

Preparation, Morphology, and Mechanical Properties of Elastomers Based on α,ω -Dihydroxy-polydimethylsiloxane/Poly(methyl methacrylate) Blends

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ABSTRACT: α,ω -Dihydroxy-polydimethylsiloxane (PDMS)/poly(methyl methacrylate) (PMMA) blends were prepared by the radical polymerization of methyl methacrylate in the presence of PDMS, with benzoyl peroxide as the initiator. The PDMS/PMMA blends obtained by this method were a series of stable, white gums, which were vulcanized into elastomers at room temperature with methyl triethoxysilane (MTES). The MTES dosage was much larger than the amount necessary for end-linking the hydroxy-terminated chains of PDMS, with the excess being hydrolyzed into crosslinked networks, which were similar to SiO₂ and acted as fillers. Investigations were carried out on the elastomeric materials by extraction measurements, swelling measurements, and scanning electron microscopy. The extraction data showed that at each composition, the

sol fraction was less than expected. The extracted materials were further studied with swelling measurements, which revealed that the material obtained from an elastomer with a higher PMMA content had an apparently larger equilibrium swelling degree. Scanning electron microscopy demonstrated that the elastomer system had a microphase-separated structure consisting of PMMA domains within a continuous PDMS matrix. Moreover, the mechanical properties of the elastomeric materials were studied in detail. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1547–1553, 2006

Key words: blends; mechanical properties; morphology; polysiloxanes

INTRODUCTION

Polymer blending is generally known as an effective route for 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.¹

α,ω -Dihydroxy-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 The conventional approach for reinforcement is to blend a particulate filler into PDMS before the matrix is cured into a network. A specific and very important example is the introduction of silica aerogel into PDMS. However, the incorporation of such a filler into PDMS is a difficult, time-consuming, and energy-intensive process.³ 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 aggregation would obviously influence the mechanical properties of the elastomer thus reinforced. To avoid such disadvantages, Mark et al.³ 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.^{4–7} Previously, we prepared a PDMS/polystyrene blend^{1,8} and a PDMS/crosslinked polystyrene blend⁹ through the free-radical polymerization of styrene in the presence of PDMS. Both blends were vulcanized into elastomers at room temperature with methyl triethoxysilane (MTES). In the elastomer systems, the mechanical properties of PDMS could be improved by the introduction of a polystyrene component, which had strong mechanical performance. Moreover, the amounts of MTES used in the vulcanization of those blends were in excess of the stoichiometrically balanced amount. MTES was used to end-link hydroxyl-terminated chains of PDMS, with the excess being hydrolyzed into crosslinked networks, which were similar to the SiO₂ structure and acted as fillers. The simultaneous curing and filling of the elastomers in this way also led to an enhancement of the mechanical performance. Each factor played its role. As

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a result, the PDMS elastomers exhibited good mechanical performance.

Because poly(methyl methacrylate) (PMMA) is a typical glassy polymer, an improvement in the mechanical properties of PDMS can be expected by the incorporation of a PMMA component into PDMS. Moreover, it has been reported that PMMA is a biocompatible polymer.¹⁰ It can be inferred that a PDMS elastomer reinforced by PMMA should not change its inherent biocompatibility and should find potential applications in biomedical and environmental fields. Some researchers introduced a PMMA component into PDMS by synthesizing a PDMS/PMMA interpenetrating polymer network (IPN).^{2,11} For example, He et al.² synthesized PDMS/PMMA IPNs by the *in situ* sequential synthesis process. In these IPNs, the PMMA network was formed by the radical copolymerization of methyl methacrylate (MMA) with 1,1,1-trimethylolpropane trimethacrylate. Through the formation of PDMS/PMMA IPNs, the poor mechanical properties of the PDMS network were improved.

In this study, PDMS/PMMA blends were prepared by the radical polymerization of MMA in the presence of PDMS, with benzoyl peroxide (BPO) as the initiator. The PDMS/PMMA blends obtained by this method were vulcanized into elastomers at room temperature with 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 elastomeric materials by extraction measurements, swelling measurements, and scanning electron microscopy (SEM). Moreover, the mechanical performances of the elastomeric materials were studied in detail.

EXPERIMENTAL

Materials

PDMS with a weight-average molecular weight of 50,000 was supplied by the Chemical Industry Factory of Shandong University (Jinan, China). The sample was kept at 80°C *in vacuo* for 24 h to eliminate the cyclic compounds and low-molar-mass components.

