

# Elastomers Based on $\alpha,\omega$ -Dihydroxy-polydimethylsiloxane/Polystyrene Blends: Morphology and Mechanical Properties

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Received 4 November 2005; accepted 8 December 2005

DOI 10.1002/app.23921

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:**  $\alpha,\omega$ -Dihydroxy-polydimethylsiloxane/polystyrene (PDMS/PS) blends were prepared by the bulk polymerization of styrene (St) in the presence of  $\alpha,\omega$ -dihydroxy-polydimethylsiloxane (PDMS), using benzoyl peroxide (BPO) as initiator. The PDMS/PS blends obtained by this method are a series of stable, white gums, which were vulcanized to elastomers at room temperature with methyltriethoxysilane (MTES). The MTES dosage was much larger than the amount necessary for end-linking hydroxy-terminated chains of PDMS, with the excess being hydrolyzed to crosslinked networks, which were similar to SiO<sub>2</sub> and acted as filler. Investigations were carried out on the elastomeric materials by extraction measurement and scan-

ning electron microscopy. The extraction data show that at each composition the sol-fraction is less than expected. Scanning electron microscopy observation demonstrates that the elastomer has microphase-separated structure consisting of PS domains within a continuous PDMS matrix, and the extracted material exhibits a porous structure. Moreover, the mechanical properties of the elastomers were studied in detail. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2565–2572, 2006

**Key words:** polysiloxanes; blends; elastomer; morphology; mechanical properties

## INTRODUCTION

Polymer blending is an effective means of obtaining new and tailor-made materials with specific desirable properties. Much research has been carried out on polymer blends, mainly because of the enhanced mechanical properties that these materials possess.

Polydimethylsiloxane (PDMS) shows several interesting properties, such as low surface energy, high permeability to many gases, and biocompatibility, but its mechanical properties are rather poor, even after crosslinking. Hence, reinforcement becomes necessary for many applications.<sup>1</sup> The conventional approach for reinforcement is to blend particulate filler into PDMS prior to the matrix being cured into a network. A specific and very important example is the introduction of silica aerogel into PDMS. However, the incorporation of such fillers in PDMS is a difficult, time-consuming, and energy-intensive process.<sup>2</sup> Another disadvantage of this standard approach is the invariable coalescence of silica aerogel into large aggregates in an essentially uncontrolled and poorly understood manner. The nature and extent of such an aggregation

would obviously influence the mechanical properties of the elastomer thus reinforced. To avoid such disadvantages, Mark et al.<sup>2</sup> originally developed an effective method to permit simultaneous curing and filling of PDMS elastomers with an excess amount of tetraethyl orthosilicate. As a result, the mechanical properties of PDMS elastomers were enhanced obviously.

An alternative approach for reinforcing PDMS is to introduce glassy polymers into the silicone.<sup>3–7</sup> Since polystyrene (PS) is a typical glassy polymer that exhibits high strength, high modulus, and excellent dimensional stability, improvement of mechanical properties of PDMS can be expected by incorporating a PS component into PDMS. However, the solubility parameter of PS is 9.1 (cal<sup>1/2</sup> cm<sup>-3/2</sup>), and PDMS has a lower solubility parameter of 7.3 (cal<sup>1/2</sup> cm<sup>-3/2</sup>).<sup>8</sup> Considering that the solubility parameters of the two polymers differ by 1.8 (cal<sup>1/2</sup> cm<sup>-3/2</sup>), the application of the Krause method of miscibility prediction<sup>9</sup> leads to the conclusion that they will be immiscible at all compositions, and we cannot obtain a stable blend based on PDMS and PS by mixing the two components directly.

Previously, we prepared a stable  $\alpha,\omega$ -dihydroxy polydimethylsiloxane/polystyrene (PDMS/PS) blend<sup>3</sup> by solution polymerization of styrene (St) in the presence of  $\alpha,\omega$ -dihydroxy polydimethylsiloxane (PDMS), using toluene as solvent. The PDMS/PS blend could

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be further vulcanized to elastomer. However, a large amount of toluene was used during the process of preparing the blend and it should be eliminated after the polymerization of St. The elimination of toluene is a difficult, time-consuming, and energy-intensive process. As a result, the remained solvent would decrease the mechanical properties of the elastomer. We also prepared PDMS/PS blend by bulk polymerization of St in the presence of PDMS with one-step feeding. The blend obtained by this method has relative stability and deposition of solid takes place in it if it has been laid for 1 month. Moreover, it is difficult to control the reaction temperature during the process of preparing the blend.

