Interpenetrating Polymer Networks Based on Poly(styrene-*co*-butylacrylate-*co*-hydroxyethyl methacrylate) and SiO₂

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ABSTRACT: Copolymer such as poly(styrene-*co*-butylacrylate-*co*-hydroxyethyl methacrylate) p (St-BA-HEMA) was prepared via free radical emulsion polymerization method. The resulting copolymer was converted to silicone secondary crosslinked interpenetrating polymer network (IPN) by condensation reaction with tetraethyl orthosilicate (TEOS). The obtained copolymers were characterized by using Fourier transform infrared spectroscopy (FTIR). Thermal properties of the copolymers were studied by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Optical microscopy (OM) is used for studying the morphology, and then the effects of silicone concentrations, the reflux time, and composition on the phase morphology of P (St-BA-HEMA)-SiO₂ IPNs were discussed. The broadening of the transition region was observed with the prolongation of the reflux time, and the tendency for aggregation of silicone on the surface was observed with Teflon as 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 P (St-BA-HEMA)-SiO₂. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 722–728, 2011

Key words: coatings; FTIR; interpenetrating networks (IPN); silicones; surfaces

INTRODUCTION

Polysiloxane has many attractive properties,[1–7] 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 been reported previously.[8–12] For example, many interpenetrating polymer networks (IPNs) with one component from a siloxane-containing polymer such as polydimethyl siloxane (PDMS) and a siloxane-containing copolymer have been synthesized and investigated. Besides the method of siloxane-containing polymers blending with other polymers (involving IPN),[13–21] another important route is chemically to incorporate siloxane into conventional polymers such as (a) the copolymerization with other conventional vinyl-type monomers, (b) grafting of siloxane onto the main polymer, (c) the condensation of siloxane, etc.[22–30]

In contrast to the above IPN, many researchers[31–35] 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 scanning electron microscope (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 to improve the surface properties of this thermosetting coating, such as acid resistance.[36] 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. Accordingly, the reactions of organosilanes with silica have been extensively studied,[37–39] and reactions of alcohols with silica have been suggested by Iler.[40] His work confirmed that alcohols should undergo surface condensation reactions with silica. Iler treated amorphous silica with alcohols at elevated temperatures (about 200°C) to prepare a hydrophobic silica. He proposed that he had prepared an organic-coated silica via condensation of the alcohol with surface silanols to give SiOC bonds. Although such a bond is hydrolytically unstable, the organic portion of the alcohol could act as a barrier to prevent the corroding H₂O from reaching the bond; thus hydrophobicity could be maintained. Although very little direct evidence has been

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TABLE I
Polymerization Recipe at 60°C

Compound	Amount (g)
Styrene (St)	18
Butyl acrylate (BA)	18
2-Hydroxylethylmethacrylate (2-HEMA)	4
Initiator: (NH$_4$)$_2$ S$_2$O$_8$	0.3
Buffer: sodium hydrogen sulfite (SHS)	0.3
Anionic surfactant: sodium lauryl ether sulfate (SLES)	1
Nonionic surfactant: Arkupal (N-300)	0.2
Demineralized water	120

reported to confirm these propositions of surface reactivity, Raymond et al.[41] have been reported first infrared spectroscopic investigation of uncatalyzed reactions of various alcohols with the surface of amorphous silica. In addition, they reported that this surface reaction can be markedly enhanced by Lewis bases. In this work, a new poly(styrene-co-butylacrylate-co-hydroxyethyl methacrylate) and SiO$_2$, p (St-BA-HEMA)-SiO$_2$ IPN was synthesized and investigated, in which the network of Si—O—Si can be formed via the hydrolysis and self-conduction of siloxane. On the other hand, siloxane can function as a crosslinker to be condensed with the hydroxyl group of 2-hydroxyethyl methacrylate (HEMA) to produce another network. The main purpose of this article is to ascertain if the (St-BA-HEMA)-SiO$_2$ IPN is able to be formed and SiO$_2$ can be aggregated in the surface of the IPN film, and to study the factors affecting the morphology of the IPN.