MMA monomer was supplied by Shanghai Reagent Co. (Shanghai, China). It was distilled *in vacuo* just before use.

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

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

General procedure for preparing PDMS/PMMA blends

A solution was first prepared through the dissolution of BPO (1.5 wt % with respect to PDMS) in a small amount of MMA. The required weight of PDMS and the solution mentioned previously were then successively introduced into a four-necked, round-bottom 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 MMA 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 MMA. At the end of the reaction, the obtained mixture was kept at 80°C *in vacuo* to remove the unreacted MMA monomer. Finally, a kind of white fluid was obtained.

Vulcanization of the PDMS/PMMA blend

An excess amount of MTES (100 wt % with respect to PDMS contained in the PDMS/PMMA blend) was added to the PDMS/PMMA blend obtained previously, and the mixture was stirred vigorously for 5 min. Dibutyl tin dilaurate (1 wt % with respect to PDMS) was then added as a catalyst. After stirring for another 5 min, the resulting mixture was transferred into a poly(tetrafluoroethylene) mold. The crosslinking reaction was allowed to proceed at room temper-

TABLE I
Compositions and Viscosities of the PDMS/PMMA Blends

| Sample | Feed ratio (PDMS/MMA) | PMMA content in the blend (wt %) | Viscosity of the PDMS/PMMA blend (mPas) |
|--------|-----------------------|----------------------------------|---|
| 1 | 90/10 | 6 | 14,100 |
| 2 | 80/20 | 17 | 27,200 |
| 3 | 70/30 | 25 | 46,000 |
| 4 | 60/40 | 39 | 61,600 |
| 5 | 50/50 | 46 | 98,200 |
| 6 | 40/60 | 56 | >100,000 |

TABLE II
Compositions and Results of Extraction for the Cured Materials

| Sample | Cured material weight composition (PDMS/PMMA) | Sol fraction (%) | |
|--------|---|---------------------|-----------------------------------|
| | | Theory ^a | Experimental (THF as the solvent) |
| 1 | 100/0 | 4.43 ^b | 4.43 |
| 2 | 94/6 | 10.16 | 4.59 |
| 3 | 83/17 | 20.68 | 7.34 |
| 4 | 75/25 | 28.32 | 8.31 |
| 5 | 61/39 | 41.70 | 10.24 |
| 6 | 54/46 | 48.39 | 11.23 |
| 7 | 44/56 | 57.95 | 17.73 |

^aAmount estimated from the composition of the cured material and the PDMS network sol fraction.

^bExperimental data.

ature for 7 days. The cured material was then removed and stored at room temperature *in vacuo* for at least 24 h before investigation.

Characterization

The viscosity of the PDMS/PMMA blend was measured at room temperature with an NDJ-5S digital viscosimeter at a shear rate of 1.26 s^{-1} .

The tensile strength, elongation at break, and tear strength of the cured material were measured with a tensile testing machine (AGS-H, Shimadzu). The measurements of the tensile strength and elongation at break were carried out at room temperature at a crosshead speed of 500 mm/min with dumbbell-shaped specimens with a gauge length of 20 mm according to GB/T528-1998. The tear strength of the cured material was measured at room temperature at a crosshead speed of 500 mm/min with unnicked angle test pieces according to GB/T529-1999.

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

The linear PMMA in the cured materials was extracted from the PDMS networks in a Soxhlet extractor. The solvent was tetrahydrofuran (THF; Tianjin Reagent Co., China). 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 *in vacuo* for 48 h, and soluble fractions of the samples were calculated. Their densities were determined with 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 SEM 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/PMMA blends

The solubility parameter of PMMA is $9.5 \text{ cal}^{1/2}/\text{cm}^{3/2}$, and PDMS has a lower solubility parameter of $7.3 \text{ cal}^{1/2}/\text{cm}^{3/2}$.¹² As the solubility parameters of the two polymers differ by $2.2 \text{ cal}^{1/2}/\text{cm}^{3/2}$, the application of the Krause method of miscibility prediction¹³ leads to the conclusion that they will be immiscible at all compositions and a stable blend based on PDMS and PMMA cannot be realized by the direct mixing of the two components. We dissolved PDMS together with PMMA in toluene. The mixture was stirred and refluxed for 5 h. When toluene was distilled out, phase separation took place between PDMS and solid PMMA. This is in accordance with the theoretical conclusion mentioned previously. This also suggests that it is difficult to improve the mechanical properties of PDMS by direct mixing with PMMA.

