Comparison of Viscoelastic Properties of Polydimethylsiloxane/Poly(2-Hydroxyethyl Methacrylate) IPNs with Their Physical Blends

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ABSTRACT: Interpenetrating polymer networks (IPNs) of polydimethylsiloxane (PDMS) and poly(2-hydroxyethyl methacrylate) (PHEMA) were prepared by sequential method. The dynamic mechanical parameters of obtained IPNs and their variations with the structural composition were evaluated. The results for the IPNs were compared with corresponding physically blended systems. The tensile properties and damping factor (tan δ) were assessed by stress–strain measurement and dynamic mechanical thermal analysis (DMTA), respectively. The glass–rubber transition temperature (T_g) was assessed by DMTA and differential scanning calorimetry (DSC). The results showed higher tensile strength and elongation at break for IPNs than those for physical blends. The shifts of T_g for that two components that make up the IPNs were greater than those for corresponding blends. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3480–3485, 2002

Key words: polydimethylsiloxane; poly(2-hydroxyethyl methacrylate); sequential IPN; physical blend; viscoelastic properties

INTRODUCTION

Considerable attention has been given to the modification of polymer properties through the use of procedures, which involve the formation of interpenetrating polymer networks.[1–12] An interpenetrating polymer network (IPN) is defined as an intimate combination of two or more polymers, both in network form, at least one of which is synthesized and/or crosslinked in the immediate presence of the other.[13] The crosslinking of one polymer in the presence of the other distinguishes an IPN system from physical blends or copolymers. For a bipolymer system, the more important IPN types are simultaneous, gradient, thermoplastic, latex and semi-IPN.[14]

Hydrogels of polyacrylates have an excellent biocompatibility but exhibit poor mechanical properties.[15] Many reports have been published that deal with the preparation and characterization of composites of polydimethylsiloxane (PDMS) having fine particles of hydrogels as dispersed phase.[16–23] Despite the advantages, such as ease of fabrication, of these materials, the main drawback of is the poor interfacial adhesion between the two phases. To improve the adhesion of a given polymer pair, the best way is to put the two polymers into the IPN system. This results in the formation of two hydrophilic and hydrophobic networks, the ratio of which can be altered and optimized. In these systems, phase separation may be controlled by the permanent interlocking of entangled chains.[24]

However, the viscoelastic characteristics of the IPN systems have a profound role in the IPNs' behaviors and therefore control the usefulness of the systems. This control has been shown to be quite important for the bioapplication of multicomponent polymeric systems as biomaterial.[13]

Although many reports can be found in the literature that deal with silicone/hydrogel composites[15–23] and hydrogel-grafted silicones,[25–39] interpenetrating polymer network systems made from hydrogels and silicone rubber have received relatively little attention. In this work, attempts have been made to study and determine the viscoelastic parameters of the PDMS/ poly(2-hydroxyethyl methacrylate) (PHEMA) IPN system and also the variation of the system's structural composition in comparison with a similar but physically blended system.

EXPERIMENTAL

Materials

The materials used and their designations are listed in Table I. HEMA was redistilled under the vacuum. AIBN was recrystallized twice from methanol.

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TABLE I
Materials Used in This Work

Designation	Description	Source
HEMA	2-Hydroxyethyl methacrylate	Merck Co.
AIBN	α,α'-Azoisobutyronitrile	Fluka Co.
EGDMA	Ethylene glycol dimethacrylate	Merck Co.
-	Toluene	Merck Co.
-	Ethanol	Riedel Co.
PDMS	Silastic MDX4-4210	Dow Corning Co.

EGDMA was used as received. Silicone rubber was used without any further purification. All other chemicals used in this study were of reagent grade and were used as received.

Methods

Preparation of IPNs

The procedure for IPN preparation is schematically shown in Figure 1. Liquid silicone rubber (Silastic MDX-4-4210) was mixed with 10% w/w of cross-linking agent. After thorough mechanical stirring, the mixture was degassed. The PDMS sheets were prepared by hot compression molding (250 psi, 75°C, 30 min), followed by a postcuring process at 90°C for a period of 3 h to establish the physical properties.