EXPERIMENTAL

Materials

The monomers St (Aldrich) and BA (Aldrich) were freed from the inhibitor by shaking with 10% aqueous NaOH, washing with distilled water, and drying over Na$_2$SO$_4$. They were then distilled under reduced pressure before use and stored at −20°C to avoid thermal polymerization. HEMA, sodium hydrogen sulfite (SHS), and tetraethyl orthosilicate (TEOS; Merck, Hohenbrunn, Germany) were analytical grades and used directly without further purification. Sodium lauryl ether sulfate (SLES) and Arkupal (N-300) were purchased from Henkel, Germany, and initiator ammonium peroxodisulfate (APS; Fisons) were used as received. Water was distilled and deionized. Tetrahydrofuran (THF) was purchased from Merck and distillated before using for reactions.

Synthesis of poly(styrene-co-butylacrylate-co-hydroxyethyl methacrylate)

St, BA, 2-HEMA, Arkupal (N-300), and SLES as well as deionized water were placed in a three-neck

round-bottom flask and emulsified prior to polymerization. The emulsion copolymerization was carried out in 250 mL three-neck flask, equipped with a reflex condenser, a stirrer, and a thermometer. A typical recipe used to prepare the copolymer latex is shown in Table I. The emulsified solution containing APS and 20 g SHS aqueous solution was added drop-wise into the three-neck flask, for about 2 h, respectively. 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 completed the copolymer precipitated in 5% NaCl solution at 50°C, and the precipitate was baked dry in an oven to constant weight. The structure of these copolymers was confirmed by Fourier transform infrared spectroscopy (FTIR; Fig. 1).

Preparation of silicone secondary crosslinked IPNs

0.3 g St-BA-HEMA copolymer, 0.075 g TEOS, 0.3 mL deionized water, 0.1 g HCl, and 0.01 g SLES were dissolved in 10 mL of THF. The same procedure has been used for the other compositions and is given in weight percent in the Tables II and III. The mixture was refluxed for 1 h, and the existing water was extracted by a Dean–Stark apparatus during refluxing. Then the mixture was poured into a substrate plate, placed at room temperature under a moist atmosphere for 24 h, and then the composition, which was formed an optically transparent film, cured at 100°C for 1 h. The final film was wiped in water, peeled off, and then dried.

Polymer characterization

Differential scanning calorimetry (DSC) thermograms were taken on a Mettler TA 4000 Model apparatus at a heating rate of 10°C/min. The glass transition temperature (T_g), was taken at the onset of the
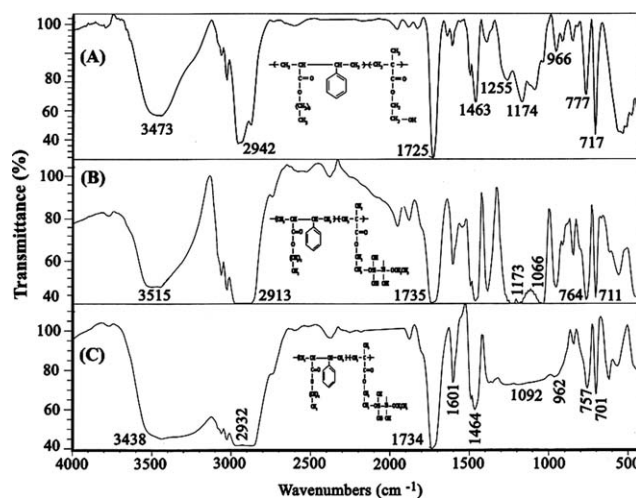

Figure 1 FTIR spectra of (A) P (St-BA-HEMA), (B) P (St-BA-HEMA) with 30% TEOS, and (C) P (St-BA-HEMA) with 50% TEOS copolymers.

TABLE II
Results of the DSC Measurement (T_g) and Properties of the IPN Films

Sample	Composition TEOS/P(St/BA/HEMA)	T_g (°C)	Remarks on the samples
1	0/100	60	Brittle, swollen in acetone and THF
2	30/70	65	Brittle, swollen in acetone and THF
3	50/50	75	Brittle, swollen in acetone and THF

corresponding heat capacity jump. Thermogravimetric analysis (TGA) measurements of copolymers were carried out by a Dupont TGA 951 under nitrogen atmosphere at a heating rate of 10°C/min. FTIR spectra of the copolymers were taken using a Nicolet Impact 400 D Model spectrophotometer.

