

Preparation, Morphology, and Mechanical Properties of Elastomers Based on Polydimethylsiloxane/Polystyrene Blends

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ABSTRACT: Polydimethylsiloxane/polystyrene (PDMS/PS) blends were prepared by radical copolymerization of styrene (St) and divinylbenzene (DVB) in the presence of α,ω -dihydroxy-polydimethylsiloxane (PDMS), using benzoyl peroxide as initiator. The PDMS/PS blends obtained by this method are a series of stable, white gums, when the feed ratio of PDMS to St is 60/40 and DVB to St is not more than 2.0 wt %. Elastomers based on PDMS/PS blends were formed by crosslinking PDMS 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 SiO₂ and acted as filler. Mechanical property measurements show that the elastomers thus formed ex-

hibit superior mechanical properties with respect to pure PDMS elastomer and the elastomers based on PDMS/PS system we prepared before. Moreover, investigations were carried out on the elastomers by extraction measurement and scanning electron microscopy (SEM). The extraction data show that the sol-fraction decreases with increasing the feed ratio of DVB to St. SEM observation demonstrates that the elastomer has a microphase-separated structure consisting of dispersed PS domains within a continuous PDMS matrix, and the extracted material exhibits a porous structure. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 985–990, 2009

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

INTRODUCTION

Polymer blending is a fast and common way to develop new polymeric materials with specific desirable properties. 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.¹ The conventional approach for reinforcement is to blend particulate filler into PDMS before 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.² Another disadvantage of this standard approach is the invariable coalescence of silica aerogel into large aggregates in an essentially uncon-

trolled 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. developed a variety of alternative techniques. Some have the potential of simplifying the process or improving reinforcement capability.^{2–4} For example, they originally developed an effective method to permit simultaneous curing and filling of PDMS elastomers with an excess amount of tetraethyl orthosilicate (TEOS). TEOS is used to end-link hydroxyl-terminated chains of PDMS with the excess present being hydrolyzed to finely divided SiO₂. As a result, the mechanical properties of PDMS elastomers were enhanced obviously with the filler thus formed.² Another example, they found that the PDMS elastomer having bimodal distribution of network chain lengths also has unusually good mechanical properties.³ The bimodal elastomeric networks were prepared by end-linking hydroxyl-terminated PDMS chains having different number-average molecular weight. The mechanical properties of this kind of elastomer depend on the relative proportions of short and long chains and are much better than those of PDMS network with a very uniform molecular weight between crosslinks.

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An alternative approach for reinforcing PDMS is to introduce glassy polymers into the silicone.⁵⁻⁹ Because 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 ($\text{cal}^{1/2}\text{cm}^{-3/2}$).¹⁰ 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 prediction¹¹ 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 α,ω -dihydroxy-polydimethylsiloxane/polystyrene (PDMS/PS) blend by bulk polymerization of styrene (St) in the presence of PDMS with step by step feeding. The PDMS/PS blend could be further vulcanized to elastomer. The elastomer thus formed exhibit superior mechanical and elastomeric properties with respect to pure PDMS elastomer.⁷

In this article, another kind of PDMS/PS blend was prepared by radical copolymerization of St and divinylbenzene (DVB) in the presence of PDMS, using benzoyl peroxide (BPO) as initiator. The PDMS/PS blends obtained by this method were directly vulcanized to elastomers at room temperature with methyl-triethoxysilicane (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. Mechanical property measurements show that the elastomers thus formed exhibit superior mechanical properties with respect to the elastomers based on PDMS/PS system we prepared before. Moreover, investigations were carried out on the elastomers by extraction measurement and scanning electron microscopy.

EXPERIMENTAL

Materials

The α,ω -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.

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

TABLE I
Compositions and Viscosities of the PDMS/PS Blends

Sample code	Feed ratio (DVB/St) (wt %)	Viscosity of PDMS/PS blend (mPa s)
1	0	46,600
2	0.5	47,900
3	1.0	49,800
4	1.5	53,700
5	2.0	70,600

1,2-Divinylbenzene (DVB) was supplied by Shanghai Reagent Company. It was used without further purification.

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

Methyl-triethoxysilicane (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.

Fumed silica with a surface area of 200 m^2/g was supplied by Xin'an Chemical Industrial Group (Zhejiang, China). It has been treated with hexamethyldisilazane.

Preparation of the PDMS/PS blends

Sample 1 (DVB/St = 0) shown in Table I was prepared by bulk radical polymerization of St in the presence of PDMS. The weight ratio of PDMS to St was 60/40. Details of the method of preparation were given in an earlier publication.⁷

Other PDMS/PS blends were prepared with the following method. A solution was first prepared by dissolving 1.5 wt % BPO in St monomer. PDMS, the required weight of DVB and the solution mentioned above were successively introduced into a three-necked round-bottomed flask. The weight ratio of PDMS to St was fixed as 60/40. The mixture was stirred vigorously at room temperature for 30 min to mix it completely. Then it was heated to 75°C. The temperature was kept at 75°C for 5 h for the copolymerization of St and DVB. At the end of the reaction, the mixture obtained was kept at 60°C under vacuum to remove the unreacted St monomer. Finally, a kind of white fluid was obtained.

