Preparation and Characterization of PDMS-PMMA Interpenetrating Polymer Networks with Indistinct Phase Separation

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Preparation and Characterization of PDMS-PMMA Interpenetrating Polymer Networks with Indistinct Phase Separation

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This paper describes the preparation and characterization of the interpenetrating polymer networks (IPNs) of polydimethylsiloxane-polymethyl methacrylate (PDMS-PMMA) via 3-(methacryloxypropyl)-trimethoxy-silane (MPS) as the crosslinking agent. The structure of synthesized IPNs was characterized by ^{1}HNMR, DSC, FT-IR, XPS, SEM and AFM, respectively. The experimental results show that, with the method adopted in this preparation process, the phase separation between PDMS and PMMA in PDMS-PMMA IPNs has been reduced to a smaller extent than other previous reports.

Keywords: interpenetrating polymer networks, polysiloxane, PDMS-PMMA, oligomer, elastomer

1 Introduction

Polysiloxane and their derivatives have many excellent properties, such as strong water repellency, high flexibility, low glass transition temperature, low surface energy and so forth (1–4). But, due to its higher cost, poor cohesiveness and film-forming property, its wide application of polysiloxane has been limited. Polyacrylate, however, seeming like the opposite of polysiloxane, is characterized by its lower cost, good cohesiveness and excellent film-forming property. Generally, it is accepted that the greater difference found in the properties of two polymers, the more likely to obtain the merits of both materials once they are complexed together in proper conditions (5). So far, based on the complexing of organic siloxane and acrylate, there are many significant studies that have been conducted by Park (6), Medda (7) and Bauer(8) et al., which have greatly promoted the technology for developing new functional materials.

The interpenetrating polymer networks (IPNs), basically, could be regarded as polymer networks in which two different polymers are crosslinked or entangled. The interlocked structure of IPNs could prevent the phase separation of different components, ensuring a good stability of the bulk and surface morphologies and making IPNs superior to some conventional materials (9). For example, IPNs could not only provide enough mechanistic strength but also the swelling property in conventional solvents (10–11).

Previous experiences have indicated that the combination of polydimethylsiloxane (PDMS) with PMMA could result in improved properties, meanwhile, the excellent properties of PDMS including low energy surface, water repellence and high gas penetrability were maintained. And, the merits of PMMA, such as good transparence and film-forming property, could also be reserved. In this way, the PMDM-PMMA IPNs become a kind of versatile materials with a wide range of applications (3, 12).

Traditionally, PMMA-PDMS semi-IPNs are prepared using trichlorosilane and silanediols as monomers, the increase of the amount of PMMA will lead to the increase of toughness, but the decrease of tensile strength of the resultant PDMS-PMMA IPNs (13). Full IPNs PDMS/PMMA are prepared by sequential crosslinking of a,ω-divinyl (dimethylsiloxane) with divinyltetramethyldisiloxane, followed by UV irradiation radical copolymerization of MMA with the existent cross-linkers (11). The full IPNs could not only possess relatively strong mechanistic strength but also high gas permeability.

Technically, crosslinking by forming firm covalent bonds is used to prevent different components from phase

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separation at the interface domains. Another effective way is to introduce specific functional groups on the precursors of one network, which could interact with the other network (10,14,15). In the present study, we reported a simple method to obtain the PDMS-PMMA IPNs. In the process of preparing PDMS, 3-(methacryloxypropyl)-trimethoxy-silane (MPS) was used to create double bonds in the host network, then once MMA was introduced into the network, MPS would react with MMA, making the two phases form a new homogeneous network. The elastomer of PDMS as well as the PDMS-PMMA IPNs were analyzed by ^{1}HNMR, DSC, FT-IR, XPS, TEM and AFM, respectively. The results show that a new PDMS-PMMS IPNs with stable phase balance could be prepared successfully.

2 Experimental

2.1 Materials

Methyl methacrylate (MMA) and tetrahydrofuran (THF) were purchased from Xilong Chemical Co. of China. Octamethyl tetracyclosiloxane (D4), 3-(methacryloxypropyl)-trimethoxysilane (MPS) were both obtained from Yudeheng Couple Agent Factory (China), and divinylbenzene was bought from Aldrich (Germany). All the monomers were purified by vacuum distillation prior to use. AIBN was purchased from Bodi Chemical Co. (China) and used without purification. All other chemicals were of analytical grade. Double distilled water was used throughout this work.