In our work, PDMS/PMMA blends were prepared by the free-radical polymerization of MMA in the

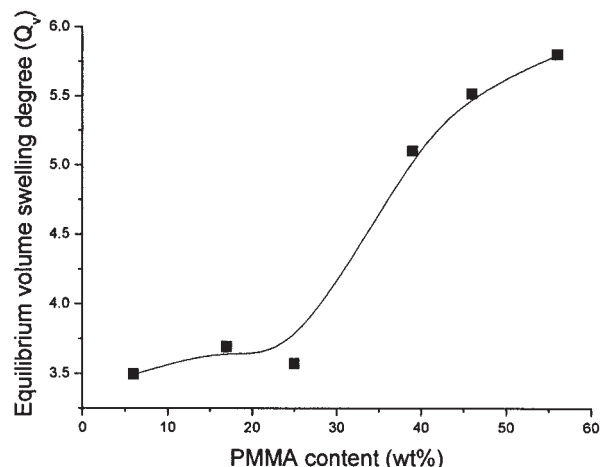


Figure 1 Effect of the PMMA content on Q_v of the extracted materials.

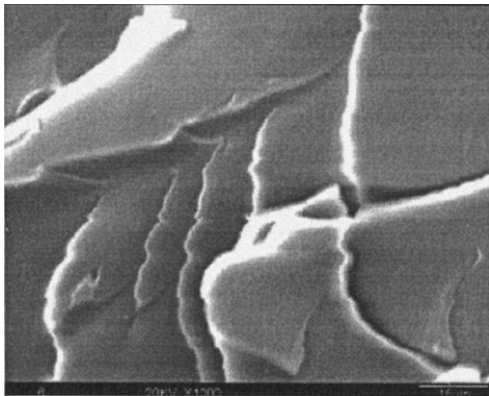


Figure 2 SEM micrograph of the PDMS elastomer.

presence of PDMS. The blends obtained by this method were a series of white gums when the feed ratio of PDMS to MMA was not less than 40/60. Furthermore, the blends could be laid for at least 2 months without macroscopic phase separation. In general, when one polymer is synthesized by radical polymerization in the intimate presence of another

polymer, it always accidentally introduces some grafting.^{1,14} Therefore, in the system that we studied, it was unavoidable to introduce the PDMS-g-PMMA copolymer during the polymerization of MMA.^{1,14,15} The graft copolymer acted as a compatibilizer, which improved the interfacial bonding of the immiscible polymer blends.¹ Moreover, we mixed PDMS with 1.0 wt % BPO. 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. Therefore, under the conditions of MMA polymerization, it is very possible that PDMS undergoes free-radical crosslinking to form an IPN consisting of either directly linked PDMS chains or chains linked via PMMA grafts. Linear PMMA is entangled in the IPN, and the entanglement can effectively restrict phase separation. These are probably the actual reasons that the PDMS/PMMA blends obtained by this method are stable. The compositions and viscosities of the PDMS/PMMA blends can be seen in Table I. Apparently, the viscosities of PDMS/PMMA blends tend to increase dramatically with a decreasing feed ratio of PDMS to MMA. When

