

Synthesis and Characterization of PDMS/PAAc Sequential IPNs

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Abstract

One limitation in the use of hydrophilic polymers as implantable devices is their inherently poor mechanical strength. Using interpenetrating polymer networks (IPNs) consisting of both hydrophilic and hydrophobic networks is an effective method to strengthen these polymers. In this work, a series of poly(dimethyl siloxane) / poly(acrylic acid) sequential IPNs was synthesized and the polymerization kinetics of acrylic acid in the presence of ethylene glycol dimethacrylate as the crosslinker was investigated using ampoule polymerization experiments and DSC analysis. The results from conversion measurements revealed the occurrence of gel effect during acrylic acid polymerization. The properties of the produced IPNs including swelling, morphological, and mechanical properties were also investigated.

Keywords: *PDMS, Interpenetrating Polymer Networks (IPNs), Kinetics, Swelling, Morphology*

1- Introduction

Loosely crosslinked polymeric materials that swell in the presence of water or other solvents are often used to make gel-like absorbent materials. These gels are typically made via a free radical polymerization mechanism, where monomer units are connected into long chains through their double bonds. The crosslinking agent, a monomer with two or more double bonds, provides the polymer network structure by connecting the long, linear chains in these polymerizations. Hydrogel networks formed from poly (acrylic acid) (PAAc) have the

ability to absorb many times their weight in water and are the basis of a class of materials called super absorbents. These polymers are used in many applications including diapers, ion exchange resins, membranes for hemodialysis and ultrafiltration and controlled release devices [1, 2].

An understanding of the kinetics of the acrylic acid polymerization process is essential for the optimization and control of commercial polymer production. Although the free radical polymerization of acrylic acid was investigated by a number of researchers, relatively little work was conducted on

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precipitation polymerization in the open literature. Given this, one of the primary objectives of this study was to quantitatively understand the precipitation polymerization of AAc toward the conceptual interpretation of interpenetrating polymer networks (IPNs) structures.

IPNs are defined as combinations of two or more polymers in network form, at least one of them being polymerized and/or crosslinked in the immediate presence of the other(s). Some important IPN types include simultaneous interpenetrating network, sequential IPN, gradient IPN, latex IPN, thermoplastic IPN, and pseudo-IPN [3].

It has been reported that the formation of an IPN structure can significantly improve the mechanical properties of polymers [4]. The poly(dimethyl siloxane) (PDMS)/polystyrene (PS) IPNs were studied by McGary et al [5]. The synergistic effect was attributed to better bonding at interfaces and an increase in crosslinking density where the two networks were formed by interpenetration into each network [6]. In the case of 2-hydroxyethyl methacrylates - terminated polyurethane (HPU)/ polyurethane (PU) simultaneous IPNs, there was an increase in swelling ratio due to a lower degree of interpenetration and the formation of new interfaces. With additional increasing of the crosslink density, the swelling ratio became approximately constant. Further increasing the crosslink density resulted in less swelling due to a highly crosslinked PU network [7].

Silicone rubbers and synthetic hydrogels are two important classes of polymeric materials for biomedical applications [8-10]. A typical characteristic of silicone rubber is its hydrophobicity [11]. Poly(acrylic acid)

(PAAc) and other synthetic hydrogels also possess good swellability and biocompatibility in many environments. Due to the high water uptake of PAAc, the biocompatibility of its IPNs with silicone polymers has been studied. To understand the properties of the PDMS/PAAc sequential IPNs accurately, in the present work, a set of experiments were established in order to study the rate of the polymerization of acrylic acid (AAc) monomer during the formation of PDMS/PAAc sequential IPNs, and then swelling behavior, morphology, and the mechanical properties of the IPNs were investigated.

