

Silicon secondary crosslinked IPN based on poly(methyl acrylate-co-hydroxyethyl acrylate) and SiO₂

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Silicon secondary crosslinked interpenetrating polymer networks (IPNs) of poly(methyl acrylate-co-hydroxyethyl acrylate) (PMA-HEA) and SiO₂ were prepared and characterized. The effects of composition, water content and substrate plate on the phase morphology of the IPNs of PMA-HEA/SiO₂ were studied by SEM, and the T_g measured by d.s.c. The broadening of the transition region was observed with the increase of water content and the prolongation of the reflux time, and the tendency of the aggregation of silicon in the surface and bottom was also observed with Teflon as a substrate plate. However, an optically transparent film was easily achieved at higher temperature due to the chemical crosslink and physical entanglement between the two phases of PMA-HEA and SiO₂. © 1997 Elsevier Science Ltd.

(Keywords: IPN's; PMA-HEA; tetraethyl orthosilicate)

INTRODUCTION

Polysiloxane has many attractive properties^{1–4}, but it is not easily compatible with other polymers, and has a tendency to aggregate to produce large-scale phase separation. Many investigations to solve the problem have appeared previously^{5–9}. For example, many interpenetrating polymer networks (IPNs) with one component from a siloxane-containing polymer such as PDMS (polydimethyl siloxane) and a siloxane-containing copolymer have been synthesized and investigated. Besides the method of siloxane-containing polymers blending with other polymers (involving IPN), another important route is chemically to incorporate siloxane into conventional polymers such as the copolymerization with other conventional vinyl-type monomers, grafting of siloxane onto the main polymer, or the condensation of siloxane, etc.

In contrast to the above IPN, Ellsworth and Novak^{10,11} prepared an organic–inorganic simultaneous IPN via incorporation of a crosslinked polymer formed *in situ* within sol–gel derived tetraalkoxy silane glasses through both radical and ring-opening metathesis. The volume shrinkage in the typical sol–gel formation was solved well, and a remarkably high degree between the two chemically dissimilar phases of these new composite materials was observed through SEM. On the other hand, the SiO₂ network can be introduced into the surface of the methoxymethyl melamine/polyol

thermosetting coatings which has been used in the automotive industry in order to improve the surface properties of this thermosetting coating, such as acid-resistance¹². Within the thermosetting coating system, the SiO₂ network was formed via hydrolysis and condensation of the silane grafted polymer which has good compatibility with the bulk phase. In this work, a new poly(methyl acrylate-co-hydroxyethyl acrylate) (PMA-HEA)/SiO₂ IPN was synthesized and investigated, in which the network of Si–O–Si can be formed via the hydrolysis and self-condensation of siloxane. On the other hand, siloxane can function as a crosslinker to be condensed with the hydroxyl group of PMAA to produce another network. Our main purpose is to ascertain if the PMA-HEA/SiO₂ IPN is able to be formed and SiO₂ can be aggregated in the surface of the IPN film, and to study the factors affecting the morphology of the IPN.

EXPERIMENTAL

Materials

Methyl acrylate (MA): Beijing Chem. Co.; hydroxyethyl acrylate (HEA): Beijing Chem. Co.; tetrahydrofuran (THF): Beijing Chem. Factory; sodium hydrogen sulfite (SDS): Beijing Chem. Factory; ammonium persulfate (APS): Beijing Chem. Factory; tetraethyl orthosilicate (TEOS): Beijing Chem. Factory; 10 units of oxyethylene containing alkyl phenol (OP-10): Tianjing Additives Factory; dodecyl benzene sulfonic acid (DBSA): Dupont, USA. MA and HEA were distilled

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under vacuum before use. DBSA was purified with a rotary evaporator. All other chemicals were used as received.

Synthesis of poly(methyl acrylate-co-hydroxyethyl acrylate)

Methyl acrylate, hydroxyl ethyl acrylate, mixed surfactant (OP-10 and DBSA) as well as deionized water were placed in a three-neck flask and emulsified prior to polymerization. The emulsion copolymerization was carried out in 250 ml three-neck flask, equipped with a reflux condenser, a stirrer, and a thermometer. A typical recipe used to prepare the copolymer latex is shown in Table 1. The emulsified solution containing APS and 20 g SDS aqueous solution were added dropwise into the three-neck flask, respectively, for about 2 h. The reactor was maintained at 60°C in a thermostated water bath and the polymerization was carried out under an inert nitrogen atmosphere for 6 h. After the reaction was complete the copolymer was precipitated in 5% NaCl solution at 50°C and the precipitate was baked-dry in an oven to constant weight. The composition and hydroxyl group content of the copolymer were characterized with n.m.r. The molar ratio of methyl acrylate/hydroxyethyl acrylate was 6:1.

