

SYNTHESIS AND CHARACTERIZATION OF POLYDIMETHYLSILOXANE/POLYSTYRENE SEMI- INTERPENETRATING POLYMER NETWORKS

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Abstract The synthesis of pseudo- and semi-interpenetrating polymer networks (IPNs) based on polydimethylsiloxane (PDMS) and polystyrene (PS) is described. IPNs were obtained by simultaneous and *in situ* sequential synthesis procedure. The preliminary studies on IPNs properties such as transition temperature, microphase separation and mechanical behaviors have been carried out by using differential scanning calorimetry (DSC) and scanning electron microscopy (SEM). The experimental evidence clearly showed that semi-IPNs obtained by sequential synthesis procedure have higher interpenetrating extent than pseudo-IPNs synthesized by simultaneous procedure. Over the full composition, the PDMS/PS IPNs are immiscible. The pseudo-IPNs microphase separation can be greatly subdued through the formation of grafting bonds between two networks as well as the kinetic rate-matching of the individual network crosslinking.

Keywords Interpenetrating polymer networks, Polydimethylsiloxane, Polystyrene, Glass transition temperature, Morphology, Mechanical properties

INTRODUCTION

Interpenetrating polymer networks (IPNs) is a novel multicomponent polymer comprised of two or more polymers in network form, at least one of which is synthesized in the presence of the other^[1]. In contrast to other multicomponent systems, the state of phase separation obtained at the end of IPNs synthesis is frozen in and cannot change by aging. IPNs are therefore well suited for the combination of highly incompatible polymer pairs. In recent years, much research have been carried out on IPNs, which is considered a superior method of polymer property modification^[2-9].

Polydimethylsiloxane (PDMS) has several unique properties such as low surface energy^[10], high permeability to many gases^[11] and good biocompatibility^[12]. But its poor mechanical properties, even after crosslinking, still limit its wide applications. IPNs systems containing organosiloxane and a rigid polymer are seldom reported in the literature^[13-20]. In our laboratory, different approaches have been used to synthesize PDMS/PS IPNs in which a PDMS network was formed by a polycondensation reaction between dihydroxypolydimethylsiloxane and oligoalkoxysiloxane (PMTS) and the rigid PS network was obtained by radical polymerization of styrene. McGarey and Richards^[21] did research on the size of phase separated regions in polydimethylsiloxane/polystyrene sequential IPNs determined by small-angle neutron scattering. On the

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assumption of spherical zone morphology, the radius of the polystyrene zones has been calculated using Porod's law. The variation of this radius with polystyrene content and polydimethylsiloxane crosslink density has been compared with the theoretical predictions of Yeo *et al.*

In this paper, the synthesis procedure and other properties such as phase separation, morphology and mechanical properties of the resulting PDMS/PS IPNs were investigated.

EXPERIMENTAL

Materials and Reagents

α , ω -Dihydroxypolydimethylsiloxane and the crosslinking catalyst, dibutyltin dilaurate (DBTDL) were purchased from Beijing No. 2 Chemical Factory. PDMS was heated at 80 °C under vacuum for 48 h to eliminate water and low molecular weight molecules. PDMS crosslinker, polyalkoxysilane (PMTS) was synthesized in our own laboratory, which is an oligomer of methyltriethoxysiloxane.

Styrene was treated with 5% NaOH solution three times, washed with distilled water until it is neutral and then dried under anhydrous Na₂SO₄ for 48 h. Styrene was polymerized using dibenzoyl peroxide as initiator.

The simultaneous IPNs synthesis consists of the following steps: Weight-calculated PDMS, PMTS and styrene were mixed with BPO and DBTDL and then blended thoroughly by electric stirrer for 0.5 h. After degassed by vacuum pump for three times, the mixture was poured into a glass mould, which was coated with mould release agent for peeling off the IPNs film conveniently. The mould was placed in a 60 °C vacuum oven under nitrogen for 2 days. The resulting IPNs was post-cured under vacuum at 120 °C for 3 days. Before examining their properties, the samples were again dried under vacuum until the weight is constant.

The *in situ* sequential synthesis procedure is as follows: The PDMS network was first formed at room temperature and then styrene and BPO (0.5% weight) was swollen into the former network film. Radical polymerization was initiated after the temperature was raised to 80 °C. The composition of IPNs was calculated according to the weight of PDMS film and the resulting IPNs.