2. Experimental

2.1. Materials

Acrylic acid (AAc) (Merck, Schuchardt, Germany) was purified by distillation *in vacuo*. α, α' -Azobisisobutyronitrile (AIBN) (Acrôs Organics, NJ, USA) was recrystallized twice from methanol. Ethylene glycol dimethacrylate (EDMA) (Merck, Darmstadt, Germany) and silicone rubber (Silbione[®]4010, A/B, DV_A: approx. 1500 mPa.s, and DV_B: 1100 mPa.s) (Rhodia, Ventura, CA) were used as received. Osmium tetroxide (OsO₄) staining agent (Merck, Schuchardt, Germany) was used without purification.

2.2. Procedures

2.2.1. Precipitation polymerization of AAc

Precipitation polymerization of AAc in toluene was carried out isothermally and conducted at a constant 80°C temperature. The time-conversion data and samples for its analysis were obtained from ampoule polymerization experiments. All isothermal

precipitation polymerizations of AAc were carried out in 5-mm diameter glass ampoules. The prescribed amount of the initiator and monomer were dissolved in the solvent, and the solution was then charged into the glass ampoules. The ampoule contents were degassed through the standard freeze-thaw cycles and sealed under a maximum pressure of 10^{-4} Torr. The reaction mixture was homogenized through agitation in order to avoid possible phase separation. In experiments like this [12, 13] ampoules containing monomer, solvent and initiator are placed into a constant temperature medium and a sampling interval of once every 30 min for low conversions and 5 min during gel effect are utilized. These samples were collected in 20 ml glass scintillation vials. The polymerization reactions in the withdrawn samples were quenched by adding 0.1 ml of a 2% hydroquinone solution in methanol and shaking it manually. The samples were then immersed in an ice-water mixture for approximately 30 min, and stored in a refrigerator at a temperature below 10°C prior to analysis. The monomer conversion was measured using a gravimetric method.

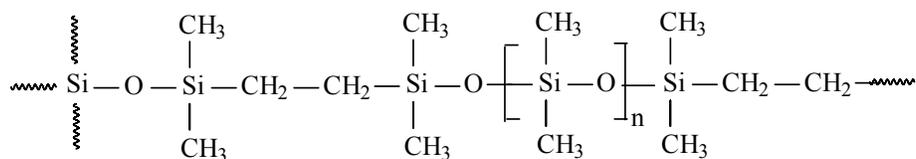
2.2.2. PDMS preparation

PDMS samples with different crosslink densities were prepared by mixing raw silicone rubber with the curing agent. The elastomer component (part A) of Silbione[®]4010 and the curing agent (part B) were mixed with PDMS/curing agent compositions of 7/1, 10/1, and 13/1 wt/wt. After thorough mechanical stirring, the

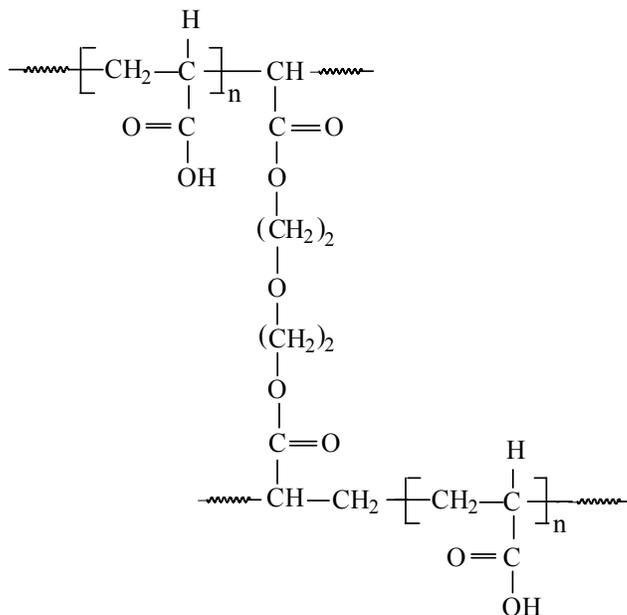
mixture was degassed. The silicone rubber strips (of about $100 \times 20 \times 1 \text{ mm}^3$) were prepared by hot compression molding (at 1700 kPa, 100°C , 45 min), followed by a post-curing process at 100°C and atmospheric pressure for a period of 12 h to establish their physical properties. The products were immersed in toluene for 24 h to remove the oligomers. The specimens were dried under vacuum at 45°C for 12 h. The final PDMS substrates with 1 mm thickness were cut into rectangular strips of about $3 \times 2 \times 1 \text{ mm}^3$.