RESULTS AND DISCUSSION

Siloxane can readily be self-condensed through formation of a Si—O—Si network via hydrolysis using acid catalyst[42,43] and possibly condensed with St-BA-HEMA to form a Si—O—C bond, which plays an important role in the preparation of silicone secondary crosslinked IPN in this work. The FTIR spectra in the region from 4000 to 500 cm^{-1} were recorded with a sample prepared by making a transparent thin film of the IPN. Figure 1 and Table V show the FTIR spectra of (A) P (St-BA-HEMA), (B) P (St-BA-HEMA) with 30%, and (C) P (St-BA-HEMA) with 50% TEOS copolymers, respectively. The comparison of A spectrum with B or C shows the following characteristics: (1) the absorption peak of the hydroxyl group at 3473 cm^{-1} changed in shape intensity and (2) in the spectra of B and C, there are three new absorption peaks appearing at 1066, 1092 and 962, which were assigned Si—O—Si and Si—O—C bonds, respectively.[42–44] The characteristics show that there are two kinds competitive condensation reactions occurring in preparation of P (St-BA-HEMA-TEOS) IPN, as shown Scheme 1, and a homogeneous, optically transparent film may also be obtained by controlling synthesis conditions as in the poly(methyl acrylate-acrylic acid) PMAA-TEOS system, but with a greatly different reaction behavior from the PMAA-TEOS system,[45] i.e., the cure temperature for P (St-BA-HEMA) film (100°C) is much higher than that for the PMAA-TEOS system (room temperature), pre-

sumably due to the higher apparent activation energy for the reaction of —OH with TEOS.
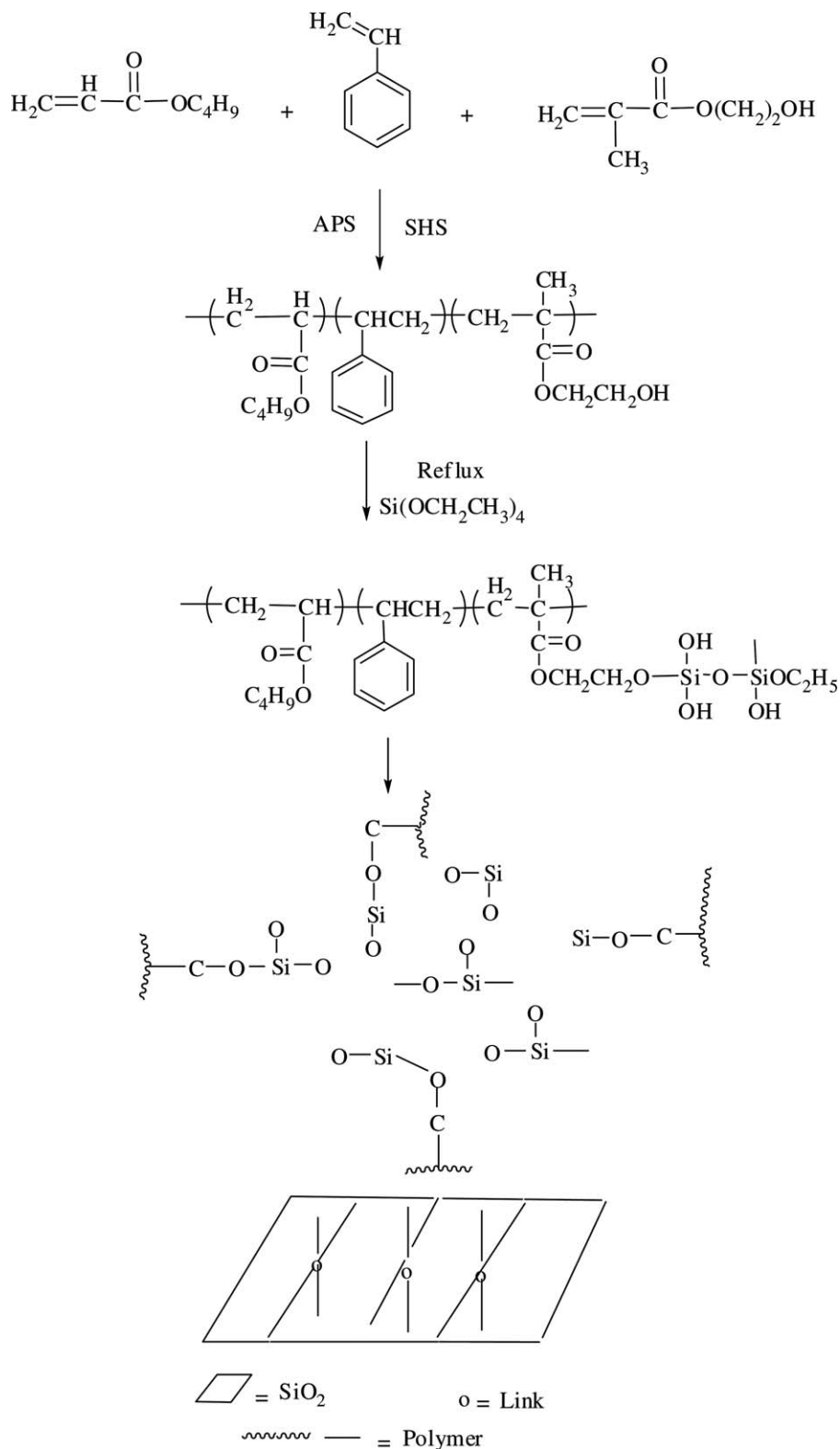
Thermal properties