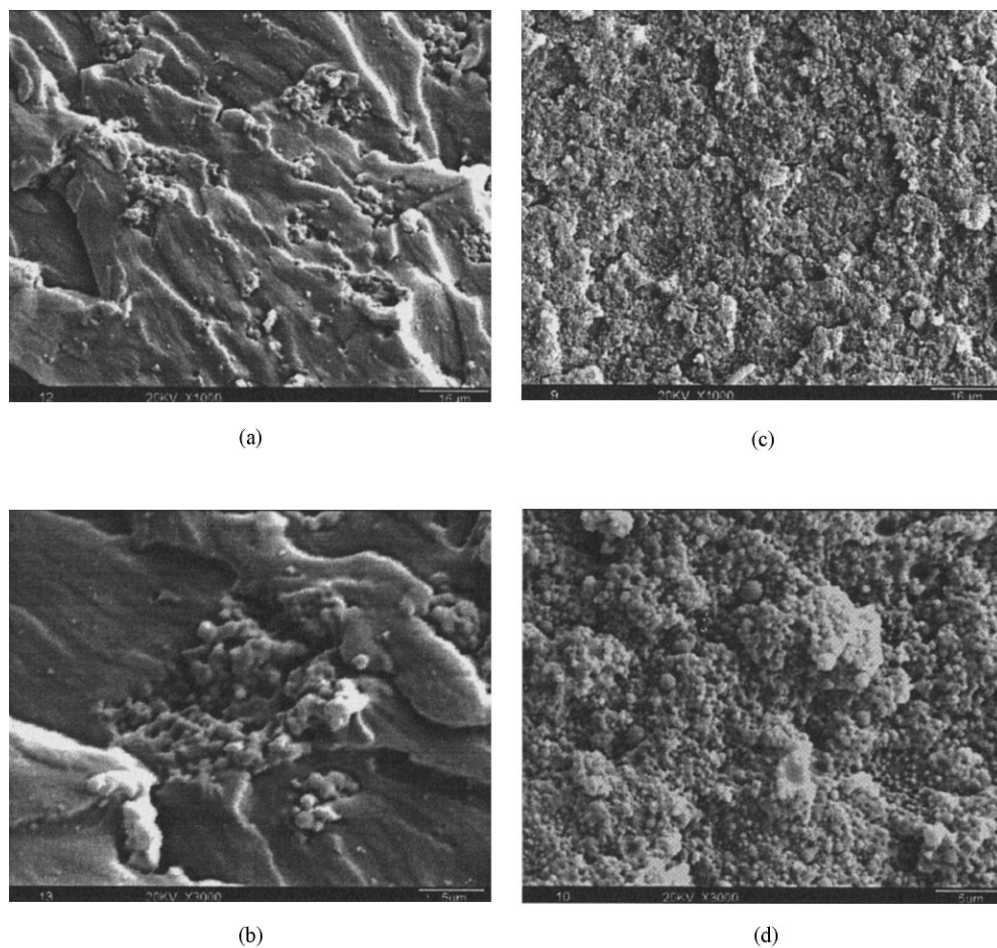


Figure 3 SEM micrographs of the cured materials: (a,b) 75/25 PDMS/PMMA and (c,d) 44/56 PDMS/PMMA.

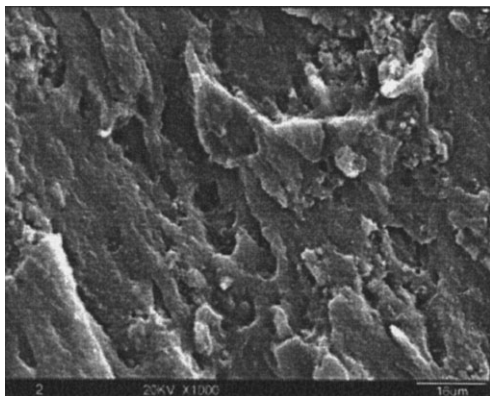


Figure 4 SEM micrograph of the extracted cured material (75/25 PDMS/PMMA).

the feed ratio of PDMS to MMA is less than 40/60, solidification takes place during the polymerization of MMA, and the obtained blend can no longer flow.

Elastomers based on PDMS/PMMA blends

Extraction and swelling measurements

THF is a good solvent for both linear PMMA and linear PDMS. The theoretical value of the soluble fraction in the cured material was assumed, including the PMMA and linear PDMS component (from the imperfect end-linking of PDMS chains with MTES). Because the formula ratio of MTES to PDMS was the same in all compositions of the cured materials, it was assumed that the soluble fraction of the PDMS component was the same, that is, 4.43%. However, the extraction data (see Table II) show that at each composition, the amount of extracted materials was less than the theoretical value. This may be due to (1) the actual grafting of linear PMMA onto PDMS during the radical polymerization of MMA or (2) the entanglement of PMMA in the IPN, which consisted of either directly linked PDMS chains or chains linked via PMMA grafts and was formed by the free-radical crosslinking of PDMS during the radical polymerization of MMA. PMMA grafted onto PDMS was insoluble, and PMMA

entangled in the IPN was difficult to extract. Both rendered the soluble fraction less than expected.

The extracted materials were studied by swelling measurements. 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 (Table II) led to the conclusion that the extracted materials could not be considered conventional PDMS networks and that there were different amounts of PMMA remaining in them. Furthermore, the SEM micrograph suggests that the extracted material was a porous material. Some THF was imbibed in the pores during swelling as a more or less pure phase. The material that had a higher PMMA content had a higher soluble fraction, which had more solvent imbibed and, hence, an apparently larger Q_V .