2.2.3. IPN preparation

For IPN preparation, the PDMS strips were immersed for 24 h at 30°C in a swelling solution consisting of AAc monomer, AIBN, EDMA, and toluene (PDMS/swelling solution = 1/4 wt/wt). The swollen samples were suspended in a sealed glass reactor including nitrogen-saturated monomer solution. The temperature was then raised and kept at 80°C for 5 h to allow monomer, initiator, and crosslinker to react. The obtained IPNs were kept at 100°C for 5 h to complete the polymerization of the monomer, and the IPNs were then immersed in ethanol for 24 h to remove homopolymers and unreacted monomers, and the specimens were dried under vacuum at 45°C for 24 h. The PAAc content of the IPNs was calculated from the difference between the weights of the final IPN and the unmodified PDMS samples. The host (PDMS) and guest (PAAc) networks are shown in Fig. 1.



(a)



(b)

Figure 1. Chemical structure of (a) crosslinked PDMS (host) and (b) PAAc (guest) networks

To maximize the PAAc content of the IPNs, the reaction parameters were optimized using the Taguchi method for experimental design

[14]. The optimized conditions are listed in Table 1.

Table 1. The optimized conditions using Taguchi approach (monomer concentration was 1.5 mol/L)

Initiator mole fraction	Crosslinker mole fraction	Polymerization Temperature (°C)	Polymerization Time (hr)	Post-curing Temperature (°C)	Post-curing Time (hr)
0.001	0.01	80	5	100	5

Swelling studies were performed by placing the previously dried polymer strips in distilled water for different time periods, drying with a filter paper, and then weighing them on a balance. This sequence was repeated until no weight change was observed. The water content of the IPNs was calculated as the difference between the combined weights of the swollen sample and the dry IPN divided by the weight of the dry IPN.

2.3. Apparatus

2.3.1. Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a direct analytical method that examines the extent of polymerization based on the assumption that heat generated during polymerization reaction is proportional to the percentage or concentration of reacted monomers. The aim of this study was to verify the ampoule polymerization data and measure the released heat of precipitation polymerization at the formulation studied. The DSC experiments were performed using a Netzsch DSC 200 Maia. Samples weighing 5.0 ± 0.1 mg were placed into aluminum pans (thickness ~ 500 μm) and then sealed. Iso-thermal polymerization experiments were conducted at 80°C . The highest value achieved for the isothermal temperature was then chosen as the total heat, ΔH_{total} , for the fully converted AAc.

2.3.2. Scanning electron microscopy

The morphology of the IPNs with different PAAc contents was studied by scanning electron microscopy (SEM) of freeze fractured samples using a LEO 440-I SEM operating at 15 kV. The broken samples were

stained with OsO_4 . The details of the staining method are described elsewhere [15]. All samples were sputter-coated with a thin layer of gold prior to viewing to enhance conductivity.

2.3.3. Measurement of mechanical properties

Tensile properties were measured according to ASTM-D412 on dumbbelled samples in both dry states using a Hounsfield H5K-S tensile machine (Elastocone, Sweden) with an extension rate of 50 mm/min at room temperature.

3. Results and Discussion

Fig. 2 shows the experimental results of monomer conversion measured during the polymerization of AAc at 80°C and initiator concentration of 8.5 mmol/l. The conversion-time behavior exhibits deviation from classical kinetics due to the onset of autoacceleration phenomena (gel effect). This effect occurred at about 20% conversion. The DSC exotherm for the precipitation polymerization of AAc initiated by AIBN at 80°C is illustrated in Fig. 3. Both Figs. 2 and 3 indicate that for the formulation studied, the recorded conversion time kinetics curve is indicative of autoaccelerated process, which is a typical feature of an autoaccelerative reaction mechanism. The amounts of heat released, induction time, peak maxima, and the ultimate percentage conversions derived from Figs. 2 and 3 are collected in Table 2.