The thermal properties of P (St-BA-HEMA-TEOS) and P (St-BA-HEMA) copolymers were evaluated by means of TGA/differential thermogravimetric (DTG) and DSC under nitrogen atmosphere. The thermograms of two copolymers are shown in Figure 2(A and B), and the result of DSC is shown in Table II. From TGA data for the 30% TEOS modified P (St-BA-HEMA) copolymer (Fig. 2A) shows that the resulting IPN is stable up to 400°C, and the maximum decomposition is around 450°C. On the other hand, the copolymer without TEOS will decompose at lower temperature around 350°C. The chemical decomposition will start after this temperature, and the maximum decomposition is around 430°C. According to these results, it can be concluded that the existence of TEOS moiety in the copolymers causes to improve thermal stability and by increasing the amount of TEOS, thermal stability increases.

According to the DSC results in Table II, the P (St-BA-HEMA) copolymer is soft, transparent, and soluble in acetone and THF. The P (St-BA-HEMA) copolymer with 30% TEOS is also soft and transparent but insoluble in the same solvents, and the P (St-BA-HEMA) copolymer with 50% TEOS is brittle, transparent, and again insoluble in them. On P (St-BA-HEMA) 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 II, we can also observe only one T_g for samples 1, 2, and 3, respectively, among which there is only a little increase with the increase of TEOS. The results indicate single phase morphology. The result of Table III shows broadening of glass transitions that was observed with increasing 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 microheterogeneity of phase domains.[46] According to these results, it is found that the presence of silicone moiety causes to change in thermal behavior and particularly affects on T_g.

TABLE III
Range of the Glass Transition Temperature of the Films

| Composition TEOS/P(St/BA/HEMA)	Reflux time (h)	$T_{onset} - T_{offset}$ (K)	Width (°C)
30/70	1	279-339	60
30/70	3	277-338	61
30/70	5	274-340	66
30/70	10	275-345	70

Scheme 1 Formation of silicone secondary crosslinked interpenetrating polymer network

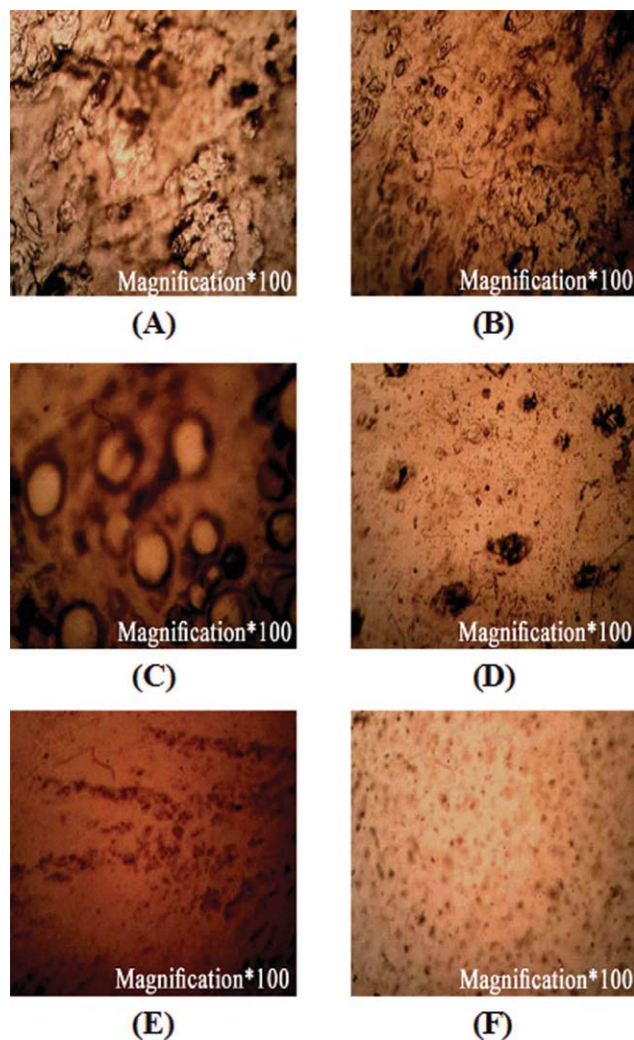## Morphologies of IPNs films at different TEOS concentrations

