

Preparation, Morphology, and Mechanical Properties of Elastomers Based on α,ω -Dihydroxy-polydimethylsiloxane/polystyrene Blends

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ABSTRACT: α,ω -Dihydroxy-polydimethylsiloxane/polystyrene (PDMS/PS) blends were prepared by the solution polymerization of styrene (St) in the presence of α,ω -dihydroxy-polydimethylsiloxane (PDMS), using toluene as solvent and 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 methyl-triethoxysilane (MTES). The use level of MTES was far more than the necessary amount used to end-link hydroxy-terminated chains of PDMS, with the excess being hydrolyzed to crosslinked networks, which were similar to SiO₂ and acted as filler. Investigations were carried out on the elastomeric materials by extraction measurement, swelling measurement, and scanning electron microscopy. The extraction data show that at each composition the amount of soluble fraction is less than expected and the difference between experimental and theoretical values becomes more and more significant as PS content increases. This is mainly due to the grafting of PS onto PDMS and the entanglement of PS in the interpenetrating polymer network (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 soluble fraction to be less than expected. As the St content in preparing PDMS/PS blends increases, the probability of grafting PS onto PDMS also increases, which may subsequently produce a higher crosslinking level of PDMS networks that linked via PS grafts by radical crosslinking. As a result, not only the amount of insoluble PS increases but also PS entangled in the IPN is more difficult to extract. Scanning electron microscopy demonstrates that the elastomer system has a microphase-separated structure and a certain amount of PS remains in the PDMS networks after extraction, which is in accordance with the extraction data. Moreover, the mechanical properties of the elastomeric materials have been studied in detail. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3542–3548, 2004

Key words: polysiloxanes; polystyrene; blends; morphology; mechanical properties

INTRODUCTION

Polymer blending is generally known to be an effective route to obtain new and tailor-made materials with specific desirable properties.¹ Much research has been carried out on polymer blends, mainly due to 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.² Usually, inorganic fillers such as silica are used. However, the incorporation of such fillers in PDMS is a difficult, time-consuming, and energy-intensive process. It can also cause premature gelation.³ To avoid such disadvantages, Mark et al.³

originally developed an essential method to permit simultaneous curing and filling of PDMS elastomers with an excess amount of tetraethyl orthosilicate (TEOS). As a result, the mechanical properties of PDMS elastomers were enhanced greatly.

An alternative approach for reinforcing PDMS is to introduce glassy polymers into the silicone.^{4–7} 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 $9.1(\text{cal}^{1/2}\text{cm}^{-3/2})$, and PDMS has a lower solubility parameter of $7.3(\text{cal}^{1/2}\text{cm}^{-3/2})$.⁸ Considering that the solubility parameters of the two polymers differ by $1.8(\text{cal}^{1/2}\text{cm}^{-3/2})$, the application of the Krause method of miscibility prediction⁹ leads to the conclusion that they will be immiscible at all compositions and we can't obtain a stable blend based on PDMS and PS by mixing the two components directly. Some researchers have introduced a PS component into PDMS by synthesizing PS-*b*-PDMS and PDMS-

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g-PS copolymers. For example, Morton et al.¹⁰ synthesized a PS-*b*-PDMS copolymer by the ring-opening polymerization of cyclic polysiloxanes with polystyryl potassium; Greber et al.¹¹ prepared a graft copolymer by anionic polymerization of styrene (St) with a macromolecular catalyst having a polysiloxane chain; Minoura et al.¹² prepared block and graft copolymers by the chain-transfer reaction of chlorosilyl compounds in the radical polymerization of St. In these copolymers, the soft PDMS component is chemically linked to the glassy PS segment, which plays a crucial role in enhancing the mechanical properties of the elastomer system.

Previously, we prepared α,ω -dihydroxy polydimethylsiloxane/polystyrene blend¹³ and α,ω -dihydroxy polydimethylsiloxane/crosslinked PS blend¹⁴ by free radical polymerization of St in the presence of PDMS. Both blends were vulcanized to elastomers at room temperature, which exhibit good mechanical performance. However, those blends have relative stability and deposition of solid takes place in both of them if they have been laid for 1 month. The stability of the blends decreases as the feed ratio of St to PDMS increases. Moreover, it is difficult to control the reaction temperature during the process of preparing both the blends, mainly due to the difficulty of eliminating heat in bulk polymerization. The viscosities of the blends are relative high, which makes them difficult to mix with the crosslinker in the process of vulcanization.

