethyl acrylate) and poly(methyl methacrylate) which are "slightly immiscible" due to their similar solubility parameters, only a rather broad transition was observed in the modulus-temperature curves (9). Therefore, in our opinion, a certain limitation exists in the miscibility improvement by crosslinking. For the case in which the components may form a miscible system due to specific interaction, what one is concerned most is whether the system can keep its miscibility on segmental scale when crosslink structure is introduced. It is reasonable to think that entire homogeneity also needs sufficient mobility of the component molecules. However, the interlocking structure of the composed networks reduces the mobility, therefore, miscible IPNs cannot be prepared unless the interaction is strong enough and the crosslinking density is not very high as we have seen in IPN A22 (B1).

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