

Sequential Interpenetrating Polymer Networks of Poly(2-Hydroxyethyl Methacrylate) and Polydimethylsiloxane

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Received 23 April 2001; accepted 20 October 2001

ABSTRACT: The preparation of interpenetrating polymer networks (IPNs) from silicone rubber and hydrogel forming poly(2-hydroxyethyl methacrylate) (HEMA) were studied. The HEMA monomer was polymerized with simultaneous crosslink formation in the presence of the swollen silicone rubber. To minimize the required number of experiments, the Taguchi method of experimental design involving the factors of temperature, monomer concentration, initiator concentration, and crosslinker concentration was used. Upon removal of the swelling solvent, an IPN was obtained which absorbed water in the manner of a hydrogel but had mechanical properties superior to a hydrogel. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1825–1831, 2002

Key words: sequential IPN; HEMA; silicone rubber; experimental design

INTRODUCTION

Interpenetrating polymer networks (IPNs) are a type of polymer blend consisting of two or more network polymers in which at least one such polymer is polymerized and/or crosslinked in the immediate presence of the others(s).¹ Some important IPN materials include simultaneous interpenetrating network (SIN), sequential IPN, gradient IPN, latex IPN, thermoplastic IPN, and semi-IPN (pseudo-IPN, PDIPN).²

Polydimethylsiloxane (PDMS)-based sequential IPNs were studied by Sperling and Sarge³ and Chang et al.⁴ These studies were directed toward ascertaining the two-phase nature of the IPNs, together with mechanical properties such as tensile, modulus, and impact resistance. Mark and Ning⁵ also prepared a sequential IPN from a tetra-functionally end-linked network by swelling it with very short vinyl-terminated PDMS chains,

which were then themselves tetra-functionally end-linked. They also prepared SINS from a mixture of the same two types of PDMS chains, with different end-linking agents and catalysts for the two separate reactions.⁵

Hourston et al.^{6,7} described the synthesis and properties of polyurethane–PDMS SINS. Frisch and coworkers studied the phase morphology of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)/PDMS SINS and compared it with corresponding blends.^{8,9}

In recent years, considerable attention was directed to investigating the properties of silicone rubber/hydrogel particulate composites.^{10–17} The main objective of these studies was to improve the hydrophilicity of silicone rubber and also to modify the limited fabricating potential and poor mechanical properties of swollen hydrogels. In this way, the poly(2-hydroxyethyl methacrylate) (HEMA)/PDMS composites were prepared and their biological properties,¹¹ hydrophilicity and permeability,^{12,15} morphology,¹³ and mechanical properties¹⁴ were studied. In all studied systems,

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Journal of Applied Polymer Science, Vol. 85, 1825–1831 (2002)
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Table I Materials Used in This Work

Designation	Description	Source
HEMA	2-Hydroxyethyl methacrylate	Merck Co., Darmstadt, Germany
AIBN	α, α' -Azoisobutyronitrile	Fluka Co., Buchs, Switzerland
EGDMA	Ethylene glycol dimethacrylate	Merck Co.
—	Toluene	Merck Co.
—	Ethanol	Riedel-de Haën Co., Seelze, Germany
PDMS	Silastic® MDX4-4210	Dow Corning Corp., Midland, MI

the particles of hydrogel and silicone rubber were dispersed and continuous phase, respectively.

Although many reports can be found in the literature dealing with silicone/hydrogel composites and hydrogel-grafted silicones,^{10–27} interpenetrating polymer network systems made from hydrogels and silicone rubber have received relatively little attention.^{28–31}

In this article, we report the results of the studies with the preparation of IPNs from poly-(HEMA) hydrogels and PDMS and the effect of several parameters on the composition and water content of the IPNs. The ultimate goal of this work was to design the optimum conditions for the preparation of silicone rubber/poly(HEMA) IPNs which contain about 33% poly(HEMA). These compositions were reported as a optimum composition in which the obtained biomaterial has a good biocompatibility as well as elastomeric properties.¹¹ We will report the results of the morphology and biocompatibility studies of the prepared IPNs in future works.

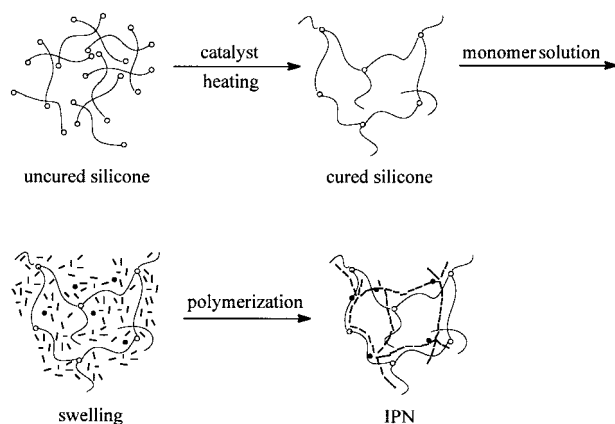


Figure 1 Schematic diagram of the synthesis of silicone rubber/poly(HEMA) sequential IPN.