Differential scanning calorimetry (DSC) was conducted on a Perkin-Elmer DSC-910S apparatus operating at a heating rate of 20 °C/min within the temperature range of -140 °C to +150 °C. Several quenching-heating cycles were performed on each sample to ensure a uniform thermal history. The glass transition temperature T_g was taken at the half-height of the corresponding heat capacity jump. The microphase structure of IPNs was observed with a JSW 5800 scanning electron microscope (SEM) at different magnification. In order to increase the electron-conducting ability, the samples were painted with gold in advance. An Instron4505 apparatus was used to measure the tensile stress of the IPN samples with a speed of 500 mm/min at room temperature.

RESULTS AND DISCUSSION

Transition Behavior

The glass transition temperature (T_g) is an important parameter, which convincingly indicates the existence of interlocking and entanglement between the two networks. The transition behavior of two series of IPNs based on PDMS/PS was examined by differential scanning calorimetry (DSC) and the results are tabulated in Table 1 and Table 2.

Table 1 and Table 2 show the T_g and T_m data of pseudo-PDMS/PS IPNs (simultaneous synthesis and PS is linear) and semi-PDMS/PS IPNs (sequential synthesis and PS is linear), respectively. Apart from the melting peak, all the IPNs exhibit a low-temperature (T_{g1}) and a high-temperature transition (T_{g2}), corresponding to the motion of elastomeric silicone segment and to that of the rigid PS segment. Considering the low-temperature transition, the IPNs from 80/20 to

50/50 have the same T_g shift to high temperature, $\Delta T_g = 2.0^\circ\text{C}$, and have almost the same T_g shift to low-temperature, $\Delta T_g = 2.0^\circ\text{C}$. The small shift of T_g could be explained by the pronounced incompatibility with silicone to PS. From the above analysis, a conclusion can be drawn that pseudo-PDMS/PS IPNs are seriously phase-separated and that the change of IPNs composition contributes little to the two phase mixing.

Table 1. Glass transition and melting temperatures of pseudo-PDMS/PS IPNs determined by DSC

Samples	IPNs composition (PDMS/PS)	Glass transition temperature ($^\circ\text{C}$)		
		T_{g1}	T_m	T_{g2}
PDMS network	100/0	-123.5	-48.0	-
Pseudo-IPNs	80/20	-121.8	-44.3	108.2
Pseudo-IPNs	70/30	-120.9	-43.4	109.2
Pseudo-IPNs	60/40	-121.6	-43.0	107.2
Pseudo-IPNs	50/50	-121.0	-42.8	108.0
Linear PS	0/100	-	-	108.0

Table 2. Glass transition and melting temperatures of semi-PDMS/PS IPNs determined by DSC

Samples (PDMS/PS)	IPNs composition	Glass transition temperature ($^\circ\text{C}$)		
		T_{g1}	T_m	T_{g2}
Semi-IPNs	50 / 50	-121.8	-42.3	67.5
Semi-IPNs	60 / 40	-118.8	-45.2	68.2
Semi-IPNs	70 / 30	-119.2	-45.9	69.1
Semi-IPNs	80 / 20	-119.1	-46.2	70.6
PDMS network	100 / 0	-123.5	-48.0	-

Different from the pseudo-PDMS/PS IPNs series, semi-IPNs shows a completely different T_g change. Table 2 gives the T_g data of this series. With the increasing weight percent of PS from 20% to 50%, the low-temperature T_{g1} shifts increasingly to the right, and the high-temperature T_{g2} increasingly to the left. This indicates that with increasing PS weight percent, the PDMS networks and PS linear chains are entangled with each other more intimately or the degree of phase mixing is greatly raised.

Through the analysis of T_g data of the two series, we can conclude that the degree of interpenetration is significantly affected by the IPNs synthesis procedure and that semi-PDMS/PS IPNs are more readily compatible than the pseudo-PDMS/PS IPNs.

Microphase Structure and Morphology

In order to confirm the results and conclusions obtained from T_g data analysis, scanning electron microscope is used to examine the IPNs samples, which can give the morphological information of IPNs. In Fig. 1, scanning electron micrographs are shown for 80/20, 70/30, 60/40 and 50/50 pseudo-PDMS/PS IPNs.

In the microphotographs, phase domains of various sizes existed in the four IPNs. Because various substances differ in the ability of reflecting electrons, so different shades of color represent different phases. In the pictures, the "white sphere" represents the discontinuous PS phase, which is evenly dispersed within the continuous dark background of the PDMS phase. With increasing PS content from 20% to 50%, the spheres become larger and larger, but the sphere boundary is very distinct and there is no indication that the two phases are interlocked with each other, which is consistent with the results obtained from the transition temperature measurement.