To avoid the disadvantages mentioned above, in this paper, PDMS/PS blends were prepared by the bulk polymerization of St in the presence of PDMS with step-by-step feeding, using benzoyl peroxide (BPO) as initiator. The PDMS/PS blends obtained by this method were directly vulcanized to elastomers at room temperature with methyl-triethoxysilane (MTES). The MTES dosage was far more than the necessary amount used to end-link hydroxy-terminated chains of PDMS, with the excess being hydrolyzed to fill the elastomer. Investigations were carried out on the elastomers by extraction measurement and scanning electron microscopy (SEM). Moreover, the mechanical performances of the elastomers were studied in detail.

## EXPERIMENTAL

### Materials

The  $\alpha,\omega$ -dihydroxy-polydimethylsiloxane (PDMS) with a weight-average molecular weight of 50,000 was supplied by the Chemical Industry Factory of Shandong University (Jinan, China). It was kept at 80°C under vacuum for 24 h to eliminate the cyclic compounds and oligomers.

Styrene (St) monomer was supplied by Shanghai Reagent Company (Shanghai, China). It was distilled under vacuum just before use.

Benzoyl peroxide (BPO) was purified by reprecipitation from a chloroform solution into a methanol solution. It was obtained from Tianjin Reagent Company (Tianjin, China).

Methyl-triethoxysilane (MTES) was provided by the Chemical Industry Factory of Shandong University. Dibutyl tin dilaurate was supplied by Tianjin Reagent Company. Both were used without further purification.

### Preparation of the PDMS/PS blends

A solution was first prepared by dissolving BPO (1 wt % relative to PDMS) in a little amount of St. The

required weight of PDMS and the solution mentioned above were then successively introduced into a four-necked round-bottomed flask. The flask was equipped with a mechanical stirrer, a reflux condenser equipped with a drying tube of calcium chloride, a constant pressure dropping funnel, and a thermometer. The mixture was stirred vigorously at room temperature for 30 min to mix it completely. Then it was heated to 92°C and the rest of the St was dropped into the flask from the constant pressure dropping funnel. The temperature was kept at 92°C for 5 h for the polymerization of St. At the end of the reaction, the mixture obtained was kept at 80°C under vacuum to remove the unreacted St monomer. Finally, a kind of white fluid was obtained.

### Vulcanization of the PDMS/PS blend

An excess amount of MTES (70 wt % relative to the PDMS contained in the PDMS/PS blend) was added to the PDMS/PS blend and the mixture was stirred vigorously for 5 min. Dibutyl tin dilaurate (1 wt % relative to PDMS) was then added as catalyst. After stirring for another 5 min, the resulting mixture was transferred into a polytetrafluoroethylene mold. The crosslinking reaction was allowed to proceed at room temperature for 7 days. (The material in the mold has two different surfaces. One surface is exposed to the air and the other is in contact with the mold during the vulcanization.) The cured material was then removed and stored at room temperature under vacuum for at least 24 h prior to investigation.

### Characterization

The viscosities of PDMS/PS blends were measured at room temperature with a NDJ-5S digital viscosimeter at a shear rate of 1.26 s<sup>-1</sup>.

The tensile strength and elongation at break of the elastomers were measured using a tensile testing machine (AGS-H, Shimadzu). The experiments were carried out at room temperature at a crosshead speed of 500 mm min<sup>-1</sup> using dumbbell-shaped specimens with the gauge length of 20 mm, according to GB/T528-1998.

The Shore A hardness of the elastomers was measured using a rubber meter (XY-1, Shanghai).

The linear PS in the elastomers was extracted from the PDMS networks in a Soxhlet extractor. The solvent used was tetrahydrofuran (THF). The extraction usually lasted for several days until no further material could be extracted. The extracted samples were deswollen in methanol. They were then dried at 60°C under vacuum for 48 h, and sol-fractions of the samples were calculated.

The elastomer and its extracted material were examined by a scanning electron microscope, Hitachi

S-520 model. The surfaces and cross section of the sample were coated with gold just before examination.