EXPERIMENTAL

Materials

The materials used and their designations are listed in Table I. HEMA was redistilled under vacuum. AIBN was recrystallized twice from methanol. Ethylene glycol dimethacrylate (EGDMA) was used as received. Silicone rubber used in this work was Silastic® MDX4-4210 medical grade elastomer, which is a pourable two-component product. The elastomer component (viscosity = 1150 P) consists of a vinyl-terminated dimethylsiloxane polymer, a reinforcing silica, and a platinum catalyst. The curing-agent component consists of a dimethylsiloxane polymer, an inhibitor, and a siloxane crosslinker. All other chemicals used in this study were of reagent grade and used as received.

METHODS

Preparation of IPNs

Figure 1 shows the schematic diagram of the synthesis of silicone rubber/poly(HEMA) sequential IPN. Silastic® MDX4-4210 was thoroughly mixed with 10% w/w of curing agent. After thorough mechanical stirring, the mixture was degassed. The silicone rubber films were prepared by hot

Table II The Three Selected Levels for Each Factor

Variable	Level 1	Level 2	Level 3
[HEMA]	0.5	1	1.5
[AIBN]	0.001	0.005	0.01
[EGDMA]	0.001	0.005	0.01
Temperature (°C)	65	73	80

Table III Design of Experiments for Four Three-Level Factors (an L-9 array)

Trial	HEMA	AIBN	EGDMA	Temperature (°C)
1	0.5	0.001	0.001	65
2	0.5	0.005	0.005	73
3	0.5	0.01	0.01	80
4	1	0.001	0.005	80
5	1	0.005	0.01	65
6	1	0.01	0.001	73
7	1.5	0.001	0.01	73
8	1.5	0.005	0.001	80
9	1.5	0.01	0.005	65

compression molding (250 psi, 75°C, 30 min), followed by postcuring process at 90°C for a period of 3 h to establish the physical properties. The crosslinked PDMS films were immersed for 24 h at 30°C in a swelling solution of HEMA, crosslinker, and initiator in toluene. The swollen samples were suspended in a sealed glass reactor. Then, the temperature was raised and kept at a definite temperature for 3 h to allow AIBN, HEMA, and EGDMA to react. The obtained IPNs were kept at 90°C for 2 h to complete the polymerization of the monomer. The produced 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 then dried under vacuum at 40°C for about 1 week.

For evaluating the effects of polymerization factors on the properties of obtained IPNs, the

Taguchi experimental design approach was used to minimize the required number of experiments. The reaction time for all experiments was 3 h and the number of variables then decreased to four parameters: temperature, monomer concentration, initiator concentration, and crosslinking-agent concentration. The concentrations of monomer, initiator, and crosslinker are defined as:

Monomer concentration [HEMA]

$$= \frac{\text{moles of monomer}}{\text{volume of solution}} \text{ (mole/liter)} \quad (1)$$

Initiator mole fraction [AIBN]

$$= \frac{\text{moles of initiator}}{\text{moles of monomer}} \quad (2)$$

Crosslinker mole fraction [EGDMA]

$$= \frac{\text{moles of crosslinker}}{\text{moles of monomer}} \quad (3)$$

Determination of Poly(HEMA) Percentage and Water Content Percentage

The amount of poly(HEMA) formed was calculated from pre- and postpolymerization dry weights, correcting for weight loss of silicone rubber during swelling in the monomer solution. This correction was based on a series of experiments, which showed an average 6% weight loss in the solution of HEMA in toluene. Water uptake capability of the IPN was defined as the weight uptake in water for 24 h after blotting between two

Table IV The Obtained Results and Their Averages and Standard Deviations for Designed Experiments