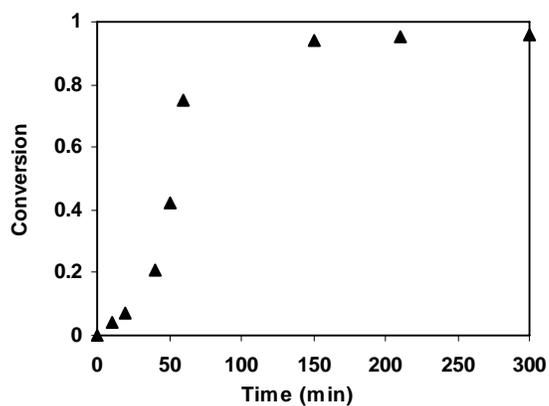


Figure 2. Conversion versus polymerization time for polymerization of AAc in toluene at 80 °C, $[M]_0 = 1.5 \text{ mol/L}$, $[I]_0/[M]_0 = 0.001$ and $[\text{EDMA}]/[M]_0 = 0.01$.

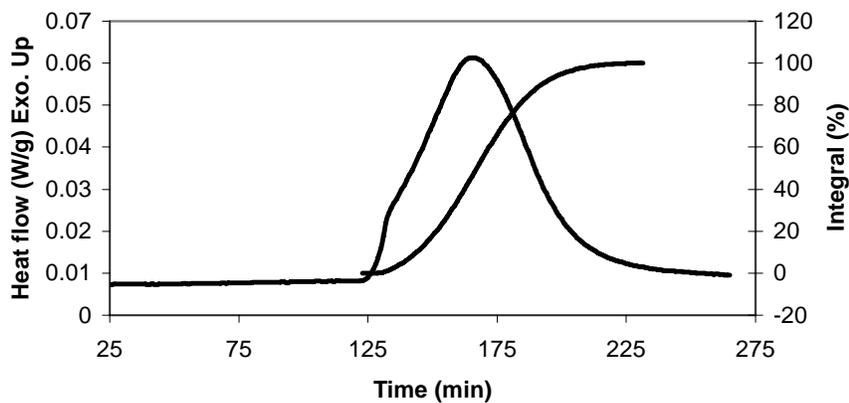


Figure 3. DSC exotherm for the precipitation polymerization of AAc in toluene at 80 °C, $[M]_0 = 1.5 \text{ mol/L}$, $[I]_0/[M]_0 = 0.001$ and $[\text{EDMA}]/[M]_0 = 0.01$.

Table 2. The results of kinetics analysis for the precipitation polymerization of AAc.

ΔH (J/g)	Induction time (min)	Peak maximum (min)	Conversion
141.5	25	160	0.95

The SEM micrographs of the cross-sectional surface of cryogenically fractured IPN samples clearly confirm the appearance of two phases in the IPN systems [Fig. 4 (a) – (c)].