Morphology

SEM micrographs of the fracture surfaces of the PDMS elastomer and cured materials based on PDMS/PMMA blends with different compositions are shown in Figures 2 and 3, respectively. The sample shown in Figure 2 had only one continuous phase of PDMS. However, the samples in Figure 3 exhibited microphase-separated structures. For the cured material containing 25% PMMA [Fig. 3(a)], PDMS was the continuous phase, and the sparsely distributed PMMA particles and some aggregates were the dispersed phase. The morphology of this sample can be better seen at the different magnification shown in Figure 3(b). From Figure 3(b), we can see that the aggregate consisted of spherical PMMA domains. Figure 3(c,d) shows the micrographs of the cured materials containing 56% PMMA. With an increase in the PMMA content, the amount of PMMA domains increased, and the aggregation degree of PMMA also increased apparently. The aggregation was due to the poor miscibility of PDMS and PMMA mentioned previously. The sample shown in Figure 4 was obtained by the extraction of the cured material shown in Figure 3(a) with THF. Comparing these two figures, we can see that the amount of disperse domains de-

TABLE III
Effect of the PMMA Content on the Mechanical Properties of the Cured Materials

| Sample | Weight composition (PDMS/PMMA) | Tensile strength (MPa) | Elongation at break (%) | Tear strength (KN/m) | Hardness (Shore A) |
|--------|--------------------------------|------------------------|-------------------------|----------------------|--------------------|
| 1 | 100/0 | 1.158 ± 0.299 | 162.540 ± 20.860 | 2.96 ± 0.15 | 16 |
| 2 | 94/6 | 1.287 ± 0.178 | 158.379 ± 11.869 | 4.34 ± 0.09 | 22 |
| 3 | 83/17 | 2.679 ± 0.400 | 138.440 ± 15.026 | 4.63 ± 0.22 | 26 |
| 4 | 75/25 | 4.061 ± 0.263 | 168.766 ± 12.873 | 5.16 ± 0.34 | 45 |
| 5 | 61/39 | 4.346 ± 0.561 | 97.535 ± 10.236 | 6.02 ± 0.21 | 49 |
| 6 | 54/46 | 3.935 ± 0.303 | 76.290 ± 4.611 | 5.20 ± 0.04 | 60 |
| 7 | 44/56 | 4.735 ± 0.023 | 61.359 ± 3.724 | 4.58 ± 0.21 | 62 |

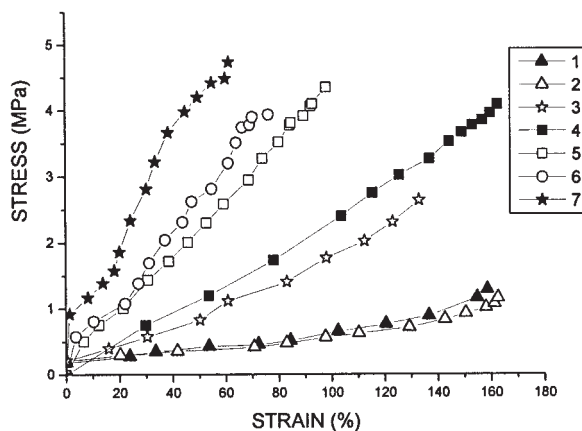


Figure 5 Effect of the PMMA content on the stress–strain behavior of the cured materials.

creased apparently after extraction. Figure 4 reveals a porous structure, in which the continuous region represents the remaining PDMS networks and the dark zone is the void in which PMMA was located. The disperse domains were unextractable PMMA and were mainly due to the actual grafting of linear PMMA onto PDMS and the formation of the IPN during the polymerization of MMA mentioned previously.

Mechanical properties

Table III shows the mechanical properties of cured materials based on PDMS/PMMA blends with various compositions. Because the weight ratio of MTES to PDMS was the same in all compositions of the cured materials, the improvement of the mechanical properties of the PDMS elastomer was mainly due to the incorporation of PMMA. Both the tensile strength and hardness (shore A) of the cured materials increased as the PMMA content increased from 0 to 56%. The elongation at break reached the maximum value at PDMS/PMMA = 75/25. The tear strength of the PDMS elastomers was enhanced by the incorporation of a PMMA component, but the improvement was not satisfactory.

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 nature to a plastic nature as the PMMA content increases. In the samples with a lower PMMA content (samples 1–5), the stress increased gradually with strain until failure. The systems underwent appreciable deformation, and the deformation was elastic in nature. However, both sample 6 and sample 7 had a relatively high initial modulus and showed definite characteristics of plastic deformation.