The cross-linked PDMS sheets were cut into strips 10.0×2.0 cm^2 and immersed for 24 h at room temperature in a swelling solution of monomer, initiator, and crosslinker in toluene. The swollen samples were suspended in a sealed glass reactor including nitrogen saturated monomer solution. The temperature was then raised and kept at a definite temperature for 3 h to allow the monomer, initiator, and crosslinker to react. The second network was the cross-linked
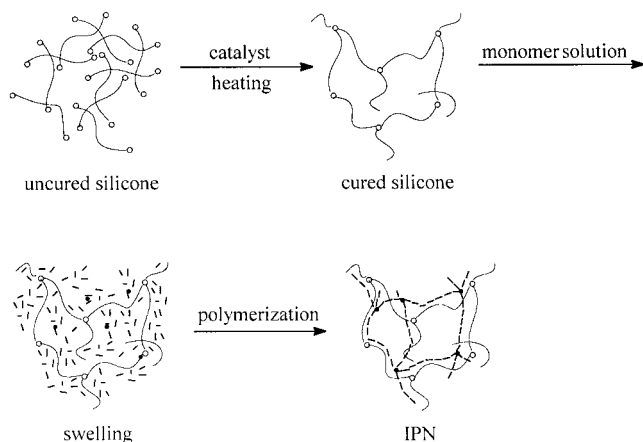

Figure 1 Schematic diagram of the synthesis of polydimethylsiloxane/poly(2-hydroxyethyl methacrylate) sequential interpenetrating polymer network.
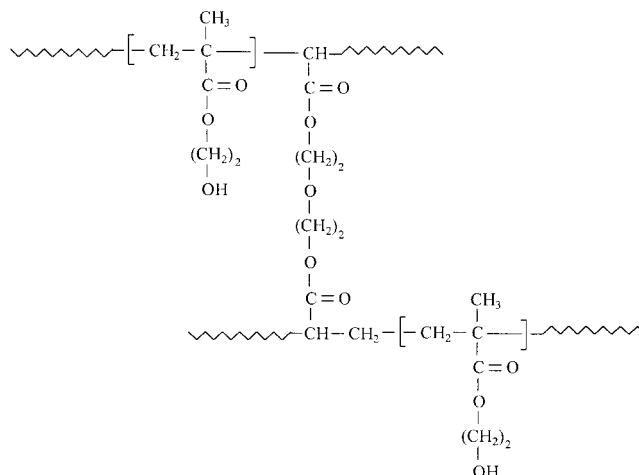

Figure 2 Schematic of cross-linked poly(2-hydroxyethyl methacrylate) (the second network).

PHEMA network (Fig. 2) that was synthesized from the monomer HEMA with EGDMA as the cross-linking agent. The free radical initiator selected was AIBN. The obtained IPNs were kept at 90°C for 2 h to complete the polymerization of the monomer. The product IPNs were immersed in ethanol for 24 h, followed by Soxhlet extraction in distilled water for 48 h to remove homopolymers and unreacted monomers. The specimens were dried under vacuum at 50°C for 48 h.

Blend preparation

Powdery cross-linked PHEMA was prepared by the precipitation polymerization of the HEMA monomer initiated by AIBN in the presence of EGDMA as a cross-linking agent. The polymerization was carried out in toluene. The obtained polymer was kept at 90°C for 3 h to complete the polymerization process. After drying, powdery PHEMA of fine particles was obtained by milling the polymer in a grinding mill and through classification on sieves.

To prepare the PDMS/PHEMA blend, the obtained powdery PHEMA was added to the 10 : 1 (wt : wt) mixture of silicone and curing agent. After thorough mechanical stirring, the mixture was degassed and the strips were prepared with a Teflon-coated mold according to the procedure described for pure silicone. The procedure used for the extraction of soluble fraction was according the method described for IPN preparation.

Determination of poly(HEMA) percentage and water content percentage

The amount of PHEMA formed in the final IPNs was calculated from pre- and postpolymerization dry weights, correcting for weight loss of silicone rubber during swelling in the monomer solution. This correc-

TABLE II
Glass Transition Temperature (T_g), Shore A Hardness, Tensile Strength, and Percentage Elongation at Break
of Sequential Interpenetrating Polymer Networks (IPNs) and Physical Blends of Polydimethylsiloxane (PDMS)
and Poly(2-hydroxyethyl methacrylate (PHEMA)