Preparation of silicon secondary crosslinked IPNs

Well defined amounts of copolymer, TEOS and deionized water, and 0.01 g DBSA were dissolved in 10 g THF. The mixture was refluxed for 1 h, poured into a substrate plate, placed at room temperature under a moist atmosphere for 24 h, and then cured at 100°C for 1 h. The final film was soaked in water, peeled off, dried

at 40°C in a baking oven for 1 h. The films were stored in a desiccator for one week before measurement.

Measurements

I.r. measurement. The film cast on a KBr plate from solution was measured using a Hitachi model 270-30.

Electron microscopy. The phase morphological characteristics of the samples were studied by scanning electron microscopy (SEM). The specimens for SEM were frozen in liquid nitrogen, fractured, mounted, and coated with gold. They were then observed with a Hitachi S-530.

Calorimetric measurements. The glass transitions (T_g s) were measured by differential scanning calorimetry (d.s.c.) (PE, 7 series thermal analysis system). Measurements were carried out from -25° to 150°C under nitrogen at a scanning rate of 20°C min⁻¹. Specimen sizes were of the order of 9 mg.

RESULTS AND DISCUSSION

Siloxane can readily be self-condensed with the product of a Si-O-Si network via hydrolysis using acid as catalyst^{13,14}, and possibly condensed with P(MA-HEA) to form a Si-O-C bond which plays an important role in the preparation of silicon secondary crosslinked IPNs in this work. The i.r. spectra of P(MA-HEA) (Figure 1a) and P(MA-HEA)/TEOS IPN (Figure 1b) are given in Figure 1. In comparison with Figure 1a, b shows the following characteristics: (1) the absorption peak of the hydroxyl group at 3450 cm⁻¹ changed in shape and intensity; (2) there were two new absorption peaks appearing at 1030 and 965 cm⁻¹, which were assigned to Si-O-Si and Si-O-C bonds, respectively^{12,15}. These characteristics show that there are two kinds of competitive condensation reactions occurring in the preparation of P(MA-HEA)/TEOS IPN, as shown in Scheme 1, and a homogeneous, optically transparent film may also be obtained by controlling synthetic conditions as in the poly(methyl acrylate-co-acrylic

Table 1 Recipe for the emulsion copolymerization of methyl acrylate and hydroxyethyl acrylate