2.2 Synthesis of the PDMS Elastomer

D$_4$ (40.0 g), H$_2$SO$_4$ (1.0 mL) and a certain amount of water was added into a 100 ml four-neck flask, which was fitted with a mechanical stirrer, nitrogen inlet and reflx condenser. After that, the temperature was raised to 80°C. Under fierce agitation of reactants, MPS (10 g) was introduced into the system slowly, and the polymerization was conducted for 2 h. The resultant PDMS elastomer did not dissolve, but swelled in tetrahydrogenfuran (THF).

2.3 Preparation of the PDMS-PMMA IPNs

The resultant elastomer (15 g) was swelled in 30 ml THF in a 100 mL four-neck flask at room temperature for 24 h before they were mixed with MMA (15 g), divinyl benzene and AIBN (0.1 g) and stirred overnight. After deairing with nitrogen for 30 min, the polymerization was carried out at 60°C for 12 h. The reaction principle for preparing PDMS-PMMA IPNs was shown in Figure 1. Then the reaction product was purified by washing with ethanol for several times and preserved for further testing.

2.4 Analysis of ^{1}H-NMR and AFM

^{1}H-NMR spectra of the oligomer were measured by a BRUKER AM 300 spectrometer and a DUAL-5 mm probe. The samples were dissolved in CDCl$_3$ (10–15 wt/vol%) at 25°C. The AFM analysis was carried out on MMAFMLN2068EX (Vecco instruments, USA).

2.5 Characterization of DSC and SEM

The sample of PDMS elastomer was dried at 60°C for 24 h for obtaining a dried elastomer. Its thermal behavior was determined by DSC at a heating rate of 20 K/min. A scanning electron microscopy (SEM, JEOL JSM-5900LV) was employed to observe the morphology of PDMS elastomer before and after Soxhlet extraction.

2.6 Measurement of XPS and FT-IR

The XPS measurement was made on a KRATOS Analytical AXISHISi spectrometer at a constant dwell time of 100 ms. A concentric hemispherical analyzer (CHA) was performed in the constant analyzer transmission mode to
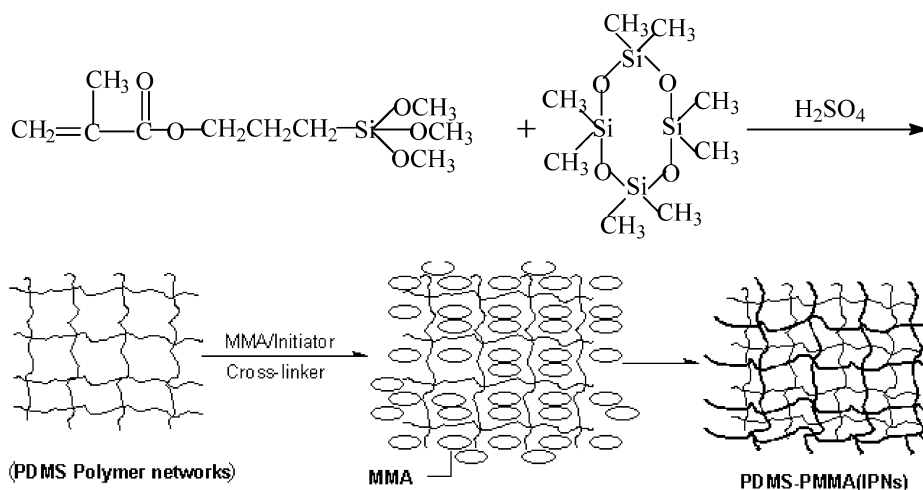