PDMS/PHEMA	T_gs of blends (°C)		T_gs of IPNs (°C)		Hardness (Shore A)		Tensile strength (kg/cm^2)		Elongation at break (%)	
	PDMS	PHEMA	PDMS	PHEMA	Blend	IPN	Blend	IPN	Blend	IPN
100/0	−36	—	−36	—	30	30	44.3	44.3	458	458
89.2/10.8	−35	129.5	−34	120.1	41	35	36.8	41.6	382	448
81.5/19.5	−35	128.2	−34	122.2	52	39	29.6	38.3	316	410
70.6/30.4	−33.5	130.1	−32	128.9	55	42	21.4	35.2	294	397
61.2/38.8	−34	133	−32	132.2	69	48	14.1	29.8	150	310
0/100	—	134	—	136	—	—	—	—	—	—

tion was based on a series of experiments that showed an average 6% weight loss in the solution of HEMA in toluene. Water content of the IPN was defined as their weight uptake in water for 24 h followed by blotting between two sheets of filter paper with 400 g pressure divided by the weight of the dry extracted IPN. Using the initial weight of silicone samples and the weight of the product IPN, the PHEMA percentage and water content percentage can be determined as

$$\frac{w_m - (0.94)w_i}{w_m} \times 100 = \text{PHEMA (\%)}; \qquad (1)$$

$$\frac{w_w - w_m}{w_m} \times 100 = \text{water content (\%)}, \qquad (2)$$

where w_m and w_i are the weights of the obtained IPN and silicone rubber, respectively, and w_w is the weight of the swollen IPN.

The PHEMA percent of the blend system can be determined as

$$\frac{w_m - w_i}{w_m} \times 100 = \text{PHEMA (\%)}, \qquad (3)$$

where w_m is the weight of the obtained blend after extraction. The water content percentage is calculated according to eq. (2).

Apparatus

Stress–strain measurements were carried out by using an Instron-type tensile tester with the crosshead speed of 50 mm min^{-1} at room temperature. The hardness of the samples was measured by static indentation tests using a Shore-A durometer. Five specimens were measured for each composition. The elongation at break, tensile strength, and hardness were obtained by averaging the results of five specimens.

Dynamic mechanical measurements were made with a Polymer-Lab DMA tester at 10 Hz over a tem-

perature range of −150° to 150°C with a heating rate of about 5°C min^{-1} under a dry nitrogen stream. The vibration mode used for the DMA tester was bending mode.

The transition temperature (T_g) of the samples were also examined by using a Dupont 9900 differential scanning calorimeter (DSC) over the temperature range of −80° to 200°C at a heating rate of 5°C min^{-1}. The sample weight was 15–20 mg. The reported results for the T_gs were taken from the second heating runs of the experiments to avoid any experimental artifacts arising from previous thermal history and any uncompleted chemical reactions.

Static contact angles were measured using the sessile drop method using contact-angle measurement equipment (Kruss G10). All reported waterdrop contact angles are the average value of five measurements on different parts of the film.

RESULTS AND DISCUSSION

Properties of the PDMS/PHEMA IPNs
in the dry state

To maximize the PHEMA content in the obtained IPN, reaction parameters were optimized according to the procedure described in our previous paper.[40] According to that work, for a given concentration of monomer, the optimum values of initiator and crosslinker, and the reaction temperature are determined by the Taguchi method for experimental design. After optimizing the reaction parameters, the IPNs having different PHEMA percentages were prepared by varying the monomer concentration. The percentages of material extracted in Soxhlet extraction procedure were, respectively, about 3% and 18%, based on the weight of PHEMA in the final material before extraction process, for the IPNs and physical blends of PHEMA and PDMS.

Table II shows the results of tensile strength, elongation at break, hardness, and glass T_g measurements. The results for the T_gs in Table II were obtained from
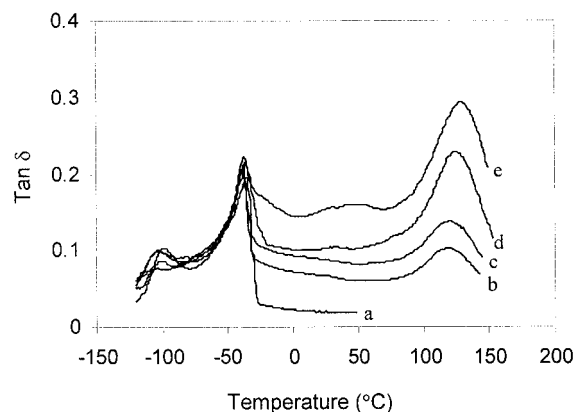
Figure 3 Bending damping factor, tan δ, versus temperature for the polydimethylsiloxane/poly(2-hydroxyethyl methacrylate) (PHEMA) interpenetrating polymer networks having PHEMA contents of (a) 0 wt %, (b) 10.8 wt %, (c) 19.5 wt %, (d) 30.4 wt %, and (e) 38.8 wt %.