To avoid the disadvantages mentioned above, in the present study, PDMS/PS blends were prepared by the solution polymerization of St in the presence of PDMS using toluene as solvent and benzoyl peroxide (BPO) as initiator. PDMS/PS blends obtained by this method were vulcanized to elastomeric materials at room temperature. Methyl-triethoxysilane (MTES) was used to end-link hydroxy-terminated chains of PDMS, with the excess being hydrolyzed to fill the elastomers. Investigations were carried out on the elastomeric materials by extraction measurement, swelling measurement, and scanning electron microscopy (SEM). Moreover, the mechanical performances of the elastomeric materials have been studied in detail.

EXPERIMENTAL

Materials

The α,ω -dihydroxy-polydimethylsiloxane with a weight-average molecular weight of 50,000 was supplied by the Chemical Industry Factory of Shandong University. The sample was heated at 80°C under vacuum for 24 h to eliminate the cyclic compounds and the low molar mass components.

Styrene monomer was supplied by Shanghai Reagent Company. It was distilled under vacuum just before use.

Benzoyl peroxide was purified by reprecipitation from a chloroform solution into a methanol solution. It was obtained from No.2 Chemical Industry Factory, Wuxi.

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

General procedure for preparing PDMS/PS blends

The required weights of PDMS and BPO (2.5 wt % relative to PDMS) were 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. Toluene was added to the mixture as solvent and the weight ratio of toluene to PDMS was 2. The mixture was stirred vigorously at room temperature for 30 min to mix it completely. It then was heated to 92°C. At that moment, the required amount of St was dropped into the flask from the constant pressure dropping funnel. We maintained the temperature at 92°C for 6 h to perform the polymerization of St. At the end of the reaction, the mixture obtained was distilled at 80°C under vacuum to rid it of toluene and unreacted styrene monomer. Finally, a kind of white fluid PDMS/PS blend was obtained.

Vulcanization of the PDMS/PS blend

An excess amount of MTES (100 wt % relative to PDMS contained in the PDMS/PS blend) was added to the PDMS/PS blend obtained above and the mixture was stirred vigorously for 5 min. Dibutyl tin dilaurate (1 wt % relative to PDMS) then was 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 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⁻¹.

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

TABLE I
Compositions and Viscosities of the PDMS/PS Blends

Sample code	Feed ratio (PDMS/St)	PS content in blend (wt %)	Viscosity of PDMS/PS blend (mPas)
1	80/20	18	17,900
2	60/40	29	19,900
3	50/50	37	36,300
4	40/60	47	82,900
5	30/70	58	>100,000

The Shore A hardness of the cured materials was measured using a rubber meter (Shanghai: XY-1).

The linear PS in cured materials 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 then were dried at 60°C under vacuum for 48 h, and soluble fractions of the samples were calculated. Their densities were determined by a pycnometer. Swelling measurements in THF at 25°C were also carried out on portions of the extracted networks.

A JXA-840 scanning microanalyzer was used to take scanning electron micrographs. The extracted samples were cooled in nitrogen and fractured with a sharp blow. The fractured sections were coated with gold.

RESULTS AND DISCUSSION

Preparation of the PDMS/PS blends

We had 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 directly mixing with PS.

In the present study, PDMS/PS blends were prepared by the solution polymerization of St in the presence of PDMS, using toluene as solvent. Since the existence of solvent is advantageous to heat elimination of the system, it is easy to control the reaction temperature during the process of preparing PDMS/PS blends. The blends obtained by this method are a series of white gums when the feed ratio of PDMS to PS is not less than 30/70. Furthermore, the blends can be laid for at least 7 months without gross 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.¹⁵ So, in the system we studied, it is unavoidable to introduce PDMS-g-PS copolymer

during the polymerization of St.^{15,16} The graft copolymer acts as a compatibilizer, which improves the interfacial bonding of the immiscible polymer blends. Moreover, 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.² These are probably the important reasons why the PDMS/PS blends obtained by this method are stable. The compositions and viscosities of PDMS/PS blends can be seen in Table I. Apparently, the viscosities of PDMS/PS blends are much lower than those of the α,ω -dihydroxy polydimethylsiloxane/polystyrene blend¹³ and the α,ω -dihydroxy polydimethylsiloxane/crosslinked polystyrene blend¹⁴ that we prepared previously. Moreover, the viscosities of PDMS/PS blends tend to increase dramatically with a decreasing feed ratio of PDMS to PS. When the feed ratio of PDMS to PS is less than 30/70, solidification takes place during the process of vacuum refining and the blend obtained can no longer flow.