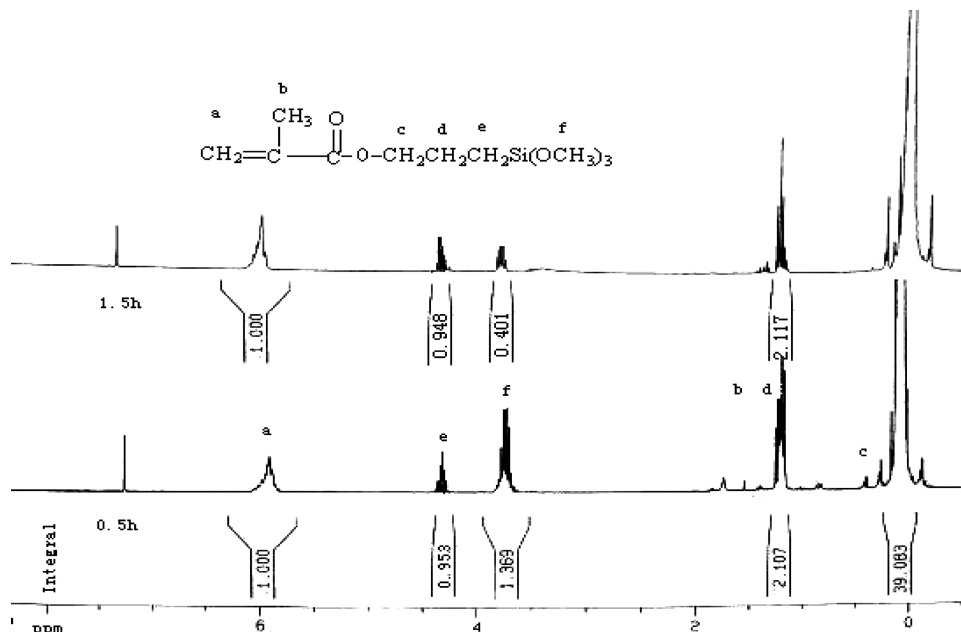**Fig. 1.** Schematic formation of PDMS-PMMA IPNs.

Fig. 2. ^{1}H-NMR spectra of elastomer at different reaction time.

measure the binding energies of emitted photoelectrons. The binding energy scale was calibrated by the Au $4f_{7/2}$ peak at 83.9 eV, as well as Cu $2p_{3/2}$ peak at 76.5 and 932.5 eV. In addition, FT-IR spectra were recorded using a NICOLET MX-1E FT-IR spectrometer.

3 Results and Discussion

3.1 Analysis of PDMS-MPS Elastomer

3.1.1. *^{1}H-NMR spectra and DSC measurement*

^{1}H-NMR is a very useful tool for probing the amount of hydrogen in different chemical shifts (16–18). The ^{1}HNMR spectrum of PDMS elastomer was shown in Fig. 2. The peaks at 0 ppm and 6 ppm correspond to the CH_3 group in the long chain of Si−O−Si and the vinyl group (CH_2=CH)

in MPS, respectively. Noticeably, with the increase of reaction time, the peak at 3.7 ppm (OCH_3) became weakened, implying that more OCH_3 groups underwent hydrolysis. In our study, 2 h was chosen as the reaction time. After cooled at room temperature, the product would turn to elastomer-like gels and did not dissolve but swell in THF.

The DSC thermogram of PDMS-MPS elastomer was shown in Figure 3(a). As could be noticed there is only one glass transition temperature (T_g) at −29.7°C, indicating a tightly enclosed structure.

3.2 FT-IR Characterization

The results of the FT-IR analysis of PDMS-MPS elastomer were shown in Figure 4. The peak at 1723.6 cm^{-1} resulted from the C=O stretching vibration of MPS. Also, the peaks at 1640.2 cm^{-1} and 3100.2 cm^{-1} corresponded to C=C
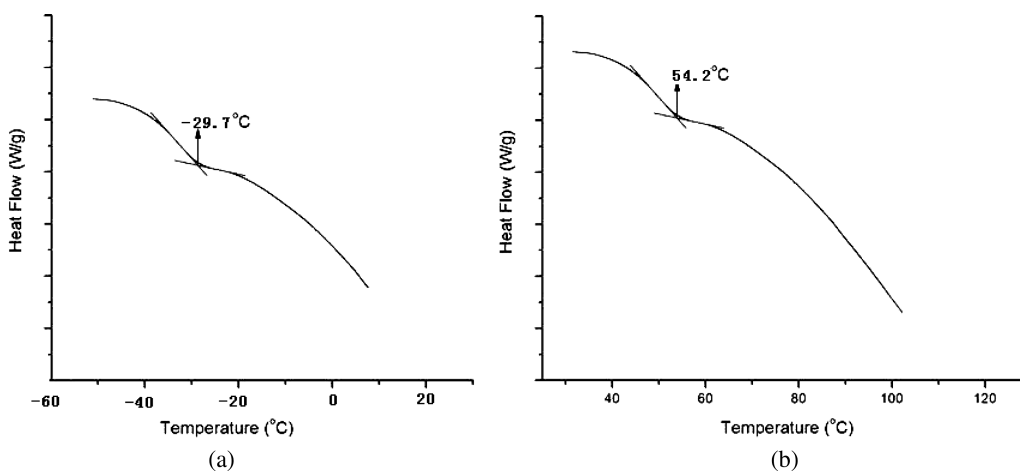