Trial	Poly(HEMA) (%)					Water Content (%)				
	Sample 1	Sample 2	Sample 3	Average	Standard Deviation	Sample 1	Sample 2	Sample 3	Average	Standard Deviation
1	0.2	0.4	-0.4	0.1	0.09	0.2	0.2	0.1	0.2	0.05
2	18.9	20.1	19.2	19.4	0.51	8.6	8.9	8.8	8.8	0.12
3	19	18.3	18.1	18.5	0.39	8.4	8.3	8.3	8.3	0.05
4	32.7	31.1	32.5	32.1	0.71	14.2	14.0	14.4	14.2	0.16
5	27.5	28.4	27.1	27.2	0.54	11.4	11.8	11.2	11.5	0.25
6	22.1	21.3	21.8	21.7	0.33	10.3	9.6	10.1	10.0	0.29
7	31.6	32	31.2	31.6	0.33	14.2	14.4	13.9	14.2	0.20
8	19.3	18.1	18.9	18.8	0.50	8.5	8.3	8.5	8.4	0.09
9	29.3	28.7	29.6	29.2	0.37	11.4	11.6	11.9	11.6	0.20

Table V Influence Percentage of Variables to the Variations of Results

Variable	[HEMA]	[AIBN]	[EGDMA]	Temperature
Influence Percentage	51.051	0.657	42.138	5.803

sheets of filter paper with 400 g pressure on the sample divided by the weight of the dry extracted IPN. By using the initial weight of the silicone samples (w_i) and the weight of the product IPN, the poly(HEMA) percentage and water content percentage can be determined as

$$\frac{w_m - (0.94)w_i}{w_m} \times 100 = \text{poly(HEMA) (\%)} \quad (4)$$

$$\frac{w_w - w_m}{w_m} \times 100 = \text{water uptake (\%)} \quad (5)$$

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.

Apparatus

Infrared spectra were obtained on a Fourier transform infrared (FTIR) spectrophotometer (Brucker IFS-48) by an attenuated total reflection (ATR) method.

RESULTS AND DISCUSSION

IPN Composition and Water Content

The effect of several parameters on the composition of the IPN were investigated by using the

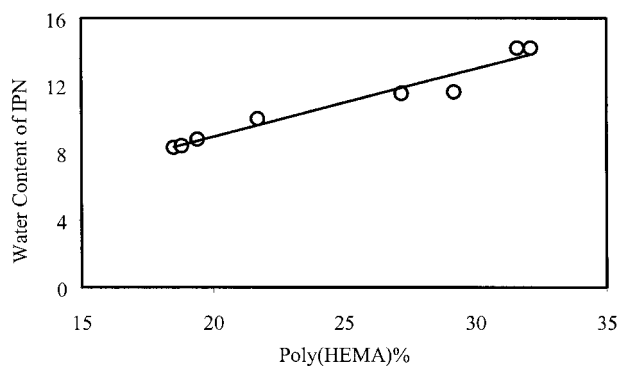


Figure 2 Dependence of water uptake of IPN on poly(HEMA)%

Taguchi experimental design approach for product optimization by analysis of variance. The Taguchi method allows the simultaneous examination of several variables having differing relative amounts and types.³² The variables and their levels are listed in Table II. According to the Taguchi approach,³³ for a four three-level factor system, we will have nine different formulations (Table III). To increase the accuracy, each designed experiment was repeated three times. The ranges used for concentrations and temperature were determined on the basis of the data in the literature^{34,35} and the carried out preliminary experiments.

The results of calculation of poly(HEMA)% and water content for product IPNs are shown in Table IV. The main reason for scattering observed in poly(HEMA)% values, in addition to error resulted from repeating the experiments, were the differences between average weight loss value considered in the calculations and real weight loss values during the swelling process for different trials.

In all cases, it was found that heating beyond 3 h did not appear to increase the fraction of poly(HEMA) in the obtained IPNs.

Of the different heating methods tested, the best results were obtained when the polymerization was carried out in the water bath equipped with a shaking system. The samples prepared in this manner were more homogeneous than those prepared by using a water bath without the shaking system. There was no increase in poly(HEMA) fraction when the vapors of refluxing toluene were used as the heat transfer agent.

As seen in Table IV, reactions carried out in the conditions of trial 1 gave products in which the percentage of poly(HEMA) was about 0%. Additional experiments were carried out to study the effect of increasing the polymerization temperature or duration of heating on the poly(HEMA) fraction in the silicone matrix. It was found that increasing the polymerization time to 4.5 h or the temperature to 73°C had no effect on the poly(HEMA) fraction in the IPN.