The results obtained from DSC measurements of the semi-IPNs of PDMS/PS were also further confirmed by SEM observation. In contrast to the SEM of pseudo-IPNs, semi-PDMS/PS IPNs show a relatively homogeneous phase (Fig. 2). The "spheres" which appeared in pseudo-IPNs

disappeared in the pictures of semi-IPNs. The dark and white phases are both continuous and dispersed within each other homogeneously. From these microphotographs, the microstructure on the molecular level shows that these two kinds of macromolecules are interlocked and entangled with each other intimately. SEM confirmed the results obtained from the DSC measurement.

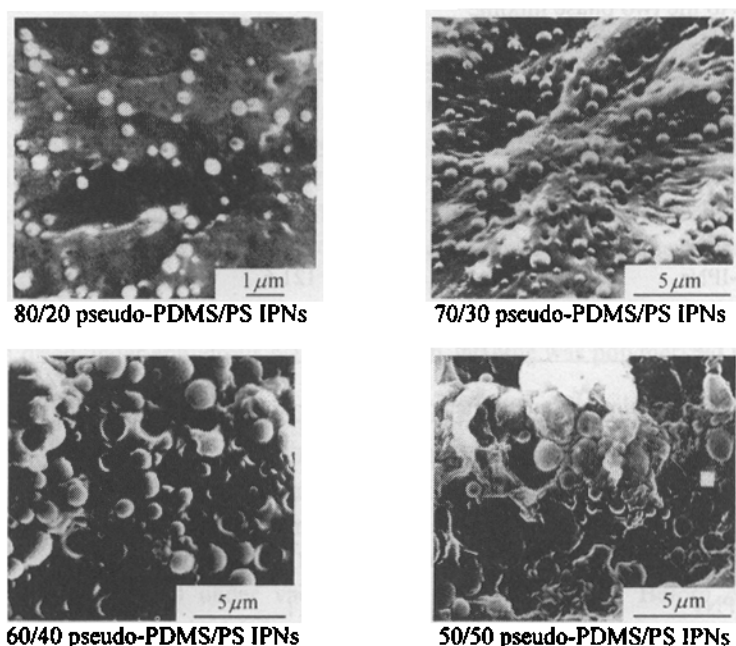


Fig. 1 Scanning electron micrographs of pseudo-PDMS/PS IPNs

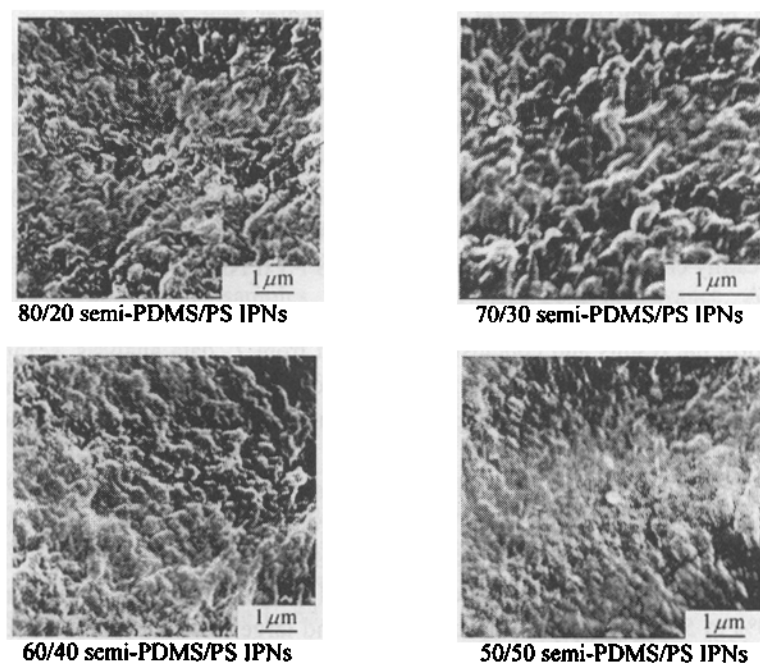


Fig. 2 Scanning electron micrographs of semi-PDMS/PS IPNs

Mechanical Properties

The tensile stress values of semi-PDMS/PS IPNs of various compositions are listed in Table 3. A

noticeable result is that the poor mechanical properties of the PDMS network is reinforced significantly by adding rigid PS, i.e. σ increases from 0.3 to 3.50 MPa. The higher the rigid PS content, the higher the IPNs tensile stress (Table 3).