Fig. 3. DSC thermogram of PDMS-MPS elastomer (a) and PDMS-PMMA IPNs (b).
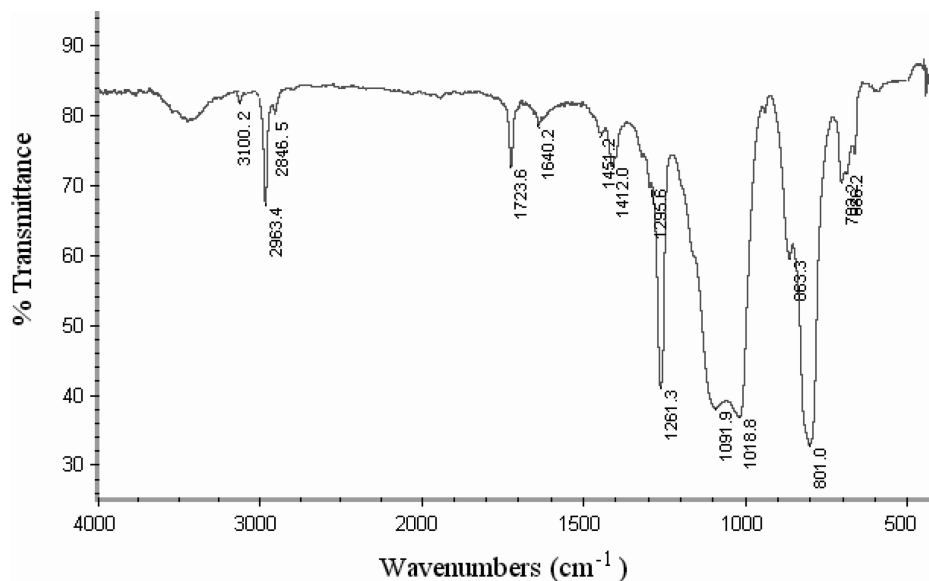
Fig. 4. FT-IR spectra of PDMS-MPS elastomer.

stretching and C–H stretching vibrations, suggesting the existence of MPS in the elastomer. Apart from that, the peaks at 801.0 cm^{-1} and 1261.3 cm^{-1} indicated the existence of Me$_2$SiO (D) groups, while the characteristic peaks of Si–O–Si were also reflected at 1018.8 cm^{-1} and 1091.9 cm^{-1} in the spectrum. It is necessary to point out that no peaks were observed in the range of 1090 cm^{-1} to 1075 cm^{-1}, suggesting that almost all D$_4$ have been consumed in the polymerization. In addition, there was only a weak peak at the point 2846.5 cm^{-1}, which indicated that almost all the Si–O–CH$_3$ groups had been hydrolyzed. This agreed well with the analysis of ^{1}H-NMR.

3.3 Analysis of PDMS-PMMA IPNs

3.3.1. *DSC measurement*

The DSC thermogram of PDMS-PMMA IPNs (50/50 wt%) was shown in Figure 3(b). The result suggested that

PDMS-PMMA IPNs also possess a tightly enclosed structure, because only one T$_g$ was observed in the experimental range. On the other hand, as could be noticed from Figures 3(a) and (b), the change of T$_g$ from $-29.7°$C to 54.2$°$C could be attributed to the introduction of PMMA as well as crosslinkers, because the value of real T$_g$ was higher than calculated value (23.1$°$C).