Ingredient	MA	HEA	APS	SDS	DBSA	OP-10	H ₂ O
Amount (g)	36	4	0.3	0.15	0.1	0.2	120

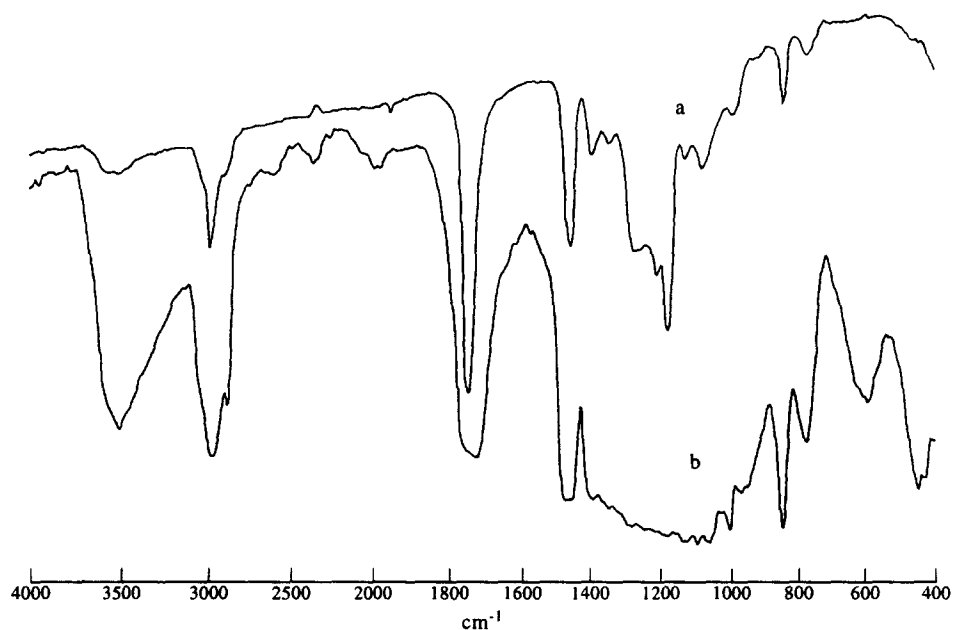
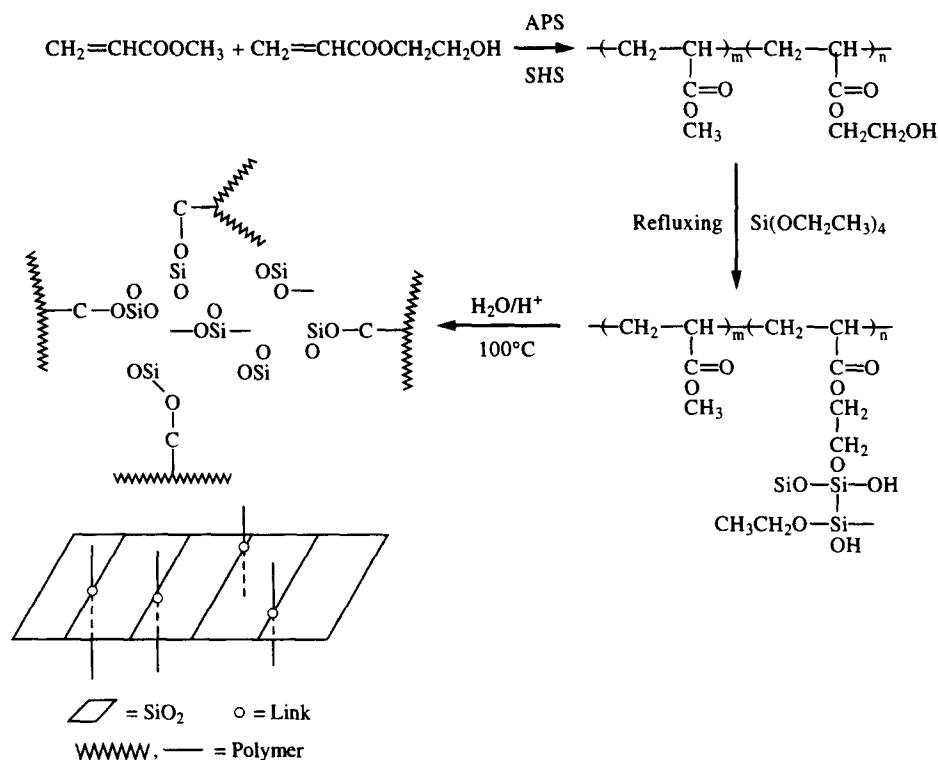


Figure 1 I.r. spectra of (a) P(MA-HEA) and (b) P(MA-HEA)/TEOS (P_{3H-5})



Scheme 1 Formation of silicon secondary crosslinked interpenetrating polymer network

Table 2 Results of d.s.c. measurement (T_g) and properties of the IPN films

Sample ^a	Composition TEOS/P(MA-HEA)	T_g (°C)	Remarks on the samples ^b
PMA-HEA	0/100	16	soft, TP, sol. in A and THF
P _H	5/95	—	soft, TP, swollen in A and THF
P _{2H}	10/90	21	soft, TP, swollen in A and THF
P _{3H}	20/80	22	soft, TP, swollen in A and THF
P _{4H}	50/50	22, 90	brittle, TP, swollen in A and THF
P _{3H-2R}	20/80	22	soft, TP, swollen in A and THF
P _{3H-5}	20/80	22	soft, TP, swollen in A and THF
P _{3H(g)}	20/80	—	soft, TP, swollen in A and THF
P _{3H(i)}	20/80	—	soft, TP, swollen in A and THF

^a H, H-5 = 1, 5% water, respectively; 2R represents 2 h refluxing time; (g), (i) denoting glass and iron as substrate plate, respectively, the others had Teflon as substrate plate

^b TP = Transparent, sol. = soluble, A = acetone

acid) (PMAA)/TEOS system, but with a greatly different reaction behaviour from the PMAA/TEOS system¹⁶, i.e. the cure temperature for P(MA-HEA) film (100°C) is much higher than that for the PMAA/TEOS system (room temperature), presumably due to the higher apparent activation energy for the reaction of -OH with TEOS. In addition, it is assumed that the stability of the -SiOOC- bond in PMAA/TEOS is less than that of -SiOC- in this system.