DSC analysis. The temperature dependence of the damping factor (tan δ) for the crosslinked silicone rubber and four IPNs, and also their corresponding blends, are, respectively, shown in Figures 3 and 4. The tan δ curve for crosslinked PHEMA, because of its different scale, was not included in these figures.

As can be seen, in the region of the glass transition of the components, the curve for the PDMS exhibits a distinct tan δ maximum at −35°C, while for the PHEMA, the glass–rubber transition occurs at 136°C. The curves for the IPNs (and physical blends) with a large content of PHEMA show a pronounced maximum in the region of α-transition of PHEMA, and for IPNs with a small content of PHEMA, the curves show a low and wide maximum (Fig. 3). The shape of the temperature dependencies of the tan δ for both systems is typical for two-phase polymer systems with incompatible components. The investigated systems are two-phase systems, but the shift of the maximum tan δ for the PHEMA in the IPN on the temperature scale from its position for pure polymer, as well as its broadening, indicate an incomplete phase separation in the IPN formation. Furthermore, the tan δ curve for the IPN having 40 wt % hydrogel content shows another maximum occurring at approximately 50°C.

For further investigation, we are studying the properties of the IPNs with hydrogel contents higher than 40 wt %. It should be noted that the fraction of PHEMA is limited by the equilibrium swelling of cross-linked PDMS strips by HEMA solution. For example, for a monomer concentration of 3.5 M/liter, an IPN having 40 wt % of PHEMA can be reached. However, by immersion of obtained IPN in the HEMA solution, the fraction of PHEMA can be increased to the values higher than equilibrium value of HEMA in the cross-linked PDMS.

Studying mechanical characteristics of the sequential IPNs based on PDMS and PHEMA demonstrated their tensile strength to be higher than that of physical blends. In contrast, the results of elongation at break measurements show that the values for elongation at break of the sequential IPNs of silicone rubber and PHEMA are substantially greater than corresponding physical blends. The lower hardness values for the IPN systems were in consistent with results of elongation measurements. These tests demonstrate that sequential IPNs have a higher fracture energy than physical blends of two components.

Thus, creating an interpenetrating polymer network structure in a multicomponent polymeric material can markedly improve its mechanical properties. There are several hypotheses to account for this phenomenon. One of them treats these types of IPNs as collections of an infinite number of layers whose compositions and elastic modulus change progressively.[41] When a sample is strained, all layers are stretched to the same degree, and the stress in every layer corresponds to its modulus. Such a stress distribution promotes plastic deformation rather than brittle fracture and thereby increases breaking elongation and fracture energy.[9]

Another hypothesis relates the higher strength of this type IPNs to a reduction of imperfections in surface layers. In the case of IPNs consisting of two components with different free energies, the concentration of a low–free energy component in the surface layer is higher than in the subsurface layers.[42] A high PDMS concentration in the surface layer prevents craze and crack initiation.

Properties of PDMS/PHEMA IPNs in the swollen state

Table III summarizes the mechanical properties of IPNs swollen in distilled water at room temperature. The samples were tested when the equilibrium water
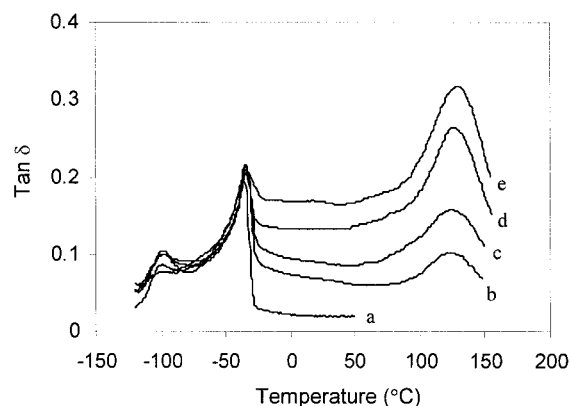

Figure 4 Bending damping factor, tan δ, versus temperature for the polydimethylsiloxane/poly(2-hydroxyethyl methacrylate) (PHEMA) physical blends having PHEMA contents of: (a) 0 wt %, (b) 10.8 wt %, (c) 19.5 wt %, (d) 30.4 wt %, and (e) 38.8 wt %.