## RESULTS AND DISCUSSION

### Preparation of the PDMS/PS blends

We dissolved PDMS together with PS in toluene. The mixture was stirred and refluxed for 5 h. When toluene was distilled out, phase separation took place between PDMS and solid PS. This is in accordance with the conclusion obtained by applying the Krause method of miscibility mentioned in the introduction. This also suggests that it is difficult to improve the mechanical properties of PDMS by direct mixing with PS.

In the present study, PDMS/PS blends were prepared by bulk polymerization of St in the presence of PDMS with step-by-step feeding. The blends obtained by this method are a series of white gums, when the feed ratio of PDMS to St is not less than 40/60. Furthermore, the blends can be laid for at least 7 months without macroscopic phase separation. In general, when Polymer 2 is synthesized by radical polymerization in the intimate presence of Polymer 1, it always accidentally introduces some grafting.<sup>3,10</sup> So, in the system we studied, it is unavoidable to introduce PDMS-*g*-PS copolymer during the polymerization of St. The graft copolymer acts as a compatibilizer, which improves the interfacial bonding of the immiscible polymer blends.<sup>11</sup> Moreover, we had introduced 1 wt % BPO into PDMS. The mixture was stirred and heated at 92°C. The viscosity of the mixture increased gradually and a gel formed 30 min later. This experiment suggests that PDMS crosslinks in the presence of BPO. So under the conditions of St polymerization, it is very possible that PDMS undergoes free radical crosslinking to form an interpenetrating polymer network (IPN) consisting of either directly linked PDMS chains or chains linked via PS grafts. Linear PS is entangled in the IPN and the entanglement can effectively restrict phase separation. These are probably the important reasons why PDMS/PS blends obtained by

**TABLE I**  
Compositions and Viscosities of PDMS/PS Blends

Sample code	Feed ratio of PDMS/St	PS content in blend (wt %)	Viscosity of PDMS/PS blend (mPa s)
1	90/10	9	12,500
2	80/20	18	23,700
3	70/30	29	28,900
4	60/40	39	46,600
5	55/45	44	71,800
6	50/50	48	88,200
7	40/60	59	>100,000

**TABLE II**  
Compositions and Results of Extraction for the Elastomers

Sample code	Elastomers weight composition of PDMS/PS	Sol-fraction (%)	
		Theory <sup>a</sup>	Experimental (THF as solvent)
1	100/0	4.7 <sup>b</sup>	4.7
2	91/9	13.3	6.4
3	82/18	21.9	15.2
4	71/29	32.3	23.5
5	61/39	41.9	27.2
6	56/44	46.6	39.1
7	52/48	50.4	43.6
8	41/59	60.9	56.6

<sup>a</sup> Estimated amount considering the composition of the elastomers and the PDMS network sol-fraction.

<sup>b</sup> Experimental data.

this method are stable. The compositions and viscosities of PDMS/PS blends are shown in Table I. Apparently, the viscosities of PDMS/PS blends tend to increase dramatically with a decreasing feed ratio of PDMS to St. When the feed ratio of PDMS to St is less than 40/60, solidification occurs during the polymerization of St and the blend obtained can no longer flow.