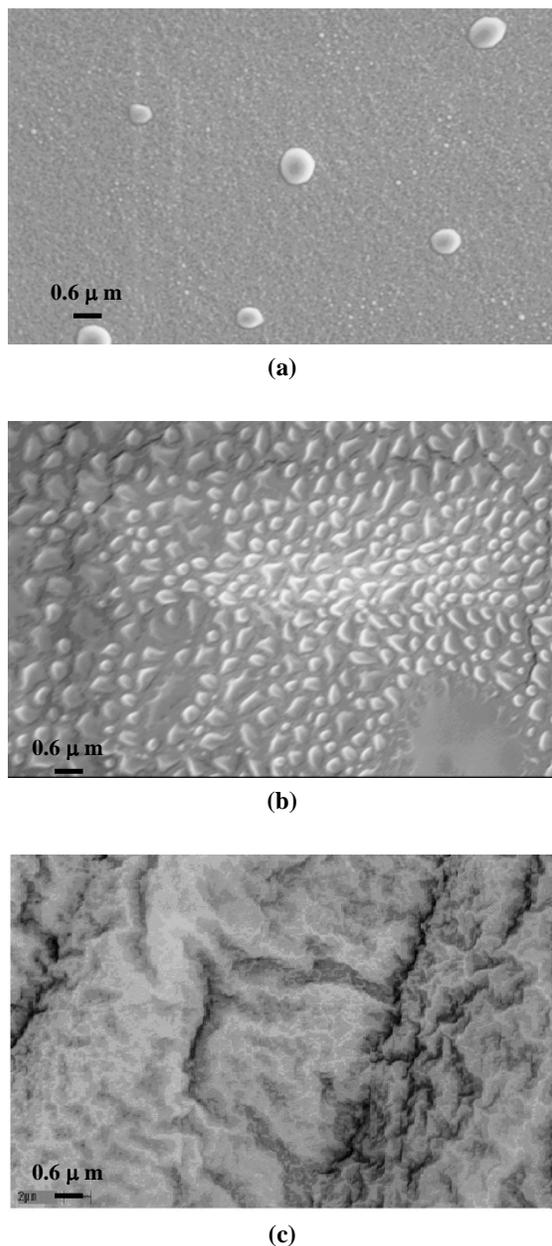


Figure 4. SEM micrographs obtained from cross sections of PDMS/PAAc IPNs having a PAAc content of (a) 20 wt%, (b) 40 wt%, and (c) 60 wt%. All micrographs were taken at a magnification of x 7000.

In sequential IPNs, the phase domain size of the second polymerized polymer is governed primarily by the crosslinking density of the first polymerized polymer and the overall composition [16]. Since the crosslink density of polymer network I (PDMS) was constant, the main factor controlling the domain size was the composition of polymer network II (PAAc) and its thermodynamic compatibility at low concentrations.