TABLE III
Mechanical properties of Polydimethylsiloxane (PDMS)/Poly(2-hydroxyethyl methacrylate) (PHEMA) Interpenetrating Polymer Networks (IPNs) Swollen in Water

Material	Swelling in water (%)	Tensile strength (kg/cm^2)	Elongation at break (%)
PDMS	—	44.3	458
PDMS/PHEMA (90.5/9.5 wt/wt) IPN	4.0	42.6	442
PDMS/PHEMA (81.7/18.3 wt/wt) IPN	8.4	40.4	409
PDMS/PHEMA (67.5/32.5 wt/wt) IPN	15.1	37.1	360
PDMS/PHEMA (61.8/39.2 wt/wt) IPN	18.2	34.3	268
PHEMA	47	5.9	64

content of the networks was reached. The swelling ratio of the samples was calculated according to eq. (2).

On the basis of the tensile strength of the PHEMA hydrogel, an increase of 629% in the tensile strength of the swollen IPN containing 67.5 wt % of PDMS was observed. A 581% increase in tensile strength was obtained with the swollen IPN that contained 61.8 wt % of PDMS. Similarly, an increase of 583% in the elongation at break was obtained for the swollen IPN containing 67.5 wt % of PDMS, and an increase of 418% was obtained for the swollen IPN containing 61.8 wt % of PDMS.

Comparing the tensile properties of the sequential IPNs of PDMS/PHEMA and PHEMA hydrogels reveals that the tensile strength and elongation at break of the IPN systems are substantially greater than the tensile strength and elongation at break of the PHEMA hydrogel. It is of interest to note that for only 258% drop in equilibrium water content for the IPN that contains 39.2 wt % of PHEMA, the tensile strength (σ = 34.3 MPa) is almost a factor of six higher compared to the PHEMA hydrogel (σ = 5.9 MPa).

The sequential IPNs of PDMS/PHEMA were characterized in terms of water contact angle. The data obtained from water contact angle measurements of the IPN systems (Table IV) showed a substantial decrease in water contact angle compared with that of the unmodified PDMS.

One of the best ways to improve the hydrophilicity of a given polymer surface is to allow water to engage its preferred interaction with the surface; that is, the short-range hydration, acid–base, and hydrogen

bonding interactions.[43] This can be done with modification techniques, like the sequential method for IPN preparation, that introduce hydrophilic groups on the substrate surface. The presence of hydrophilic groups on the surface of PDMS/PHEMA sequential IPNs has been confirmed by surface characterization methods.[40] The basis of surface hydrophilization is to maximize hydration and hydrogen bonding interaction. Hydroxyl, carbonyl, carboxyl, and carboxylate groups contain lone pairs, unshared electrons, and asymmetric charge distributions. All sorts of oxygen-containing organic functionals can interact with water more effectively than methyl groups. For these reasons, higher PHEMA contents IPNs have lower water contact angles (Table IV).

CONCLUSIONS

Results of DMA analysis for physical blends and sequential IPNs consisting from silicone rubber and PHEMA exhibit transitions in the regions of T_g of the two phases. In comparison with physical blends, the T_g of the IPNs having about 10 wt %, 20 wt %, 30 wt %, and 40 wt % hydrogel contents was, however, shifted from those for the pure components because of an incomplete phase separation of the components and the formation of two varying composition regions. The higher tensile strength and elongation at break values and the decreased hardness for the IPNs were consistent with DMA results. The results of mechanical behavior and water contact angle measurements of the IPN materials in the hydrogel state show that the PDMS/PHEMA sequential IPN systems have potential for applications in which PHEMA is compounded to improve the wettability of pure silicone rubber.

TABLE IV
Water Contact Angle Data for Modified and Control Polydimethylsiloxane (PDMS) Samples

Samples	Contact angle
Control PDMS	105.6
PDMS/Poly(2-hydoxyethyl methacrylate (PHEMA) (90.5/9.5 wt/wt) IPN	86.0
PDMS/PHEMA (81.7/18.3 wt/wt) IPN	78.2
PDMS/PHEMA (67.5/32.5 wt/wt) IPN	63.8
PDMS/PHEMA (69.8/39.2 wt/wt) IPN	57.0

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