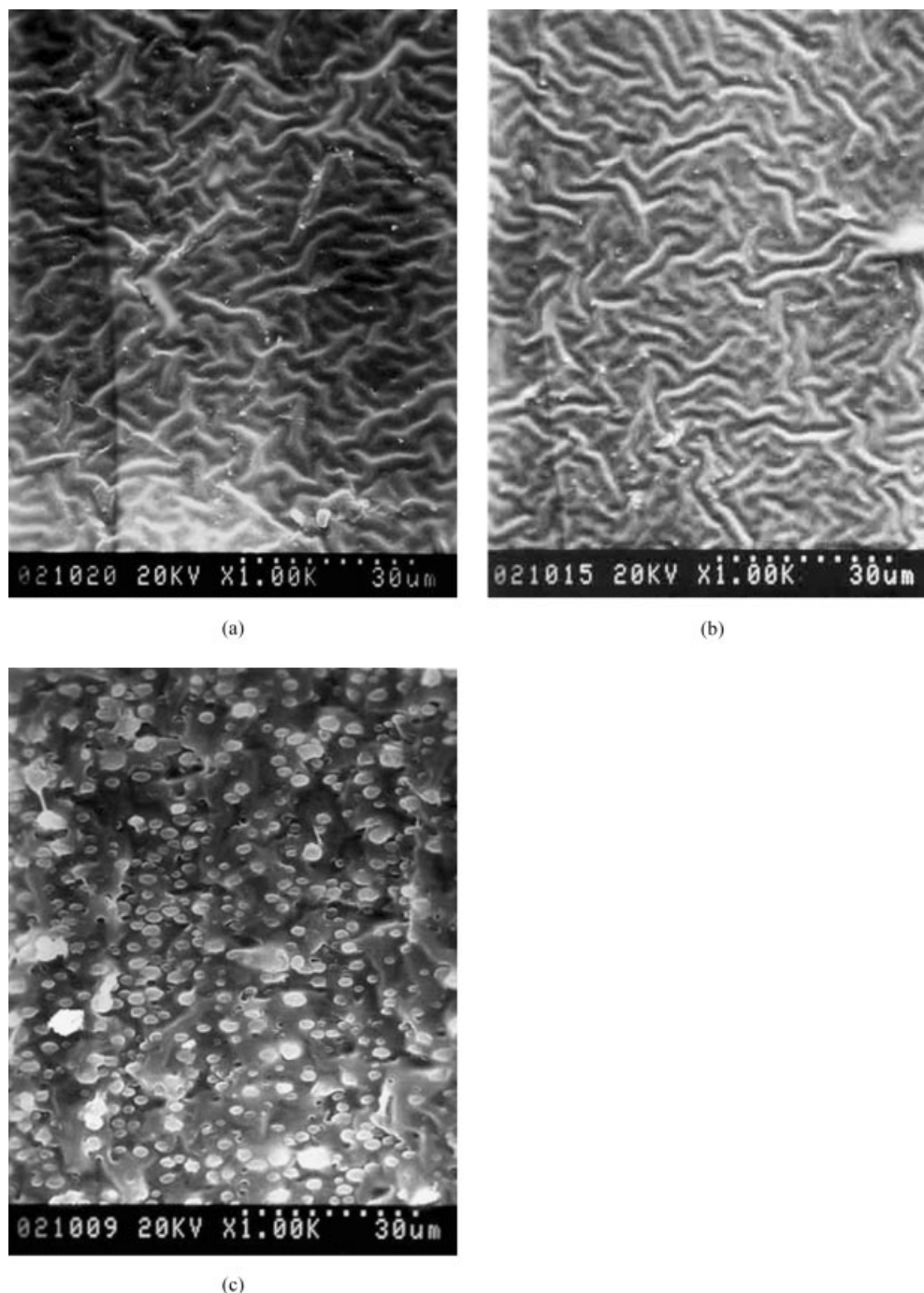
### Elastomers based on PDMS/PS blends

#### Extraction measurement

Tetrahydrofuran (THF) is a good solvent for both linear PS and linear PDMS. The theoretical value of sol-fraction in the elastomer is assumed including PS and linear PDMS component (from imperfect end-linking PDMS chains with MTES). Since the formula ratio of MTES to PDMS is the same in all compositions of the elastomers, it is assumed that the sol-fraction resulting from PDMS component is the same, i.e., 4.7% of PDMS component. However, the extraction data (Table II) show that at each composition the experimental sol-fraction is less than the theoretical value. This may be due to (1) the actual grafting of linear PS onto PDMS during the radical polymerization of St or (2) the entanglement of PS in the IPN, which consists of either directly linked PDMS chains or chains linked via PS grafts and is formed by free radical crosslinking of PDMS during the radical polymerization of St. PS grafted on PDMS is insoluble and PS entangled in the IPN is difficult to extract. Both render the sol-fraction to be less than expected.