Crosslinking of the PDMS/PS blend

An excess amount of MTES (70 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) 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 crosslinking.). The cured material was then removed and stored at room temperature under vacuum for at least 24 h before investigation.

Elastomer (Sample 1 shown in Table IV) was prepared using the following method: Enough of the fumed silica was added to PDMS/PS blend (Sample 2 shown in Table I) to make up 13.5 wt % of the mixture. MTES in an amount sufficient to react with all of the PDMS hydroxyl groups was then added, along with 1 wt % Dibutyl tin dilaurate as catalyst. The mixture was stirred vigorously at room temperature to mix it completely. Then it was poured into a polytetrafluoroethylene mold, and the crosslinking reaction was permitted 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 before mechanical property measurement.

Characterization

The viscosity of PDMS/PS blend was 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 elastomers 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.

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

The elastomers were extracted 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

Silicone-containing polymers are particularly incompatible with all other polymers, and a classical me-

chanical blend would be most unstable. 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 radical copolymerization of St and DVB in the presence of PDMS. The blends obtained by this method are a series of stable white gums when the feed ratio of PDMS to St is 60/40 and DVB to St is not more than 2.0 wt %. During the formation of PS network by copolymerization of St and DVB, PDMS undergoes free radical crosslinking to form a PDMS network. An interpenetrating polymer network (IPN) consisting of PDMS network and PS network forms in the system. The interpenetration of PDMS and PS improves the interfacial bonding of the immiscible polymer blends and effectively restricts phase separation. It is probably the important reason that the PDMS/PS blends obtained by 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 with an increasing feed ratio of DVB to St. When the feed ratio of DVB to St is more than 2.0 wt %, solidification occurs during the copolymerization of St and DVB, and the blend obtained can no longer flow.

Elastomers based on PDMS/PS blends

Extraction measurement

THF is a good solvent for both linear PS and linear PDMS. The theoretical value of sol-fraction in the elastomer is assumed including linear PS (from imperfect crosslinking with DVB) and linear PDMS component (from imperfect end-linking PDMS chains with MTES). Because 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. The extraction data (Table II) show that the sol-fraction decreases when the feed ratio of DVB to St is increased due to the increasing crosslinking level of PS network.

TABLE II
Compositions and Results of
Extraction for the Elastomers

Sample code	Feed ratio (DVB/St) (wt %)	Sol fraction (wt %)
1	0	27.2
2	0.5	21.2
3	1.0	21.0
4	1.5	19.1
5	2.0	14.5

TABLE III
Effect of the Feed Ratio of DVB to St on the Mechanical Properties of the Elastomer

Sample code	DVB/St (wt %)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
1	0	2.7	149	34
2	0.5	3.1	161	46
3	1.0	2.8	158	47
4	1.5	2.7	154	49
5	2.0	2.8	152	50

Mechanical properties

Table III shows the mechanical properties of elastomers based on PDMS/PS blends with various feed ratios of DVB to St. It is clear that both the tensile strength and the elongation at break increase first and then drop down as the feed ratio of DVB to St increases. The tensile strength and elongation at break reach the maximum value at DVB/St = 0.5 wt %. Moreover, all the elastomers exhibit superior mechanical properties with respect to pure PDMS elastomer. The Shore A hardness of the elastomers was also determined. As DVB content increases, the crosslink density increases and the hardness values also correspondingly increase.

The effect of MTES dosage on the tensile strength, elongation at break, and hardness of sample 2 shown in Table I was determined respectively. The values are given in Figures 1–3. As the MTES dosage increases, the tensile strength and hardness of elastomers increases, while the elongation at break decreases. This is due to the reinforcing effect of the filler which precipitated from MTES. In the present study, the amount of MTES used in the crosslinking of PDMS/PS blends was in excess of the stoichio-

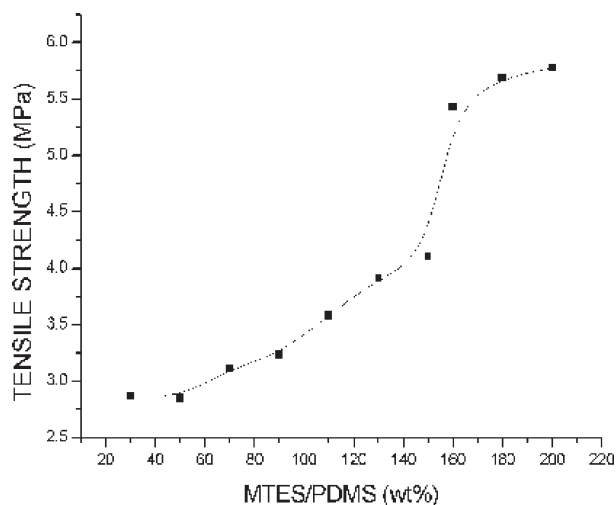


Figure 1 Effect of MTES dosage on the tensile strength of the elastomers.