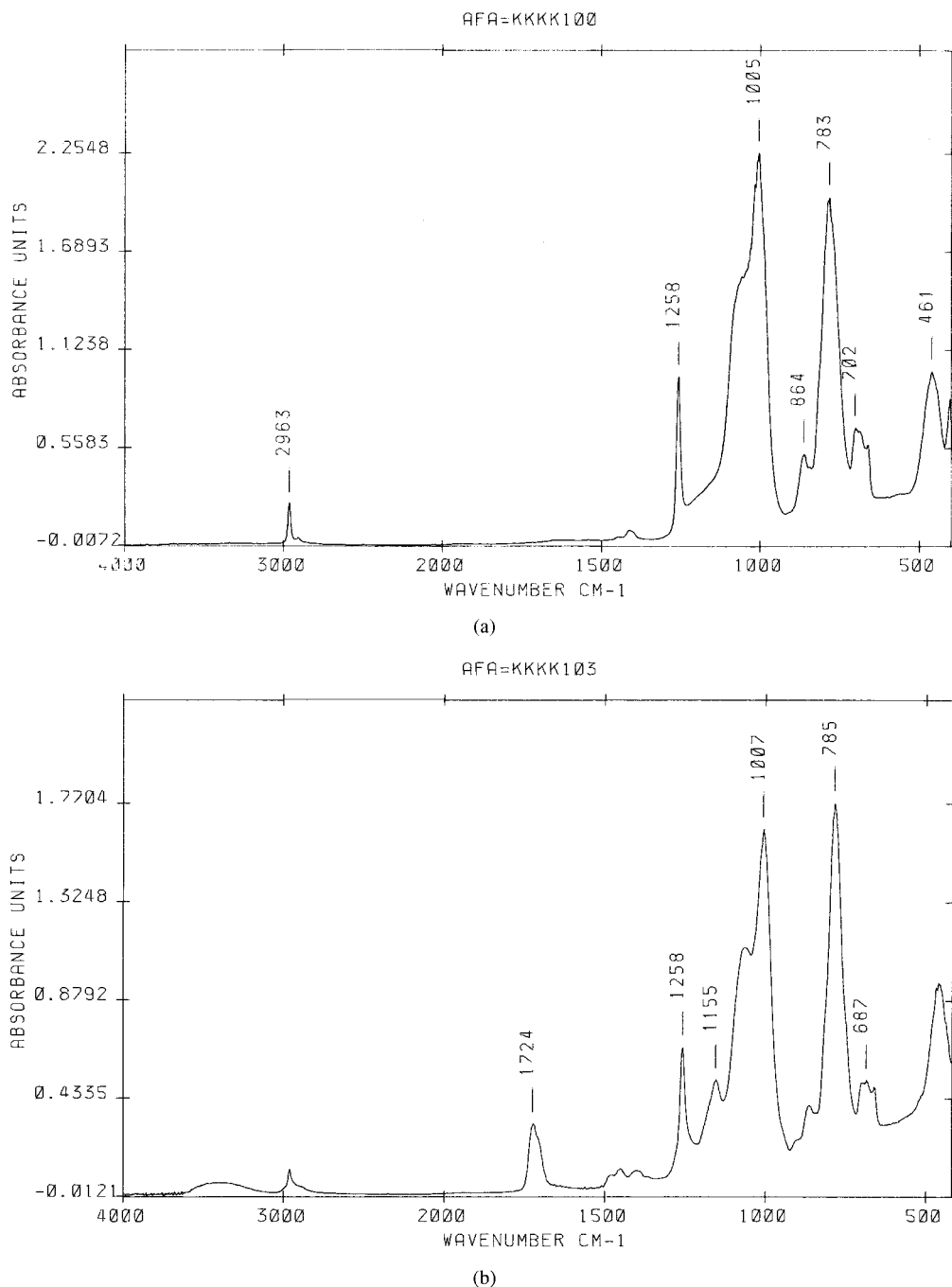


Figure 3 (a) FTIR-ATR spectra of contol silicone rubber film. (b) FTIR-ATR spectra the silicone rubber/poly(HEMA) IPN.

From the poly(HEMA)% point of view, trials 2–9 can be divided into two categories: experiments in which the poly(HEMA) fractions are 18.5–21.7%, and experiments in which the poly(HEMA)% are 27.2–32.1%. Considering trial 2 as the baseline, we see that in constant concentration of monomer, increasing temperature and

mole fractions of initiator and crosslinker did not have a significant effect on poly(HEMA)% in the obtained IPNs. On the other hand, the results obtained for trials 6 and 8 show that for a low value of crosslinker, increasing the monomer concentration and/or temperature did not have a significant effect on poly(HEMA) percentage.