#### Morphology

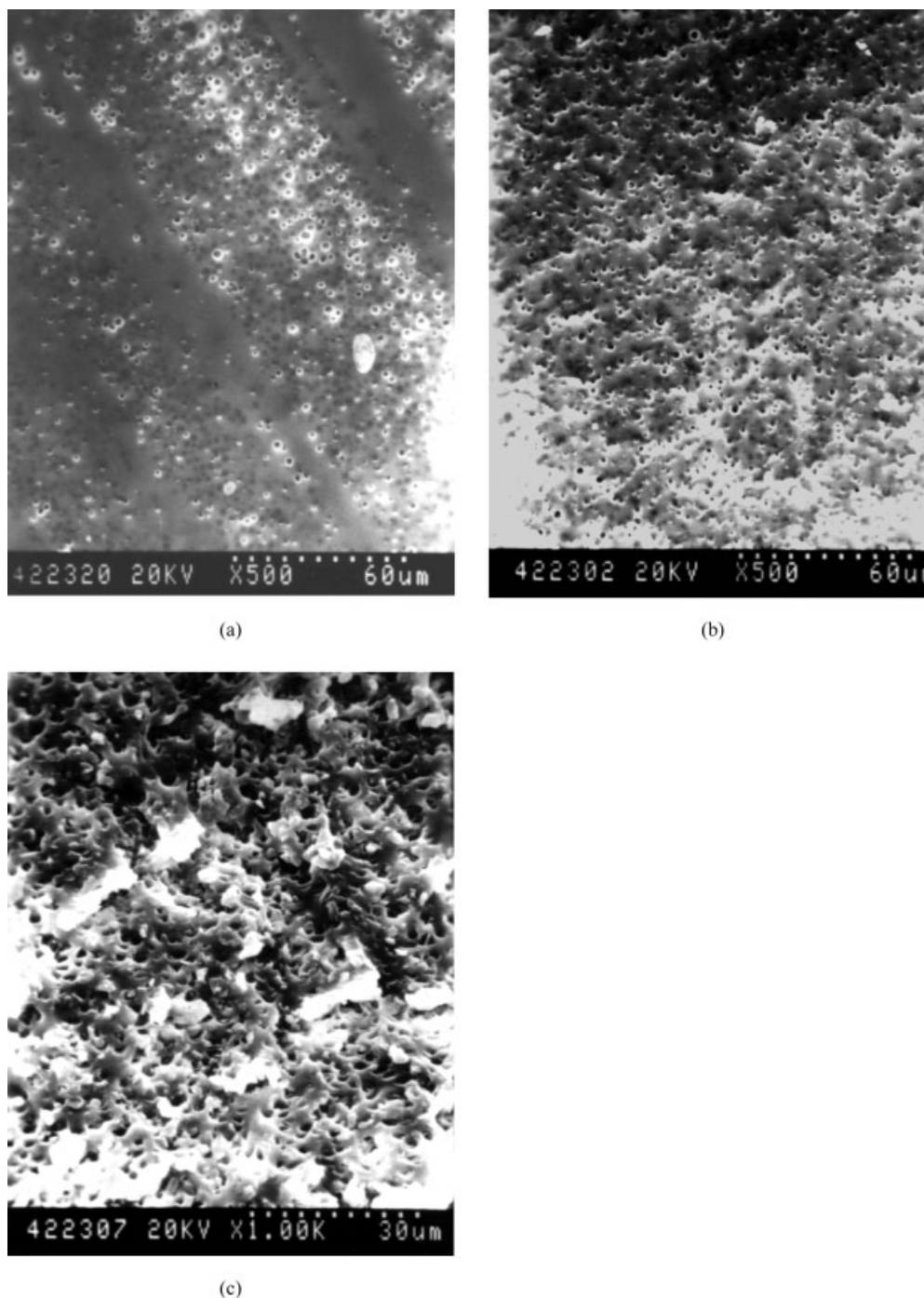
Figures 1(a–c) show the SEM photographs of an elastomer based on PDMS/PS blend (PDMS/PS, 61/39).