3.4 FT-IR Spectrum

The FT-IR spectrum of PDMS-PMMA IPNs was shown in Figure 5. The peak at 1728.8 cm^{-1} attributed to the C=O stretching vibration of acrylate. There were no peaks at 1640 cm^{-1} and 3102 cm^{-1}, corresponding to C=C and C–H stretching vibration, respectively, thus suggesting that almost all the monomers be consumed in the reaction, and that no C=C bonds existed in the resulting product. Similar
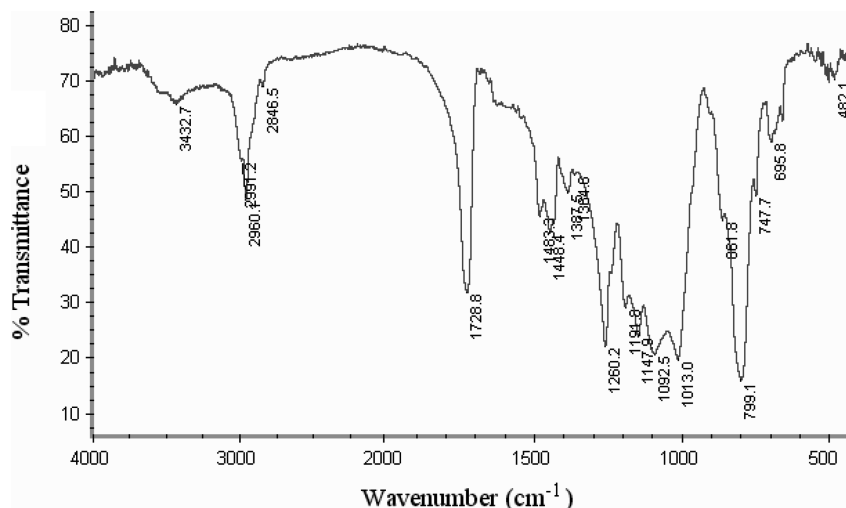

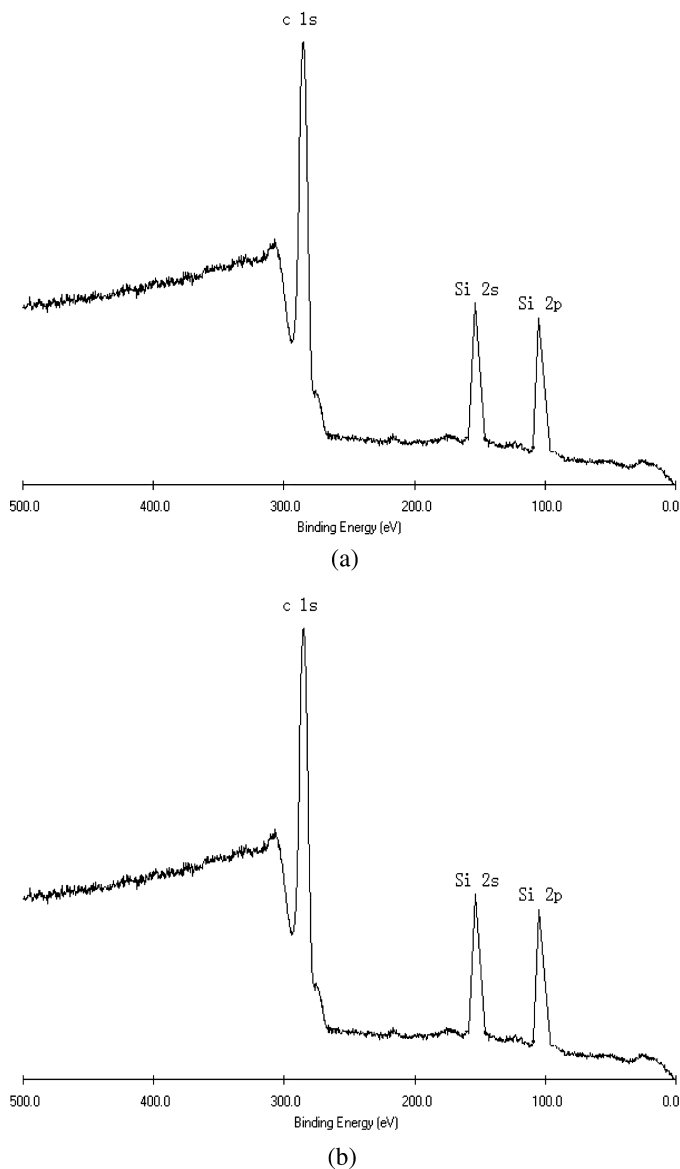**Fig. 5.** FT-IR spectra of PDMS-PMMA IPNs.

(a)

(b)

Fig. 6. XPS characterization of PDMS-PMMA IPNs before (a) and after (b) Soxhlet extraction.

to the spectrum in Figure 4, the peak of Si–O–CH$_3$ group could also be reflected at 1013.0 and 1092.5 cm^{-1}.

3.5 X-ray Photoelectron Spectroscopy (XPS)

XPS is frequently used for the element analysis for material's surface, from which some important parameters such as C/Si ratio could be obtained (19–21). Logically, if PDMS could totally combine with PMMA, there would appear some characteristic peaks of Si element, and the atomic ratio of C/Si in the sample would be consistent with the value calculated by the monomers' ratio. To confirm this idea, the elements in the surface of PDMS-PMMA IPNs before and after Soxhlet extraction were measured by XPS (Fig. 6).