T_g obtained from P(MA-HEA), P_{2H}, P_{3H}, P_{3H-2R}, P_{3H-5} and P_{4H}, and solubility obtained for P(MA-HEA), P_{2H}, P_{3H}, P_{3H-2R}, P_{3H-5}, P_{2H(g)}, P_{2H(i)} and P_{4H} are given in Table 2. All crosslinked films except P_{4H} (brittle) were soft and transparent, and insoluble in good solvent such as acetone and THF for P(MA-HEA), indicating P(MA-HEA) can easily be condensed with TEOS at higher temperature, in good agreement with the i.r.

spectra. While Si(OC₂H₅)₄ reacting with ROH (alcohol) using acid as catalyst, the longer the chain length of R, the more easily the transesterification reaction can be carried out^{17,18}, confirming the result obtained in this study. Upon P(MA-HEA) reacting with TEOS, the formation of the Si-O-C link and physical interpenetration between the -SiOSi and -SiOC- networks compress the two chemically dissimilar phases, so that the homogeneous, transparent film is obtainable.

From Table 2, we can also observe only one T_g for P_{2H}, P_{3H}, P_{3H-2R}, and P_{3H-5}, respectively, among which there is only a little increase with the increase of TEOS. The results indicate a single phase morphology. There are two distinct glass transition temperature for P_{4H} suggesting a phase separation in the material¹⁹. From Figure 2 a broadening of glass transitions (see Table 3) was observed with increasing water content as well as

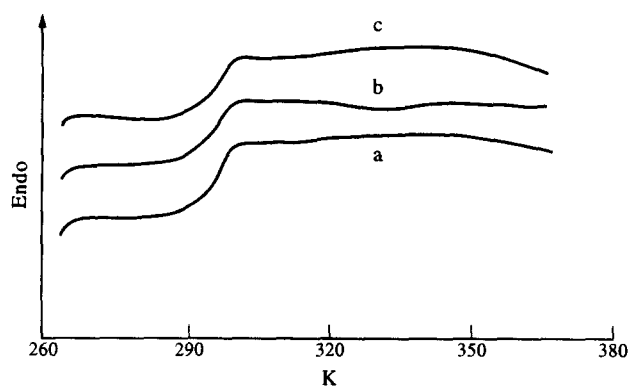


Figure 2 D.s.c. thermograms of 80/20 P(MA-HEA)/TEOS system: (a) P_{3H} (1% water, 1 h of refluxing), (b) P_{3H-5} (5% water, 1 h of refluxing), (c) P_{3H-2R} (1% water, 2 h of refluxing)

Table 3 Range of the glass transition temperatures of the films

Code	$T_{onset} - T_{offset}$ (K)	Width ($^{\circ}C$)
P_{3H}	279–303	24
P_{3H-2R}	271–304	33
P_{3H-5}	275–306	31

refluxing time, although no obvious change in the temperature was observed. This leads to some difficulties in obtaining the best T_g values. The broadening of the transition region may reflect a microheterogeneity of phase domains²⁰.

SEM fracture studies of P_{3H} and P_{4H} (Figure 3) revealed a common characteristic that there is a tendency for Si–O–Si phase to aggregate in the two surfaces of the IPN film and more particles (Si–O–Si phase)

appeared in the bottom, more obvious submicrometre sized particles can be observed at 50% TEOS (P_{4H}). The water content and refluxing time also strongly affect the morphologies of these samples (Figure 4) due to the competitive reaction rates being changed by these factors in this system, such as increasing hydrolysis and condensation of TEOS with increasing water content. Submicrometre sized holes resulting from the removal of large Si–O–Si particles exist in P_{3H-5} , indicating the particles are not embedded in the bulk phase, but there were no holes in P_{3H} . With increasing refluxing time, more homogeneously dispersed particles can be observed in P_{3H-2R} than that in P_{3H} (Figure 3), suggesting a high density crosslink network has been formed with 2 h refluxing time, which inhibits the migration of the component with the lower surface tension.

The SEM observation of $P_{3H(i)}$ and $P_{3H(g)}$ (Figure 5) showed that substrate plates with different surface tension also greatly affect the morphologies of the samples. One difference is that more spherical particles appear in $P_{3H(g)}$ with glass as substrate plate than that in $P_{3H(i)}$ with iron as substrate plate. Another difference is that more spherical particles appear at the bottom than at the surface of $P_{3H(g)}$, while such a phenomenon is not observed in $P_{3H(i)}$, indicating the particles of Si–O–Si network have a trend of segregation due to the different interfacial tension as reported in other systems^{21,22}.