**Figure 1** SEM photographs of the elastomer (PDMS/PS 61/39; MTES/PDMS = 130 wt %).

Figures 1(a,b) show its surfaces, which are in contact with air and with the polytetrafluoroethylene mold, respectively. Both surfaces exhibit a corrugated morphology, which is due to the material shrinkage occurring during the vulcanization. Figure 1(c) shows the cross section of the elastomer, which exhibits a microphase-separated structure. We can see the PS dispersed as domains in the continuous PDMS matrix. The elastomer shown in Figure 1 was extracted with THF. Figures 2(a–c) are micrographs of the extracted

sample and they are corresponding to Figures 1(a–c), respectively. Comparing Figures 1 and 2, we can see the amount of dispersed PS domains decrease obviously after extraction, and the extracted material was found to have a porous structure. It is caused by the good solubility of linear PS in THF. Comparing Figures 2(a,b), the latter has a larger pore density. This suggests that the surface in contact with polytetrafluoroethylene mold is rich in PS component. The silicone component, owing to its low surface energy, tends to



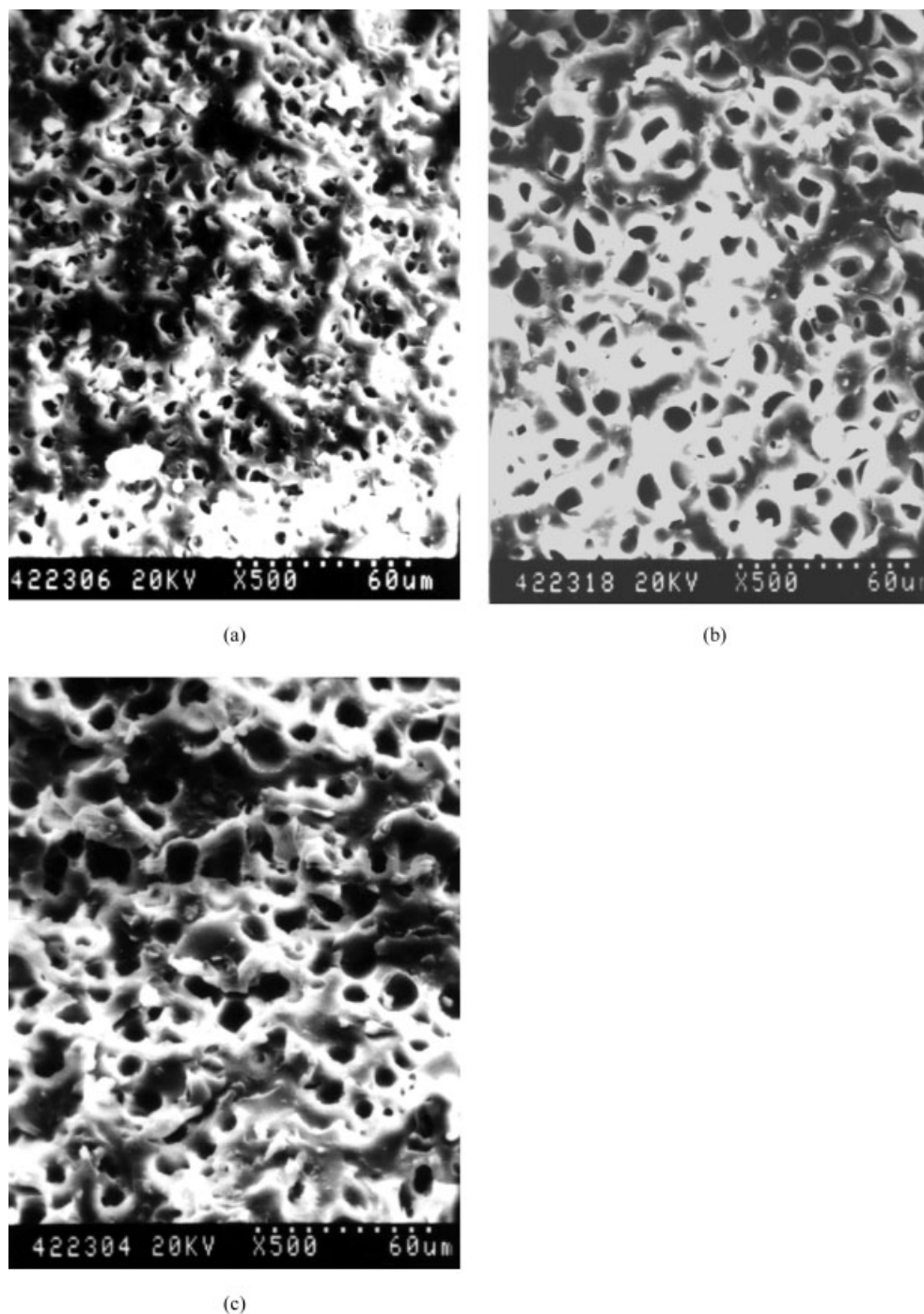
**Figure 2** SEM photographs of the extracted material (PDMS/PS 61/39; MTES/PDMS = 130 wt %).