Table 1. The atomic ratio of C/Si of PDMA-PMMA IPNs before and after Soxhlet extraction

Sample	Element	CPS	Sensitivity	Atomic ratio (C/Si)
Before	C	6145.746	0.25	3.375
	Si	2112.286	0.29	
After	C	4936.64	0.25	3.285
	Si	2096.081	0.29	

The atomic ratios of C/Si before (3.375) and after (3.285) Soxhlet extraction (Table 1) were smaller than the theoretical value calculated with the monomer (6.93). Previous studies have indicated that polysiloxane has the tendency of surface segregation in copolymers, which is derived from its lower surface tension, in particular for Si- or F-containing copolymers (22). Therefore, the lower C/Si ratio found in PDMS-PMMA IPNs could be assigned to the surface enrichment of polysiloxane, i.e. the outer layer was enriched in PDMS, while PMMA network was mainly distributed in the inner layers. In addition, the small difference between the C/Si ratio before (3.375) and after (3.285) Soxhlet extraction suggested that an even monomer concentration profile be obtained.

3.6 SEM Characterization

The morphology for fracture surface of PDMS-PMMA IPNs was further observed by means of SEM (Figs. 7 and 8). Although some small cavities could be noticed in Figure 7, the phase separation was not obvious. However, the size of these cavities were enlarged and the numbers of cavities were increased too after the sample was treated with Soxhlet extraction (Fig. 8(a)). These experimental results are associated with the loss of low molecular weight polymers during the solvent extraction. Apart from that, it could be observed from Fig. 8(b) that some aggregates or blocks were distributed inside the sample. It was postulated that these aggregates with irregular shapes were mainly PMMA. By a rough estimation, the domain size (no more than 0.5 μm) of these aggregates was much smaller than reported in other literature (about 3 μm) (23).

3.7 AFM Analysis

Recently, atom force microscope (AFM) has become an advanced analytical tool used for examining the surface properties of various materials, such as engineering plastics, paint and coating, rubber, packing, fiber and a wide range of consumer goods. In particular, AFM analysis could yield some important parameters, such as the elastic modulus and surface flatness of materials (24–26).

Figure 9 showed the AFM micrographs of PDMS-PMMA IPNs. Because of surface enrichment, polysiloxane occupied most of the surface of the sample, as was reflected as the bright regions in Figure 9(a). This result
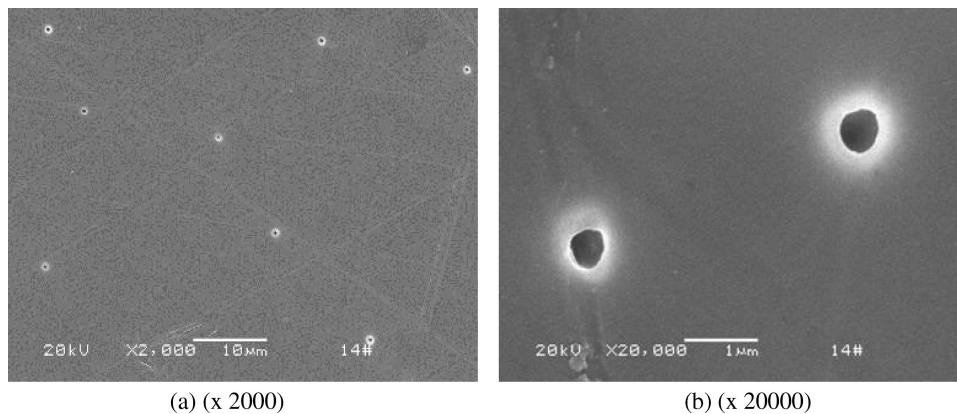
(a) (x 2000)   (b) (x 20000)

Fig. 7. SEM of PDMS-PMMA IPNs (before Soxhlet extraction).