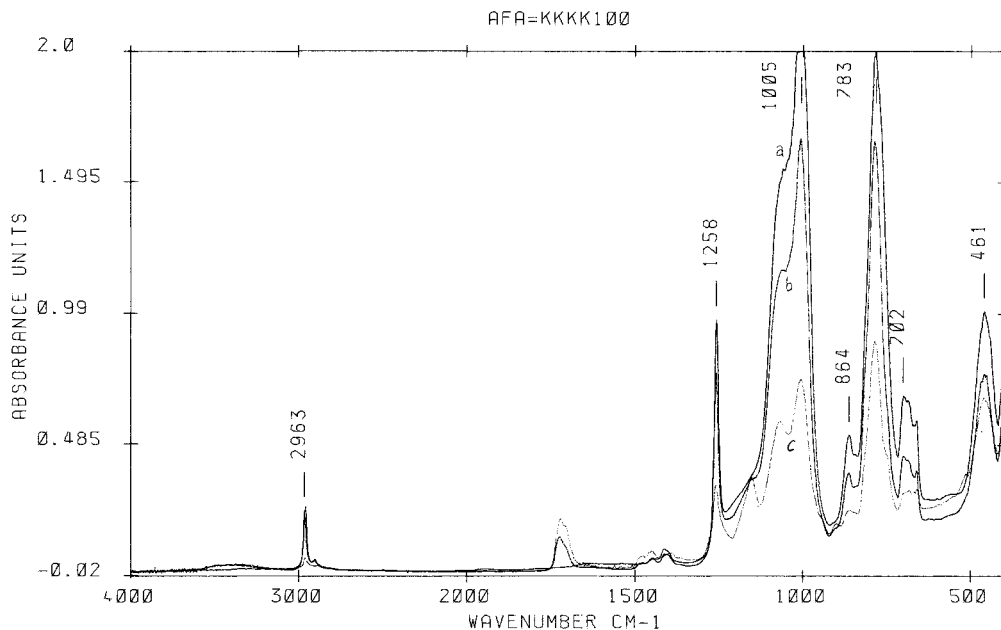


Figure 4 FTIR-ATR spectra of (a) control silicone rubber; (b) silicone rubber/poly(HEMA) IPN having 18.5 wt % poly(HEMA); and (c) silicone rubber/poly(HEMA) IPN having 32.1 wt % poly(HEMA).

Comparing the results and conditions of trial 4 with those for trials 2 and 3 shows that for a low concentration value of the initiator, increasing the monomer concentration and crosslinker mole fraction together have a significant effect on poly(HEMA)% in the IPN. Furthermore, results of trial 5 show that increasing the temperature in trial 4 had a slight effect on the poly(HEMA) percent in the IPN.

Statistical analysis for the calculation of the influence of factors to the variation of results³⁶ confirms the above claims (see Table V). As expected, increasing the monomer and crosslinker concentrations had the greatest effects on the poly(HEMA)% in the obtained IPNs.

Increasing the monomer concentration results in the presence of more monomers inside the silicone network. However, lower crosslink density of the formed poly(HEMA) results in the leaching out the macromolecules. The fact that increasing the crosslinker mole fraction resulted in increased poly(HEMA)% may be due to the interlocking of the poly(HEMA) networks with the crosslinked silicone rubber. Furthermore, increasing the initiator concentration results in low molecular weight polymer chains and in decreased in physical entanglements. It means that above a minimum value, increasing the initiator concentration not only had no effect on the poly-

(HEMA) fraction in the IPN, but also probably had a negative effect.

Water uptake measurements [in the range of 18–32% poly(HEMA)] showed that the water uptake capability increases linearly with poly(HEMA) fraction (Fig. 2), because for the poly(HEMA) fraction in this range, the hydrogel domains are connected together so that water can easily diffuse to these domains.³⁷ For samples 2–9, the calculated water uptake values based on the poly(HEMA) weight were between 41 and 46%, but the dependencies of these values (as well as water uptake values based on IPN weight) on polymerization variables were not clear.

FTIR-ATR Study

The presence of poly(HEMA) was confirmed by FTIR-ATR spectra, as illustrated in Figure 3(a) for the pure silicone rubber and in Figure 3(b) for its IPN with poly(HEMA). The absorption bands occurring at approximately 1720 cm^{-1} are the characteristic absorption bands for carboxyl group, which demonstrates that the second component in the IPN is indeed poly(HEMA).

Figure 4 shows that the intensity of the C=O stretching absorption at 1720 cm^{-1} increases with increasing poly(HEMA)% in the IPN. This observation by FTIR-ATR spectroscopy is consis-

tent with those of gravimetric determination and water-uptake measurements.

CONCLUSION

Interpenetrating polymer networks provide a unique method for preparation of polymeric materials having the characteristics of good mechanical properties and hydrophilicity. Sequential interpenetrating polymer networks of polydimethylsiloxane/poly(2-hydroxyethyl methacrylate) were synthesized. The design of experiments was carried out by using the Taguchi method and optimum conditions to prepare an IPN containing about 33% poly(HEMA) were determined.

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