In summary, the formation of a Si–O–C link which plays an important role in the preparation of the silicon secondary IPNs was characterized through FTi.r. The solubility of the films, and IPNs based on PMA-HEA and TEOS can be easily achieved at a high cure temperature. The SEM fracture studies for this PMA-HEA/SiO₂ system and the T_g measured by d.s.c. indicate

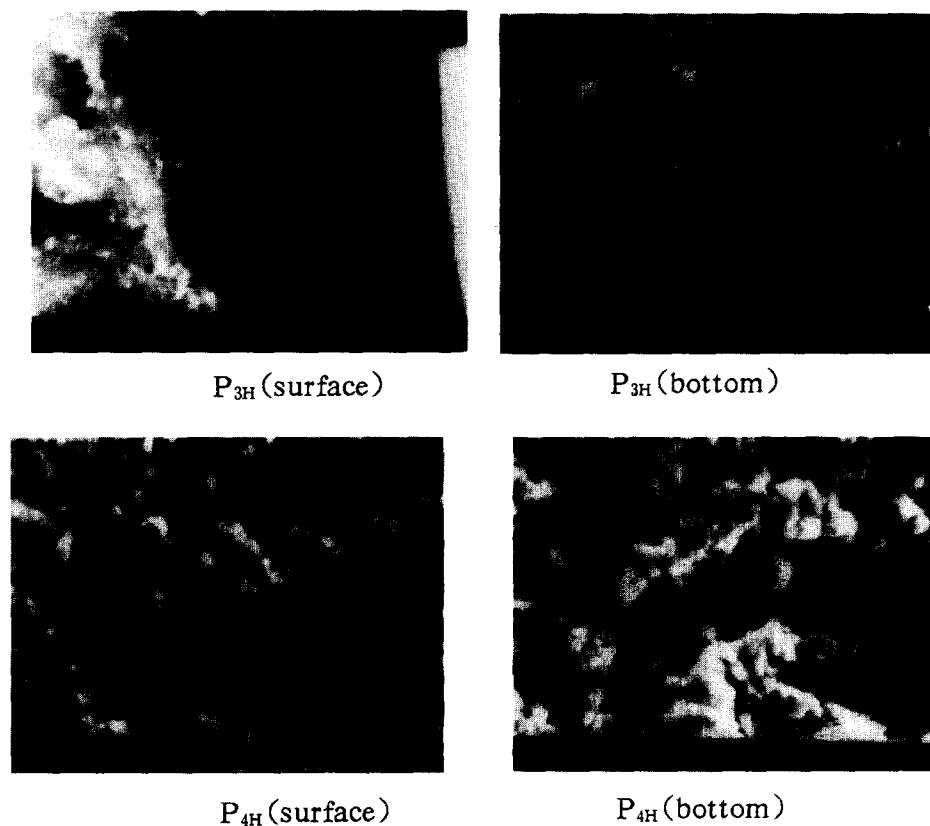


Figure 3 SEM of the fracture sections of IPNs for P_{3H} (20% TEOS) and P_{4H} (50% TEOS)