Table 3. Mechanical properties of semi-PDMS/PS IPNs

Sample	IPNs composition	Tensile stress	Elongation at break
	PDMS/PS	σ , MPa	ϵ , %
PDMS	100/0	0.30	256
Semi-IPNs	80/20	2.68	199
Semi-IPNs	70/30	2.92	175
Semi-IPNs	60/40	3.02	164
Semi-IPNs	50/50	3.50	160

Hardness

Figure 3 shows the hardness of various IPNs samples as a function of PDMS content. The hardness reached a maximum value of 65.3 when the PS content was 40%, then the value does not change any more when the rigid component predominates.

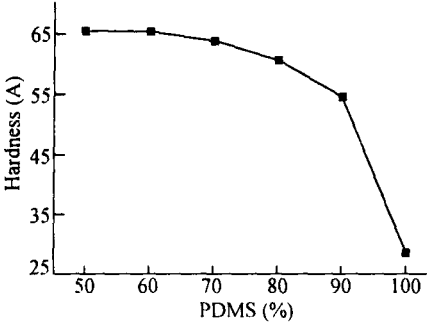


Fig. 3 Hardness H of semi-PDMS/PS IPNs versus PDMS content

Improvement of Pseudo-PDMS/PS IPNs Phase Separation

As mentioned above, the pseudo-PDMS/PS IPNs show phase separation, which is proven by the appearance of double T_g in DSC measurement and the existence of various phase domains in SEM observation. In our studies, we have attempted to enhance the phase morphology. One method was to introduce grafting bonds between the PDMS network and the PS linear chains (Fig. 5), which can be realized by replacing PDMS crosslinker PMTS with vinyltriethoxysilane. The other method was to speed up the slow PDMS crosslinking rate by adding a kind of accelerator NDZ-401 (Fig. 6).

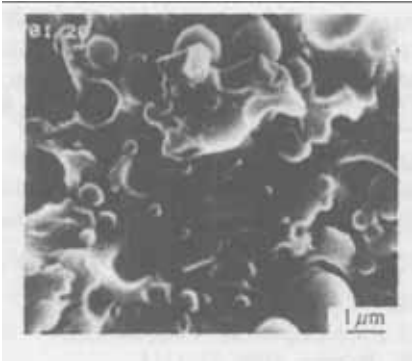


Fig. 4 SEM of pseudo-PDMS/PS IPNs ($T_{g1} = -123.5^{\circ}\text{C}$, $T_{g2} = 108.2^{\circ}\text{C}$)

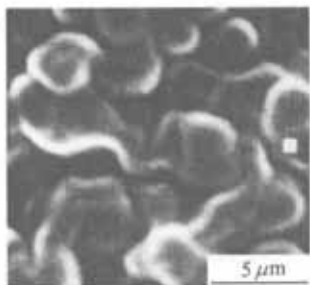


Fig. 5 SEM of pseudo-PDMS/PS IPNs ($T_{g1} = -118.9^{\circ}\text{C}$, $T_{g2} = 86.7^{\circ}\text{C}$)

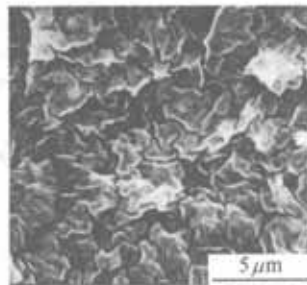


Fig. 6 SEM of pseudo-PDMS/PS IPNs ($T_{g1} = -120.6^{\circ}\text{C}$, $T_{g2} = 87.5^{\circ}\text{C}$)

Figures 4, 5 and 6 are the microphotographs of various pseudo-PDMS/PS IPNs with the same composition: 80/20. Compared with picture of pure pseudo-PDMS/PS IPNs (Fig. 4), the “spheres” in Figs. 5 and 6 are deformed and interpenetrated with the PDMS phase intimately to form a dual-phase morphology. The introduction of grafting bonds and accelerator into PDMS networks will both subdue the phase separation.

CONCLUSION

Through the formation of PDMS/PS interpenetrating polymer networks, the poor mechanical properties of the silicone network are improved. Semi-PDMS/PS IPNs series show higher degrees of interpenetration than pseudo-IPNs series. The existence of grafting bonds between the bi-component networks can subdue the phase separation as well as the rate-matching of the individual crosslinking reaction. It can be expected that with an improved mechanical behavior, PDMS/PS IPNs would have potential applications.

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