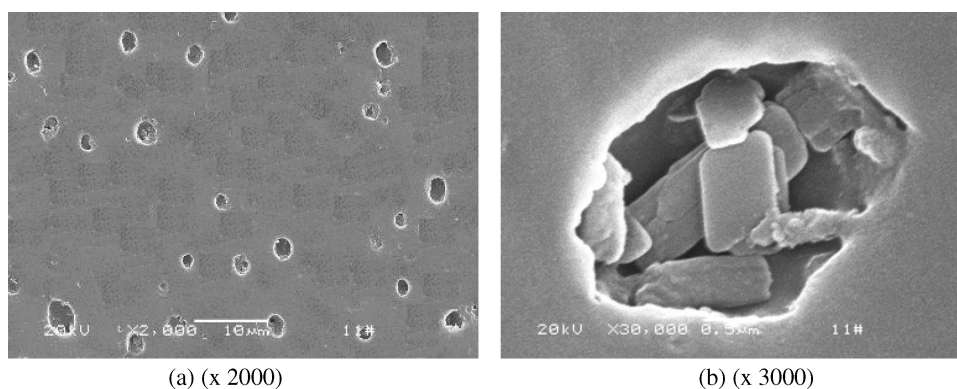(a) (x 2000)   (b) (x 3000)

Fig. 8. SEM of PDMS-PMMA IPNs (after Soxhlet extraction).

agreed well with the conclusion of XPS analysis, namely the outer layer was almost covered by PDMS. Besides, the contrast of bright and dark regions in Figure 9(a) was not very intensive, showing that the IPNs' surface was almost homogeneous and smooth. However, the modulus difference between PDMS and PMMA was large enough: the bright regions possessed a higher modulus, and vice versa. Since the networks generally possessed a high modulus, the
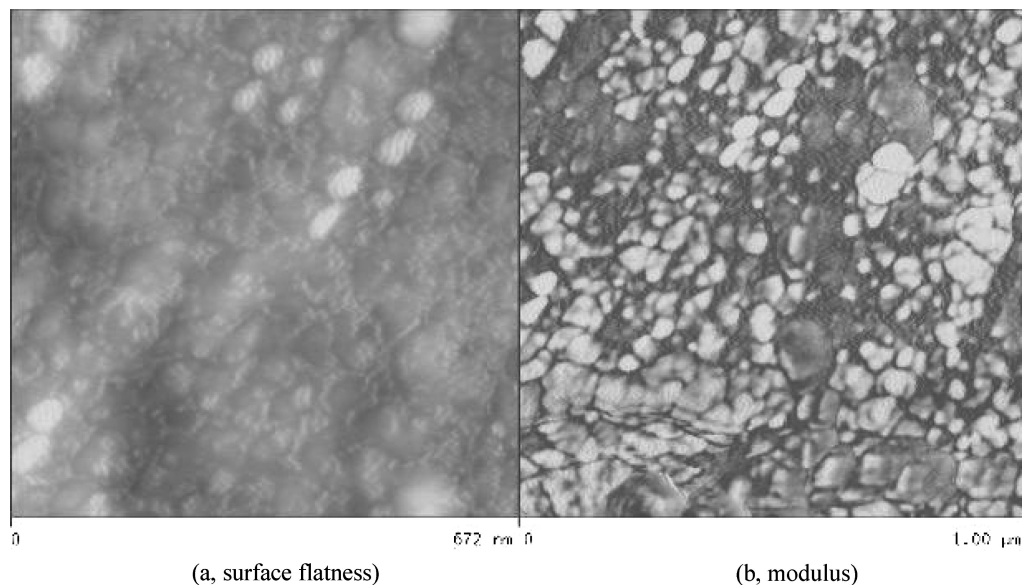

(a, surface flatness)   (b, modulus)

Fig. 9. AFM analysis of PDMS-PMMA IPNs.

bright area in Figure 9(b) was obviously larger than the case in Figure 9(a).

4 Conclusions

In this study, we developed a simple method for preparing PDMS-PMMA interpenetrating polymer networks. Firstly, the PDMS elastomer was prepared in the presence of MPS, and the polymerization reaction was catalyzed by H_2SO_4. The experimental results indicated that almost all the MPS had been hydrolyzed and incorporated with PDMS. Secondly, the MMA monomer was introduced in the networks of PDMS, through a further polymerization, the PDMS-PMMA IPNs, without obvious phase separation, could finally be produced.

Because of the obvious difference in solubility parameters of PDMS (d = 7.5) and PMMA (d = 9.1), the phase separation in PDMS-PMMA IPNs would still occur to a certain extent as observed in TEM micrographs. However, the phase separation could be well controlled by setting up a proper reaction conditions, and the domain size of PMMA aggregates could be reduced and became much smaller than other cases in the literature.

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