introduce a strong phase separation and migrates towards the surface exposed to the air.<sup>1</sup>

Figures 3(a–c) are the micrographs for the extracted materials with various compositions, which reveal a porous structure, where the continuous region represents the remaining PDMS networks, and the dark zone is the void where PS is located. The dispersed domains are unextractable PS, and they are mainly due to the actual grafting of linear PS onto PDMS and

the formation of IPN during the polymerization of St mentioned above. Moreover, as the PS content increases, the pores tend to get larger. This means the PS component of the elastomers tends to form larger domains.

The samples shown in Figures 2(c) and 3(b) are prepared with different MTES dosage. We can see that the pores in Figure 2(c) are much smaller than those in Figure 3(b). This suggests that with the increase of



**Figure 3** SEM photographs of the cross sections of the elastomers with various compositions (MTES/PDMS = 70 wt %): (a) (PDMS/PS 71/29); (b) (PDMS/PS 61/39); (c) (PDMS/PS 52/48).

crosslinker, the PS component is liable to form small domains in the continuous PDMS matrix.

#### Mechanical properties

In the elastomer system we prepared, the mechanical strength of PDMS can be improved by the introduction of a PS component that has strong mechanical properties. Moreover, the amount of MTES used

in the vulcanization of PDMS/PS blends was in excess of the stoichiometrically balanced amount. MTES was used to end-link hydroxyl-terminated chains of PDMS, with the excess being hydrolyzed to crosslinked networks, which were similar to  $\text{SiO}_2$  and acted as fillers. The simultaneous curing and filling the elastomers in this way also lead to an enhancement in mechanical performances. Each factor plays its role.

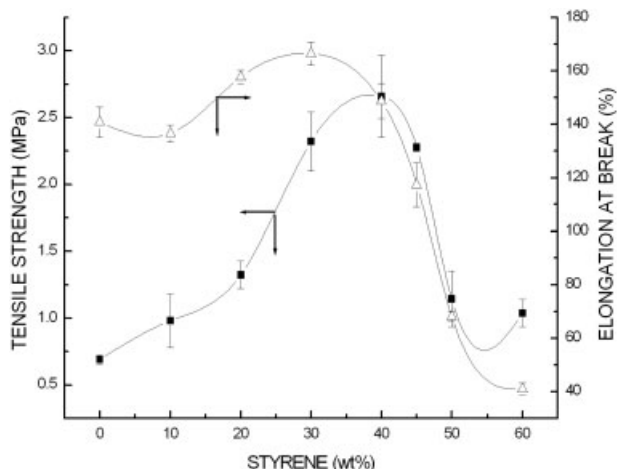


Figure 4 Effect of feed ratio of PDMS/PS blends on the tensile strength and elongation at break of the elastomers.

Figures 4 and 5 show the mechanical properties of the elastomers based on PDMS/PS blends with various feed ratios. Since the weight ratio of MTES to PDMS was the same in all compositions of the elastomers, the effect of the incorporation of PS probably predominated. It is clear that both the tensile strength and the elongation at break increase first and then drop down as the St dosage increases. The tensile strength reaches the maximum value at a St dosage of 40 wt %, while the elongation at break reaches its maximum value at St dosage of 30 wt %. With the increase of St dosage in preparing PDMS/PS blends, PS component of the elastomers tends to form large domains, which are revealed in the SEM photographs above. This leads to disadvantageous effects on the reinforcement of elastomers. This is the probable reason for the decrease of tensile strength at high St

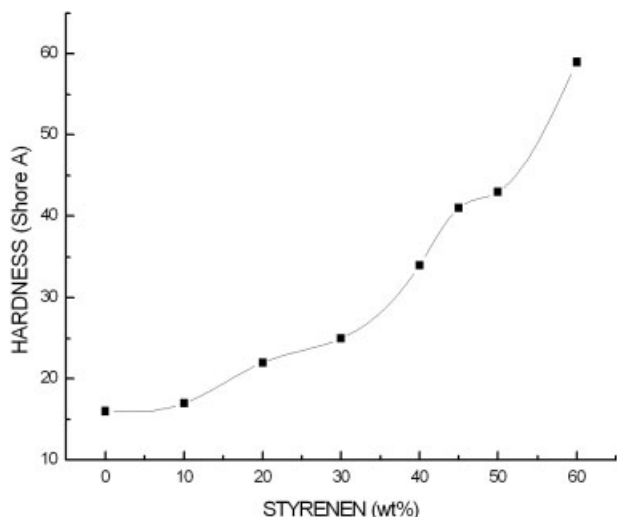


Figure 5 Effect of feed ratio of PDMS/PS blends on the hardness of the elastomers.