Elastomers based on PDMS/PS blends

Extraction and swelling measurement

THF is a good solvent for both linear PS and linear PDMS. The theoretical value of soluble fraction in the cured material 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 cured materials, it is assumed that the soluble fraction of PDMS component is the same, i.e., 4.4% of PDMS component. However, the extraction data (see Table II) show that at each composition the amount of extracted materials is less than the theoretical value. This

TABLE II
Compositions and Results of Extraction for the Cured Materials

Sample code	Cured materials wt composition PDMS/PS	Sol fraction (%)	
		Theory ^a	Experimental (THF as solvent)
1	100/0	4.4 ^b	4.4
2	82/18	21.6	19.2
3	71/29	32.1	20.7
4	63/37	39.8	26.9
5	53/47	49.3	32.0
6	42/58	59.8	41.1

^a Estimated amount considering the composition of the cured material and the PDMS network sol fraction.

^b Experimental data.

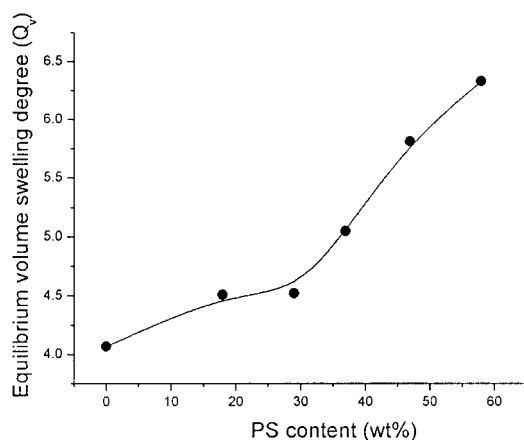


Figure 1 Effect of PS content on the equilibrium swelling degree of the extracted materials.

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 soluble fraction to be less than expected. From Table II, we can see that, as PS content increases, a larger difference between experimental data and theoretical values is observed. This may be explained by the following: as the St content in preparing PDMS/PS blends increases, the probability of grafting PS onto PDMS also increases, which may subsequently produce a higher crosslinking degree of PDMS networks that linked via PS grafts by radical crosslinking. As a result, not only the amount of insoluble PS portion, i.e., PS grafting on PDMS, increases but also PS entangled in the IPN is more difficult to extract. Both render a larger difference between experimental data and theoretical values.

The extracted materials were characterized by swelling studies. For each composition mentioned in Table II; the equilibrium swelling degree (Q_v) in THF was calculated, and the results are shown in Figure 1. The extraction results (seen in Table II) lead to the conclusion that the extracted materials cannot be considered to be conventional PDMS networks and there are different amounts of PS remaining in them. Furthermore, the SEM micrographs presented below suggest that the extracted materials are porous materials. Some THF is imbibed in the pores during swelling as a more or less pure phase. The material that has a higher PS content has a higher soluble fraction, which has more solvent imbibed and, hence, an apparently larger Q_v .

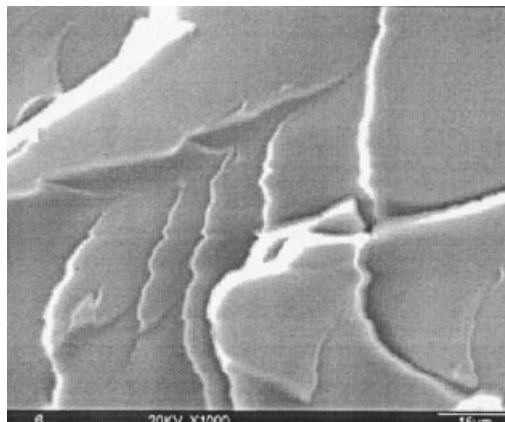


Figure 2 Scanning electron micrograph of PDMS elastomer.