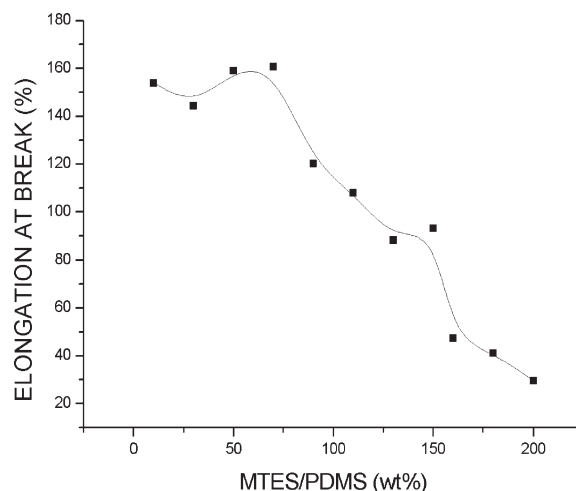


Figure 2 Effect of MTES dosage on the elongation at break of the elastomers.

metrically 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 SiO_2 and acted as fillers. As the MTES dosage increases, the amount of filler thus formed increases. This is the reason why the tensile strength and hardness of the elastomers increase. Moreover, as the MTES dosage increases, the network structure should become more highly cross-linked. This tighter structure imposed higher restrictions on the incorporated chains and led to the decrease of the elongation at break.

Table IV shows the comparisons between the reinforcing effects provided by surface-treated fumed silica and the crosslinked networks *in situ* precipitated during curing. The amount of crosslinked networks *in situ* precipitated was estimated from the change in weight of the polymer. It can be seen that

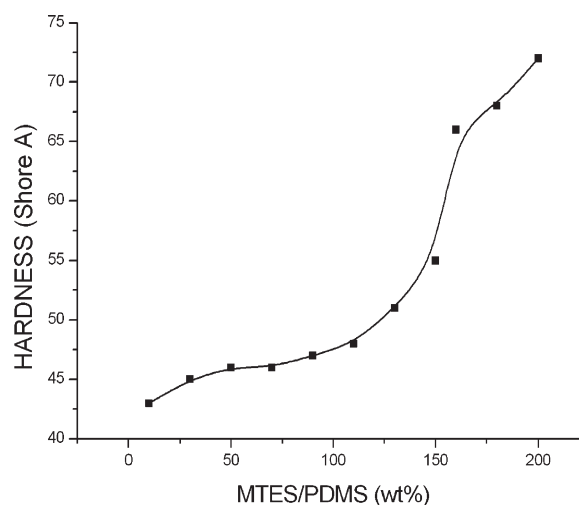


Figure 3 Effect of MTES dosage on the hardness of the elastomers.

TABLE IV
Filler Characteristics and the Mechanical Properties of the Elastomer

Sample code	Filler characteristics		Tensile strength (MPa)	Elongation at break (%)	Hardness (shore A)
	Type	wt % introduced			
1	Surface-treated fumed silica	13.5	2.2	148	37
2	Crosslinked networks in situ precipitated during curing	13.5	3.1	161	46

the PDMS elastomer filled with crosslinked networks *in situ* precipitated has values of the tensile strength and elongation at break obviously higher than those of the elastomer filled with fumed silica.

Morphology

Figure 4(a–c) show the SEM photographs of an elastomer based on sample 2 (shown in Table I, DVB/St = 0.5 wt %). Figure 4(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 crosslinking. Figure 4(c) shows the cross section of the elastomer, which