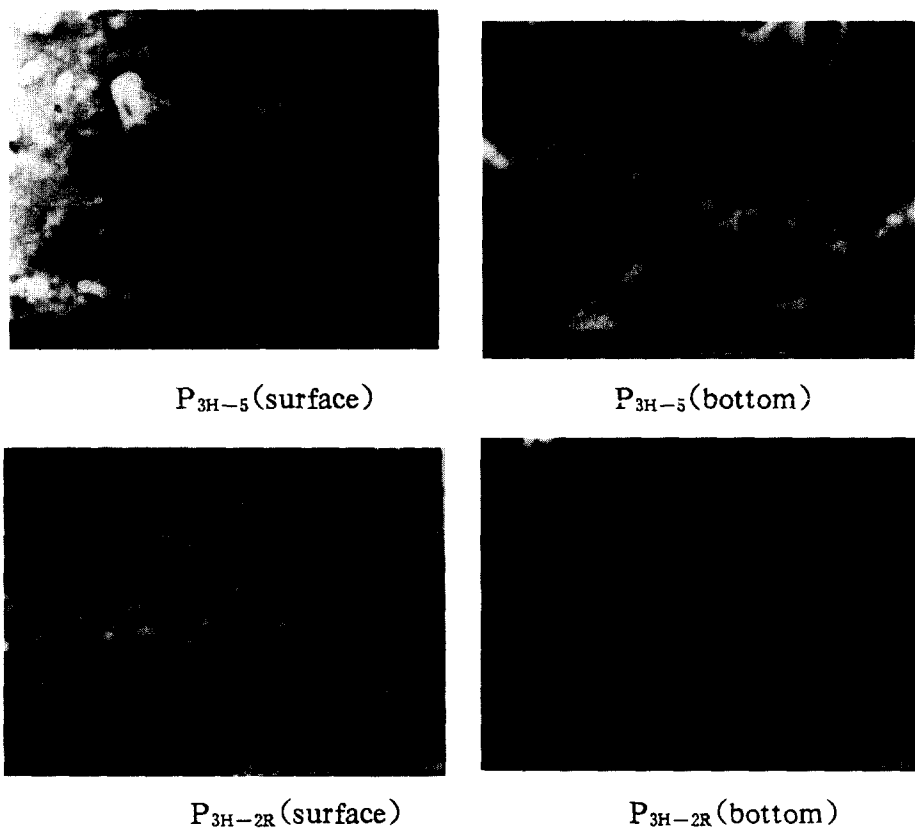


Figure 4 SEM of the fracture sections of P_{3H-5} and P_{3H-2R}

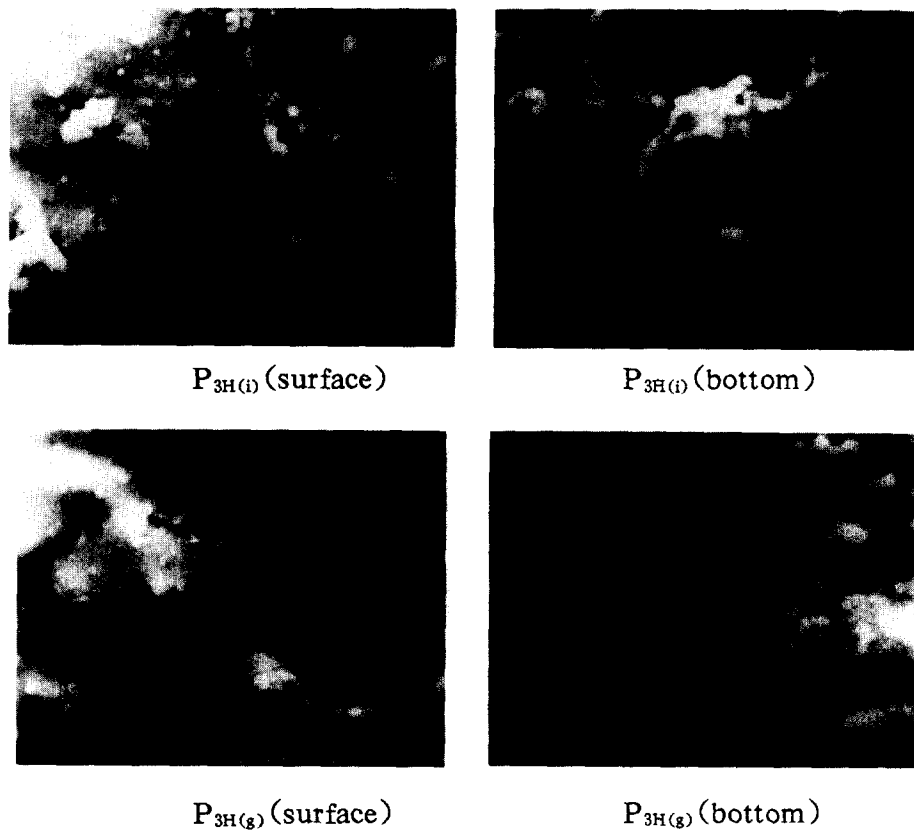


Figure 5 SEM of the fracture sections of P_{3H(i)} and P_{3H(g)}

the degree of phase separation of the IPNs corresponds to a definite composition range of PMA-HEA and TEOS, corresponding to water content as well as to the refluxing time, due to the corresponding change of competitive crosslink rates in the PMA-HEA/TEOS system. With the addition of 5% water, the IPNs with submicrometre sized holes exhibited a high micro-phase separation between the two incompatible phases of crosslinked PMA-HEA/SiO₂, and above 50 wt% of TEOS content, evidence of phase separation were observed by SEM and the two *T_g*s. In addition, the surface morphology strongly depends on the substrate plate and a trend of segregation of the Si–O–Si network in the two surfaces of most samples (e.g. P_{3H}), can be observed.

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