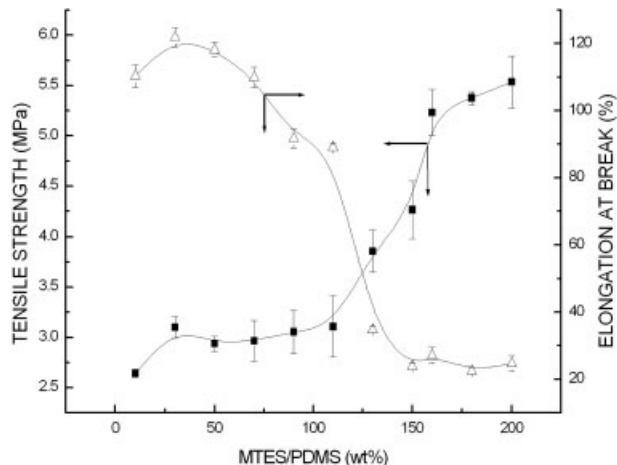


Figure 6 Effect of MTES dosages on the tensile strength and elongation at break of the elastomers.

dosage. As the St dosage increases, the hardness (Shore A) of the elastomers increases.

There was also ample evidence for a very strong reinforcing effect by simultaneous curing and filling of the elastomers with an excess amount of MTES.

The effect of MTES dosage on the tensile strength and elongation at break of Sample 4, shown in Table I, was determined. The values are given in Figure 6. As the MTES dosage increases, the tensile strength of elastomers increases, while the elongation at break decreases. The Shore A hardness values of these elastomers are given in Figure 7. The hardness increases with increasing MTES dosage.

CONCLUSIONS

PDMS/PS blends were prepared by the bulk polymerization of St in the presence of PDMS with step-by-

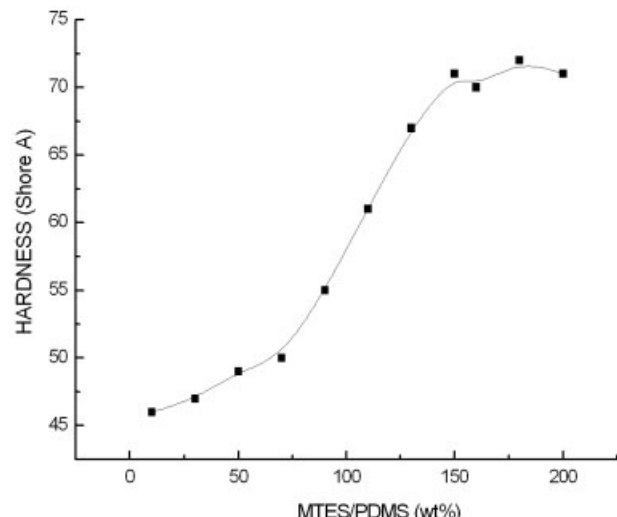


Figure 7 Effect of MTES dosages on the hardness of the elastomers.

step feeding, using BPO as initiator. PDMS/PS blends obtained by this method are a series of white stable gums, when the feed ratio of PDMS to PS was not less than 40/60.

Extraction measurement and SEM study on the elastomers based on PDMS/PS blends showed that the actual grafting of PS onto PDMS and the entanglement of PS in the IPN that formed by radical crosslinking of PDMS rendered the extraction difficult. The two components in the elastomers are incompatible as predicted by solubility parameter considerations, and the system is microphase separated.

Study on the mechanical performances of the elastomers based on PDMS/PS blends demonstrated that both the incorporation of appropriate amount of PS and the simultaneous curing and filling of elastomer with excess amount of MTES led to the improvement of the mechanical properties of the elastomers.

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