There was also ample evidence for a very strong reinforcing effect by the simultaneous curing and fill-

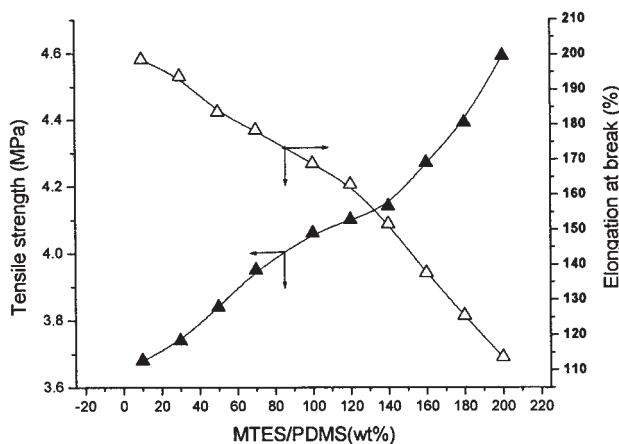


Figure 6 Effect of the MTES amount on the tensile strength and elongation at break of the cured material.

ing of the elastomers with an excess amount of MTES. The effect of the MTES dosage on the tensile strength and elongation at break of sample 3 (Table I) was determined. The values are given in Figure 6. As the MTES amount increased, the tensile strength of the cured materials increased, whereas the elongation at break decreased. The tear strength and shore A hardness values of those cured materials are given in Figures 7 and 8, respectively. With an increase in the MTES amount, the tear strength decreased, whereas the hardness increased.

CONCLUSIONS

PDMS/PMMA blends were prepared by the free-radical polymerization of MMA in the presence of PDMS, with BPO as the initiator.

PDMS/PMMA blends obtained by this method were a series of white, stable gums when the feed ratio

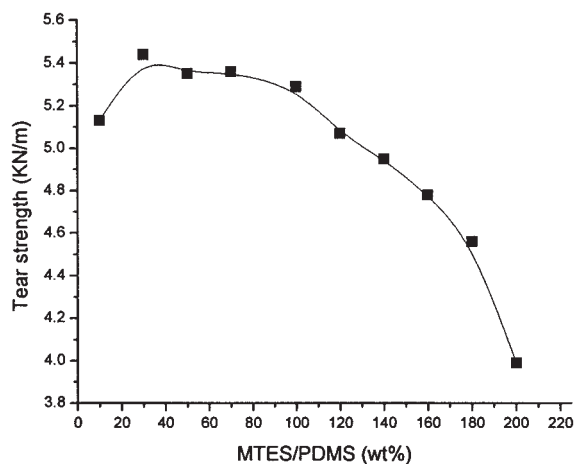


Figure 7 Effect of the MTES amount on the tear strength of the cured material.

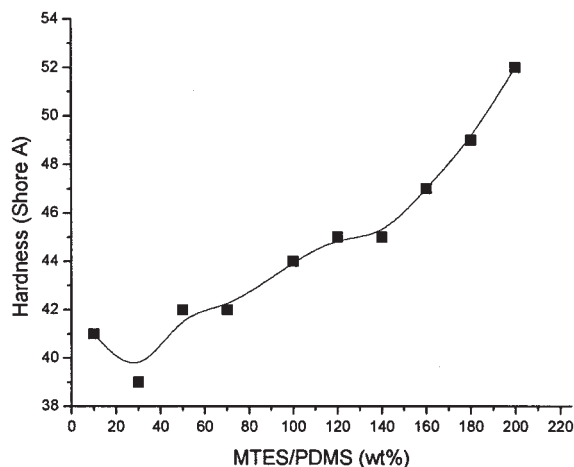


Figure 8 Effect of the MTES amount on the hardness of the cured material.

of PDMS to MMA was not less than 40/60. Furthermore, the blends could be laid for at least 2 months without macroscopic phase separation.

Extraction measurements and SEM study of the cured materials of the PDMS/PMMA blends showed that the actual grafting of PMMA onto PDMS and the entanglement of PMMA in the IPN that was formed by radical crosslinking of PDMS rendered extraction difficult. The two components in the cured materials were incompatible as predicted by solubility parameter considerations, and the system was phase-separated. Swelling measurements of the extracted materials indicated that the material that had a higher PMMA content had an apparently larger Q_V .

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

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