Optical microscopic image studies of A–F (Fig. 3) revealed a common characteristic that there is a tendency for Si—O—Si phase to aggregate in the sur-face of the IPN film, and more obvious submicro-metre-sized particles can be observed at 50% TEOS (Fig. 3F). The morphologies of these samples (Fig. 4) are also strongly influenced by the water content and refluxing time. This is due to the competitive
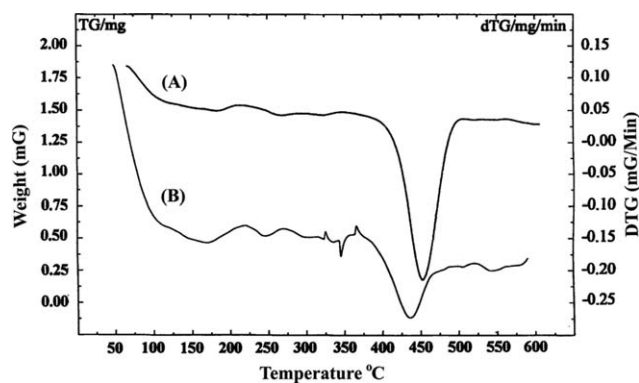
Figure 2 TGA/DTG thermograms of (A) TEOS modified P (St-BA-HEMA) and (B) P (St-BA-HEMA) in N_2 atmosphere.

reaction rates, which are changed as a result of increasing hydrolysis and condensation of TEOS. With increasing water content, submicrometre-sized

holes due to the removal of large Si—O—Si particles are seen in Figure 4A. This indicates that the particles are not embedded in the bulk phase, but there were no holes in Figure 4C. With increasing refluxing time, more homogeneously dispersed particles can be observed in Figure 4C than that in Figure 3C. These observations suggest that a high density cross-link network has been formed with 4 h refluxing time, which inhibits the migration of the component with the lower surface tension.

Chemical resistance

Chemical resistance in a series of standard reagents was studied as per Iranian Standard Test Method (ISTM) C. 44 (2007), and the results are furnished in Table IV. The pieces of IPNs (20 × 20 × 0.78 mm) were kept in 100 mL standard reagents for 30 days.
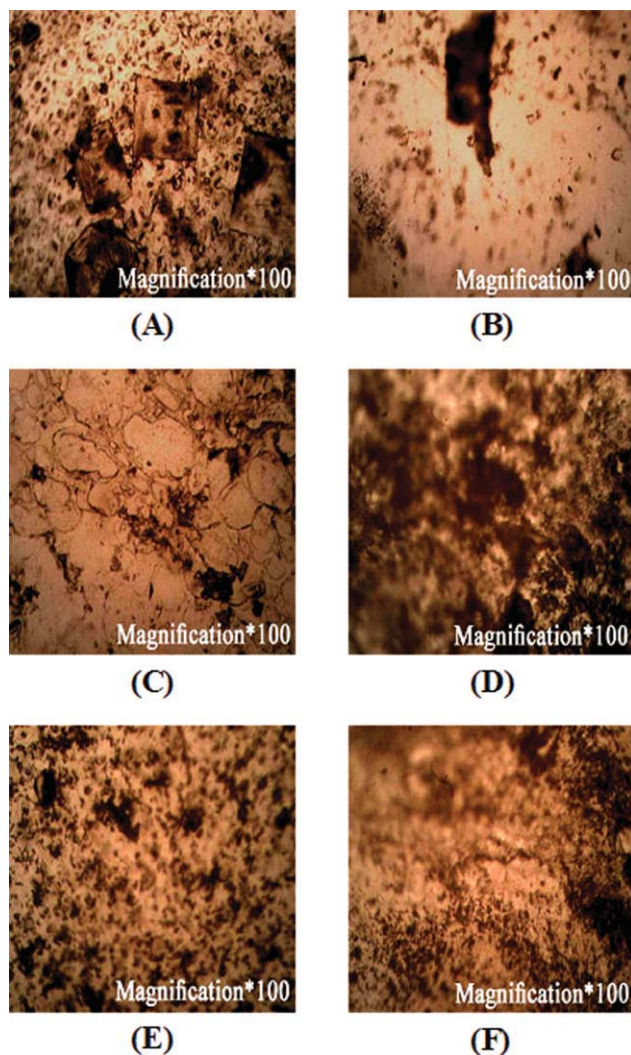