Morphology

In general, for a polymer blend, even if the two polymer components are well mixed with each other, they are often phase separated to some extent. The two components then tend to form two mutually continuous phases in which the first-formed network is predominant.⁴ SEM micrographs of the fracture surfaces of PDMS elastomer and cured material based on PDMS/PS blend (PDMS/PS, 82/18) are shown in Figures 2 and 3, respectively. The sample seen in Figure 2 has only one continuous phase of PDMS. But in Figure 3 the sample exhibits a microphase-separated structure. We can see some spherical dispersed PS domains with a diameter of about 1 μm exist in a continuous PDMS matrix. The sample seen in Figure 4(a) was obtained by extracting the cured material seen in Figure 3 with THF. Comparing these two micrographs, we can see the amount of disperse domains decreased apparently after extraction due to the good solubility of THF to linear PS; this also demonstrated that PS formed a disperse phase in a continuous PDMS phase.

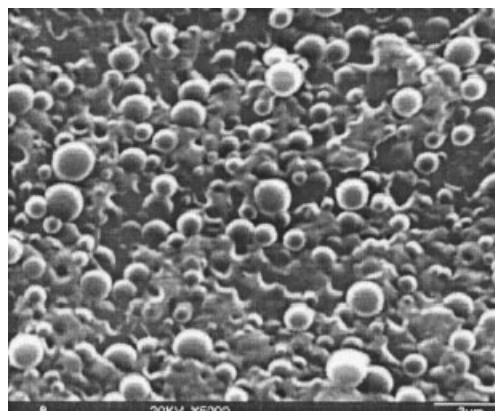


Figure 3 Scanning electron micrograph of cured material (PDMS/PS 82/18).