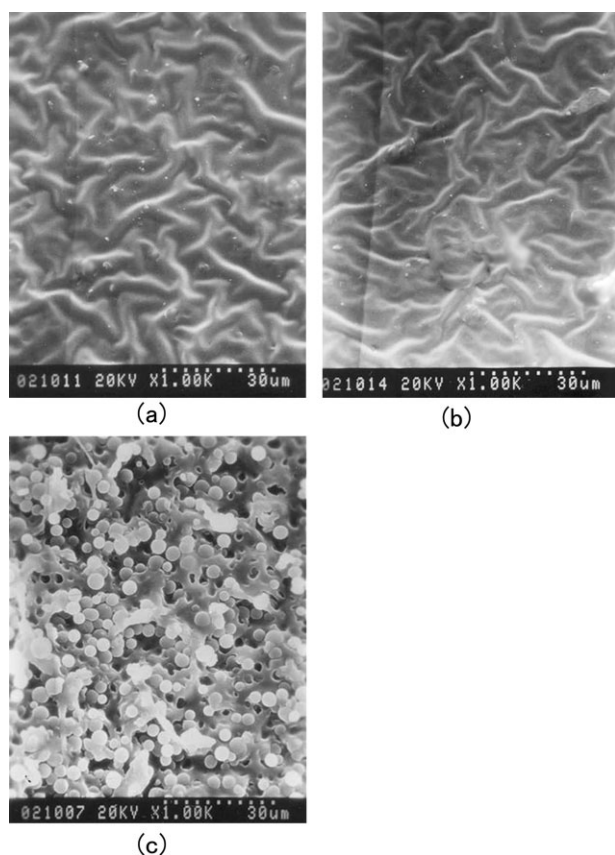


Figure 4 SEM photographs of the elastomer (DVB/St = 0.5 wt %; MTES/PDMS = 130 wt %): (a) surface exposed to the air, (b) surface in contact with the polytetrafluoroethylene mold, (c) cross section.

exhibits a microphase-separated structure. The PS is uniformly dispersed as spherical particles with a number-average diameter of about 3 μm in the PDMS matrix. Figure 5 was obtained by extracting the elastomer shown in Figure 4 with THF. Comparing Figures 4(c) and 5, we can see the amount of dispersed PS domains decreases obviously after extraction, and the extracted material is shown with a porous structure, in which the continuous region represents the remaining PDMS networks, and the dark zone is the void where linear PS (from imperfect crosslinking with DVB) is located. The dispersed domains remained are unextractable PS, and they are mainly due to the formation of IPN during the copolymerization of St and DVB mentioned above.

SEM micrograph of cross section of the elastomer based on sample 1 (shown in Table I, DVB/St = 0) is given in Figure 6. The morphology consists of a large number of small PS particles along with a small number of large PS particles in the PDMS matrix. The particle size is in the range of 2–6 μm . The comparison of Figures 4(c) and 6 indicates that the dispersed phase has different domain size distribution and shape. The domains of the dispersed phase on Figure 4(c) are much better distributed in the matrix than those on Figure 6, which leads to

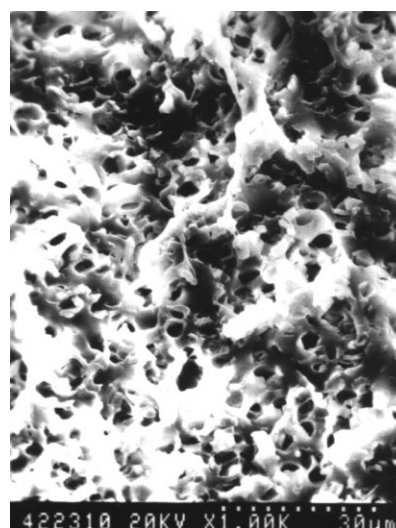


Figure 5 SEM photograph of the extracted material (DVB/St = 0.5 wt %; MTES/PDMS = 130 wt %).

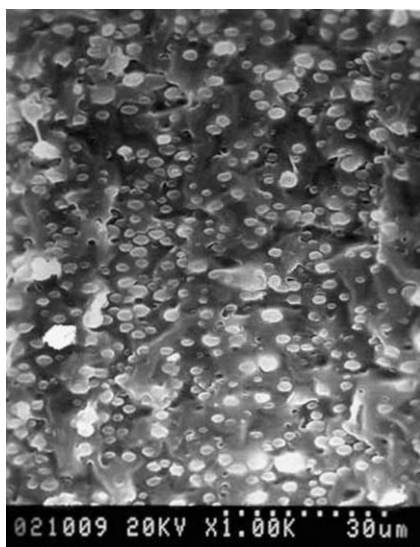


Figure 6 SEM photograph of cross section of the elastomer (DVB/St = 0; MTES/PDMS = 130 wt %).

advantageous effects on the reinforcement of the elastomers. So the elastomer 2 (shown in Table III) exhibits superior mechanical properties with respect to the elastomer 1 (shown in Table III).

CONCLUSIONS

PDMS/PS blends were prepared by the copolymerization of St and DVB in the presence of PDMS with BPO as initiator. The PDMS/PS blends obtained by this method are a series of stable, white gums, when the feed ratio of PDMS to St is 60/40 and DVB to St is not more than 2.0 wt %.

Extraction measurement and SEM study on the elastomers based on PDMS/PS blends show that the sol-fraction decreases when the feed ratio of DVB to St is increased due to the increasing crosslinking level of PS network. The two components in the elastomers are incompatible as predicted by solubility parameter considerations. However, the phase separation of the system is restricted to some extent by the crosslinking and interpenetration of the chains.

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

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