Figure 3 Optical microscopy pictures of IPNs for P (St-BA-HEMA), with (A) 0.0, (B) 5, (C) 10, (D) 20, (E) 30, and (F) 50% TEOS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4 Optical microscopy pictures of IPNs for P (St-BA-HEMA), and (30%) TEOS with reflux time of (A) 1 h, (B) 3 h, (C) 4 h, (D) 5 h, (E) 7 h, and (F) 10 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV
The Chemical Resistance of Different Samples

Solvents	IPN films (damaged % in 30 days)
CH$_3$OH	64
Butylamine	51
HCl 37%,	21
NaOH 0.2 mol L^{-1}	8

The percentage change in weight loss of some of the IPNs was measured. Table IV showed that the chemical resistance of IPN films is poor in the methanol and butylamine and have more chemical resistance in NaOH 0.2 mol L^{-1} and HCl 37%. The IPN films were easily damaged in the butylamine and methanol comparing with other mediums. The reason might be that —Si—O— linkage is quite easy to be attacked under methanol and butylamine conditions.

Water absorption ratio of the IPNs films

The water absorption ratio of the IPNs films is an important parameter for characterization of the hydrophobicity. Saturated water absorption (A_w) of the films was performed gravimetrically at 20°C, as described below. In brief, about 2 g of dried film was placed a definite volume of double distilled water for 14 days, then taken out, wiped in between two filter papers by gently pressing, and finally weighed. This process was continued until an almost constant weight of the swollen button was noticed. The dry buttons were almost fully transparent in unswollen state and became opaque white after water sorption. The equilibrium water content was calculated by the following equation:

$$A_w(\%) = ((W_1 - W_2)/W_2) \times 100$$

where W_1 and W_2 are the weight of the film before drying and after drying of the IPN buttons, respec-

tively. As shown in Figure 5, the absorption ratio was greatly influenced by the content of the TEOS %. With the increase of the TEOS content, the water absorption ratio of the IPNs films decreased, which can be contributed to the excellent hydrophobicity of this monomer. We could make a conclusion that higher TEOS content would give better water resistance.