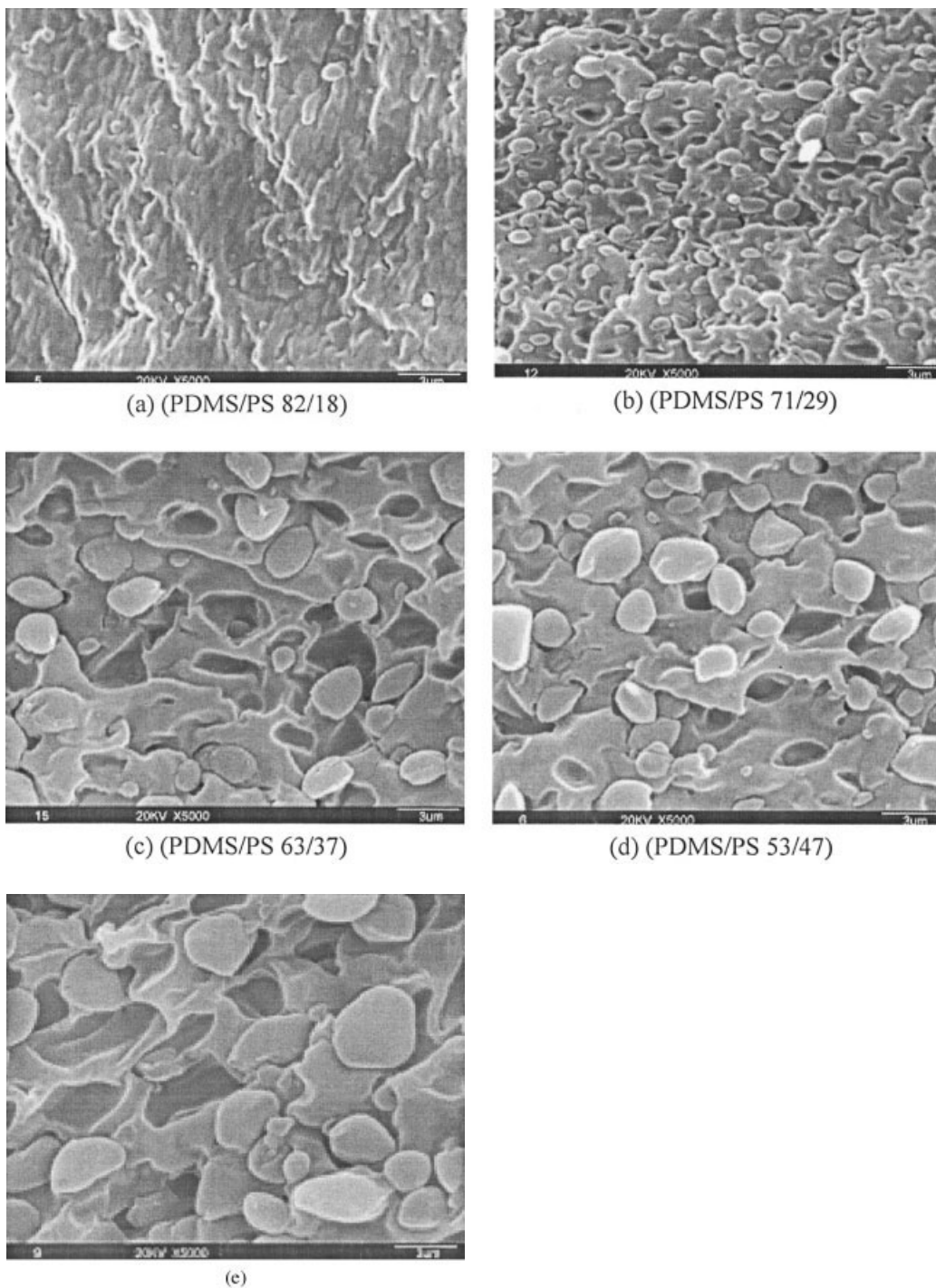


Figure 4 Scanning electron micrograph of extracted cured materials. (a) PDMS/PS 82/18; (b) PDMS/PS 71/29; (c) PDMS/PS 63/37; (d) PDMS/PS 53/47; (e) PDMS/PS 42/58.

In the cured materials of PDMS/PS blends, linear PS, which was introduced in the solution polymerization of St. exists in PDMS networks. Therefore, with the increase of PS content, the PS component is liable to form large domains in the continuous PDMS phase. These can be confirmed in Figure 4. Figure 4 shows the micrographs for the extracted cured materials with various compositions, which reveals a porous struc-

ture in which the continuous region represents the remaining PDMS networks and the dark zone is the void where the PS is located. The disperse domains are unextractable PS, and are mainly due to the actual grafting of linear PS onto PDMS and the formation of IPN during the polymerization of St mentioned above. For the cured materials containing 18 and 29% PS [Figs. 4 (a) and (b)], PDMS is the continuous phase and

TABLE III
Effect of Feed Ratio of PDMS/PS Blends on Mechanical Properties of Cured Materials

Sample code	Feed ratio (<i>r</i>) PDMS/St (wt)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
1	100/0	1.158 ± 0.299	162.540 ± 20.860	16
2	80/20	1.366 ± 0.206	201.720 ± 22.491	21
3	60/40	3.804 ± 0.588	287.564 ± 9.233	24
4	50/50	3.154 ± 0.315	168.561 ± 4.163	35
5	40/60	2.854 ± 0.074	103.302 ± 5.362	44
6	30/70	2.505 ± 0.041	25.109 ± 2.883	60

PS is the dispersed phase. Figures 4(c–e) are micrographs of the cured materials at midrange compositions. Obviously, PDMS is still the continuous phase, but the PS domains seen in Figures 4(c–e) are about three times larger than those in Figures 4 (a) and (b). This means the PS component of the cured material tends to form large domains, which is in accordance with the theoretical conclusion mentioned above.

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 SiO₂ and acted as fillers. The simultaneous curing and filling of the elastomers in this way also leads to an enhancement in mechanical performance. Each factor plays its role.

Table III shows the mechanical properties of cured materials based on PDMS/PS blends with different feed ratios. Since the weight ratio of MTES to PDMS was the same in all compositions of cured materials, the effect of the incorporation of PS probably predominated. It is clear that the tensile strength and elongation at break increases as the feed ratio of PDMS to PS, i.e., *r*, decreases from 100/0 to 60/40 and at *r* = 50/50 the strength and elongation drop. Both reach the maximum value at *r* = 60/40. With the decrease of *r* in the preparation of PDMS/PS blends, the PS component of cured materials tends to form large domains, which are revealed in SEM micrographs above. This leads to disadvantageous effects on the reinforcement of curing materials. This is the probable reason for the decrease of tensile strength at the low feed ratios of PDMS to St. The hardness (shore A) of the cured materials increases with the decrease of *r*.

The stress–strain behavior of the cured materials in Table III is shown in Figure 5. The stress–strain curves show a gradual transition from a rubbery to a plastic

nature as *r* decreases from 100/0 to 30/70. In the samples with a higher feed ratio of PDMS to St (samples 1–4), the stress increases gradually with strain until failure. The systems undergo appreciable deformation and the deformation is elastic in nature. However, both sample 5 and sample 6 have a relatively high initial modulus and show definite characteristics of plastic deformation.