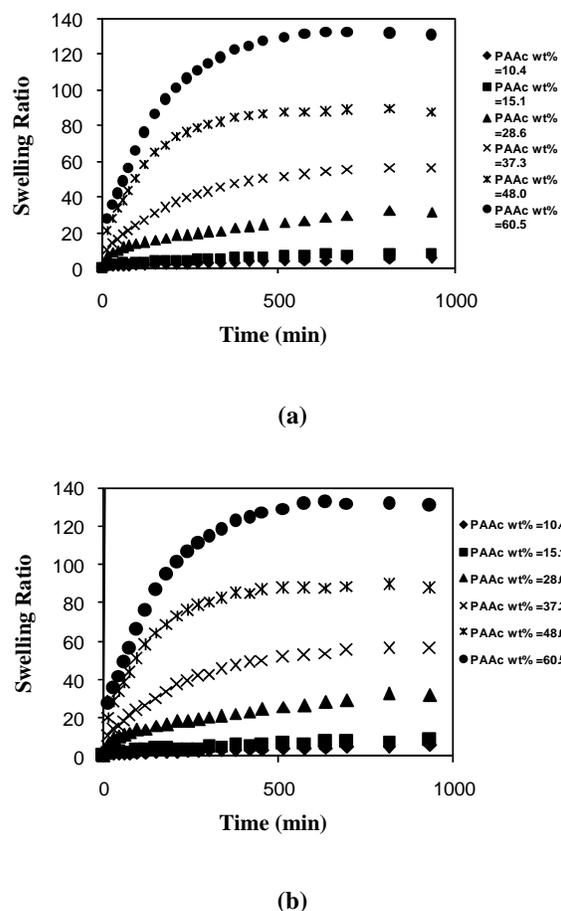


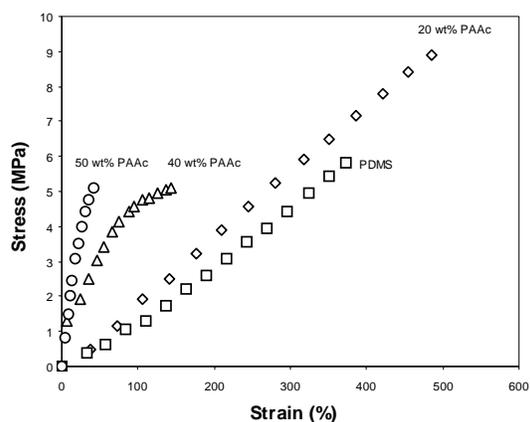
Figure 5. Swelling behavior of PDMS/PAAc IPNs with different crosslink densities of PDMS network: (a) PDMS/curing agent=13/1 wt/wt and (b) PDMS/curing agent=7/1 wt/wt. All IPNs were prepared at 80°C, $[M]_0 = 1.5 \text{ mol/L}$, $[I]_0/[M]_0 = 0.001$ and $[EDMA]/[M]_0 = 0.01$.

Figs. 5 (a) and (b) show the variation of swelling with time for the IPNs with different PAAc concentrations and different PDMS network crosslink densities.

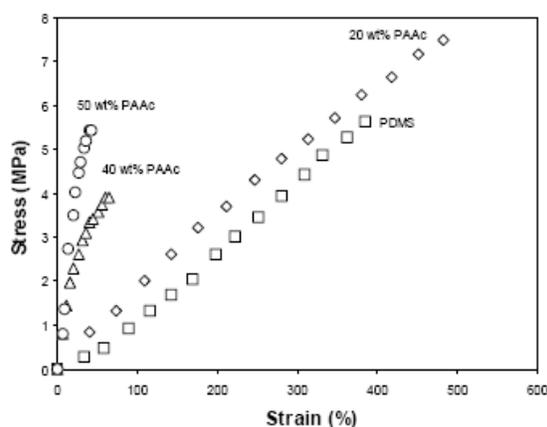
In an IPN consisting of both hydrophilic and hydrophobic polymers, the swelling capability of the IPN in water results from the hydrophilic component, but it may be limited by hydrophobic continuous phase. As shown in Fig. 5, nearly all of the IPNs swelled and reached equilibrium swelling within about 10 h. The effect of crosslink density on equilibrium swelling of the IPNs appeared beyond PAAc wt% around 25. After this concentration, increasing the crosslink density of a PDMS network (with increasing the amount of curing agent) lowers the equilibrium swelling of the IPNs.

Figs. 6 (a) and (b) show the results of the stress-strain measurements of IPN samples having different crosslink density respectively, in the dry state.

In comparison with unmodified PDMS, the moduli of all IPNs increased with the incorporation of PAAc in the silicone network. However, except for the concentration of 20 wt%, their elongation at break decreased. Increasing the moduli of the IPNs compared with the pure silicone rubber was due to stiffening of the silicone network by increasing PAAc content. The reinforcing effect with the addition of PAAc to PDMS was observed for the IPNs having around 20 wt% of PAAc. As shown in Fig. 4(a), the IPNs with 20 wt% of PAAc exhibited a bimodal size distribution of dispersed phase. In this IPN the micron sizes of PAAc particles coexisted with nanosize particles.



(a)



(b)

Figure 6. Uniaxial stress-strain curves in dry state for (a) PDMS/curing agent = 7/1 wt/wt and (b) PDMS/curing agent = 13/1 wt/wt.

Conclusions

AAC was isothermally polymerized by precipitation polymerization in toluene using ampoule polymerization technique. The DSC was used to investigate the kinetics of AAC precipitation polymerization and the heat of the reaction as an important kinetic parameter was successfully determined. The effect of crosslink density on equilibrium swelling of the IPNs appeared beyond PAAc wt% around 25. It seems that in a swollen

state phase inversion occurs at around 25 wt% of PAAc. The synergistic effect with the addition of PAAc to PDMS was observed for the IPNs having about 20 wt% of PAAc component, where the dispersed phase was formed as fine particles.

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