CONCLUSIONS

Copolymer such as St-BA-HEMA was prepared via free radical emulsion polymerization method. The resulting copolymer was converted to silicone secondary crosslinked IPN by condensation reaction with TEOS. The formation of a Si—O—C link, which plays an important role in the preparation of the silicone secondary IPNs, was characterized through FT-IR. The solubility of the films and IPNs based on P (St-BA-HEMA-TEOS) can be easily achieved at a high cure temperature. The optical microscopy (OM) studies for this St-BA-HEMA-SiO$_2$ system and the T_g measured by DSC indicate that the degree of phase separation of the IPNs corresponds to a definite composition range of P (St-BA-HEMA) and TEOS, corresponding to the refluxing time, due to the change of competitive crosslink rates in the P (St-BA-HEMA-TEOS) system. With the addition of 3% water, the IPNs with submicrometre-sized holes exhibited a high micro-phase separation between the two incompatible phases of crosslinked P (St-BA-HEMA-SiO$_2$), and up to 50% of TEOS content, evidence of phase separation was not observed by OM. In addition, it was observed that the surface morphology strongly depends on the substrate plate and a trend of segregation of the Si—O—Si network in the surface of most samples (50/50). On the other hand, the obtained results showed that the chemical resistance of IPN films is poor in the methanol and
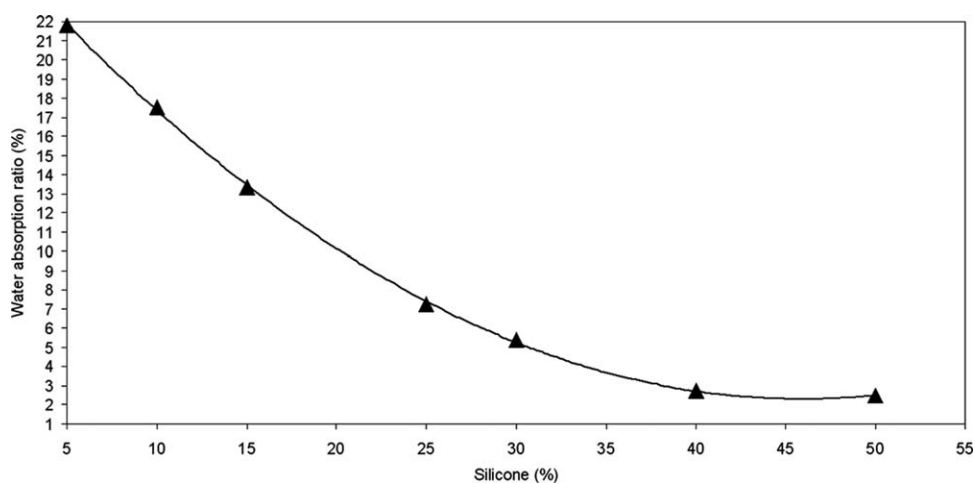
Figure 5 Effects of the TEOS percent on the water absorption ratio of the IPNs films.

TABLE V
FTIR Data of Different IPNs Films

Compounds	Wavenumber (cm^{-1})	Stretching and banding vibration zone
P (St/BA/HEMA)	3473	O—H stretching
	3036–2942	Asymmetric+symmetric CH$_2$ stretching
	1725	C=O stretching
	1463	Symmetric/asymmetric bending vibration of CH$_3$ group
P (St/BA/HEMA) with 30% Si	3515	O—H stretching
	3036–2913	Asymmetric+symmetric CH$_2$ stretching
	1735	C=O stretching
	1464	Symmetric/asymmetric bending vibration of CH$_3$ group
	1066	Si—O—Si
P (St/BA/HEMA) with 50% Si	3438	O—H stretching
	3036-2932	Asymmetric+symmetric CH$_2$ stretching
	1734	C=O stretching
	1464	Symmetric/asymmetric bending vibration of CH$_3$ group
	1092	Si—O—Si

butylamine and have more chemical resistance in NaOH 0.2 mol L^{-1} and HCl 37%. Also the water absorption ratio of the IPNs films was greatly influenced by the content of the TEOS %. With the increase of the TEOS content, the water absorption ratio of the IPNs films decreased, which can be contributed to the excellent hydrophobicity of this monomer.