There was also ample evidence for a very strong reinforcing effect by simultaneous curing and filling the elastomers with an excess amount of MTES. The effect of MTES amount on the tensile strength and elongation at break of sample 2 shown in Table I was determined. The values are given in Figure 6. The tensile strength of cured materials increases as the MTES amount increases. Furthermore, the elongation at break increases at a low MTES amount and then is followed by a linear decrease. The shore A hardness values of those cured materials are given in Figure 7. The hardness increases with increasing MTES amount.

CONCLUSION

PDMS/PS blends were prepared by the solution polymerization of St in the presence of PDMS, using toluene as solvent and BPO as initiator.

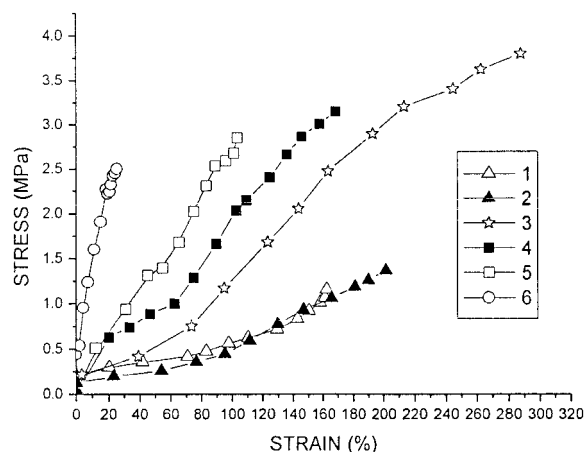


Figure 5 Effect of feed ratio on the Stress–strain behavior of the cured materials.

The incorporation of solvent can effectively avoid the disadvantages resulting from the bulk polymerization. PDMS/PS blends obtained by this method are a series of white stable gums when the feed ratio of PDMS to PS is not less than 30/70. The stability of PDMS/PS blends enhanced greatly compared with those we prepared before.

Extraction measurement and SEM study of the cured materials of 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 cured materials are incompatible as predicted by solubility parameter considerations and the system is phase separated. Swelling measurement of the extracted materials indicated that the material that had a higher PS content had an apparently larger Q_v .

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

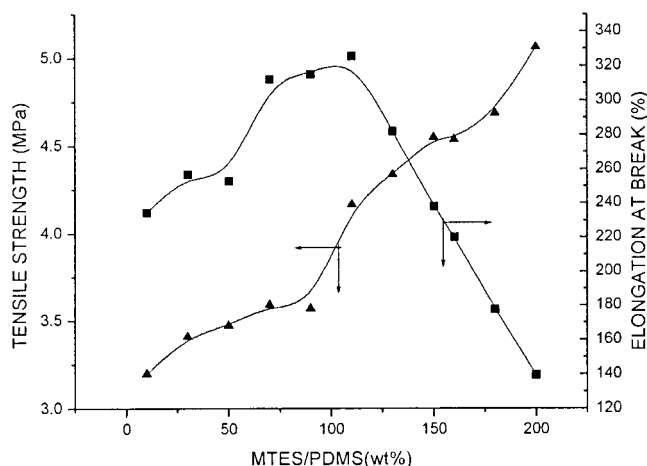


Figure 6 Effect of MTES amount on the tensile strength and elongation at break of cured material.

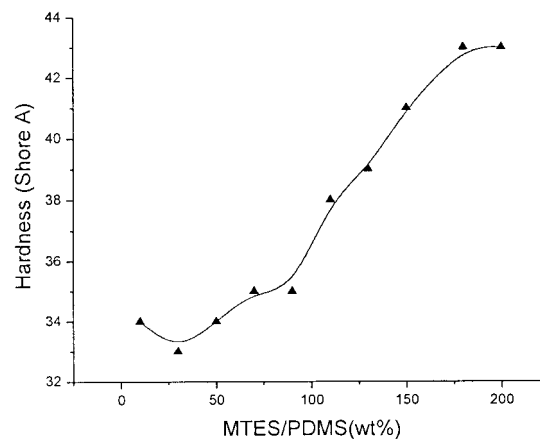


Figure 7 Effect of MTES amount on the hardness of cured material.

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