References

1. Gaines, G. L. Macromolecules 1981, 14, 208.
2. W.Noll. In Chemistry and Technology of Silicones, Academic Press: New York, 1968.
3. Duc, L. L.; Blanchard, L. P.; Malhorta, S. L. J Macromol Sci Chem A 1980, 14, 389.
4. Okkema, A. Z.; Fabrizius, D. J.; Grasel, T. G.; Cooper, S. L.; Zdrahala, R. J. Biomaterials 1989, 10, 23.
5. Maria, Z.; Elzbieta, B. Prog Org Coat 2006, 55, 160.
6. James, G. K.; Andrew, J. B.; Enrico, L. L. L.; Frank, G. J. Prog Org Coat 2007, 59, 278.
7. Tao, W.; Zi Wen H.; Xiao, L. M.; Jie, Y.; Kuai, L. Prog Org Coat 2008, 62, 219.
8. Klein, P. G.; Ebdon, J. R.; Hourston, D. J. Polymer 1988, 29, 1079.
9. Holohan, A. T.; George, M. H.; Barrie, J. A. Polymer 1994, 35, 977.
10. He, X. W.; Widmair, J. M.; Herz, J. E.; Meyer, G. C. Polymer 1992, 33, 866.
11. He, X. W.; Widmair, J. M.; Herz, J. E.; Meyer, G. C. Polymer 1989, 30, 364.
12. Xiao, H.; Ping, Z. H.; Frisch, H. L. J Polym Sci A: Polym Chem 1990, 28, 585.
13. Shimizu, T.; Goda, T.; Minoura, N.; Takai, M.; Ishihara, K. Biomaterials 2010, 31, 3274.
14. Wang, J.; Wang, C.; Jiao, G. S.; Wang, Q. Y. Mater Sci Eng A 2010, 527 2045.
15. Soldani, G.; Losi, P.; Bernabei, M.; Burchielli, S.; Chiappino, D.; Kull, S.; Briganti, E.; Spiller, D. Biomaterials 2010, 31, 2592.
16. Jiang, D. X.; Jiang, F. P.; Yu, L. J.; Zhang, W. Gaofenzi Cailiao Kexue Yu Gongcheng. 2010, 26, 155.
17. Suresh, K. I.; Vishwanatham, S.; Bartsch, E. Polym Adv Technol 2007, 18, 364.
18. Nowers, J. R.; Broderick, S. R.; Rajan, K.; Narasimhan, B. Macromol Rapid Commun 2007, 28, 972.
19. Dhoke, S. K.; Palraj, S.; Maruthan, K.; Selvaraj, M. Prog Org Coat 2007, 59, 21.
20. Sun, H.; Lin, J. M.; Wu, J. H.; Li, W. J. Gaofenzi Cailiao Kexue Yu Gongcheng. 2008, 24, 42.
21. Tang, E.; Tian, B.; Fu, C. Colloids Surf A: Physicochem Eng Asp 2009, 333, 7.
22. Miura, S.; Naito, H.; Kanemitsu, Y.; Matsuura, Y. Thin Solid Films 2003, 438, 253.
23. Ivanova, Y.; Gerganova, T. S.; Dimitriev, Y.; Salvado, M. M.; Fernandes, M. H. V. Thin Solid Films 2006, 515, 271.
24. Gupta, N.; Srivastava, A. K. Macromolecules 1995, 28, 827.
25. Bajpai, A. K.; Bajpai, J.; Shukla, S. React Funct Polym 2001, 50, 9.
26. Dean, K. M.; Cook, W. D.; Lin, M. Y. Eur Polym Mater 2006, 42, 2872.
27. Chang, T. C.; Liao, C. L.; Wu, K. H.; Chen, H. B.; Yang, J. C. Polym Degrad Stab 1999, 66, 127.
28. Liu, L.; Sheardown, H. Biomaterials, 2005, 26, 233.
29. Bastani, S.; Moradian, S. Prog Org Coat 2006, 56, 248.
30. Erdodi, G.; Kennedy, J. P. Prog Polym Sci 2006, 31, 1.
31. Ellsworth, M. W.; Novak, B. W. J Am Chem Soc 1991, 113, 2756.
32. Novak, B. W.; Ellsworth, M. W.; Davies, C. Polym Prep (Am Chem Soc Div Polym Chem) 1990, 31, 698.
33. Qiu, L.; Zhai, J.; Shen, Y.; Guo, L.; Ma, G.; Liu, Y.; Mi, J.; Qian, S. Thin Solid Films, 2005, 471, 96.
34. Fichet, O.; Vidal, F.; Laskar, J.; Teyssie, D. Polymer 2005, 46, 37.
35. Wu, T.; Ke, Y. Thin Solid Films 2007, 515, 5220.
36. Murthy, P. S. K.; Mohan, Y. M.; Sreeramulu, J.; Raju, K. M. React Funct Polym 2006, 66, 1482.
37. White, T. E. 20th Annu SPI Reprints, Chicago, February 1965, Section 3B.
38. Hair, M. L.; Hertl, W. J Phys Chem 1969, 73, 2372.
39. Broun, E. V. Russ J Phys Chem 1970, 44, 443.
40. Iler, R. K. U.S. Patent 1953, 2,657,149.
41. Raymond, G. A.; Angel1, C. L. J Phys Chem 1973, 77, 7973.
42. Roberts, R. J.; Evans, P. D. Composites A 2005, 36, 95.
43. McNeil, K. J.; Dicaprio, J. A.; Walsh, D. A.; Pratt, R. F. J Am Chem Soc 1980, 102, 1859.
44. Schmidt, H.; Scholze, H.; Kaiser, A. J Non-Cryst Solids 1982, 48, 65.
45. Smith, A. L. In Analysis of Silicone, Wiley: New York, 1974; p 271.
46. Olabisi, O.; Robeson, L. M.; Shaw, M. T. Polymer–Polymer Miscibility, Academic Press: New York, 1979.