

## Novel PDMS-Based Membranes: Sodium Chloride and Glucose Permeability

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**ABSTRACT:** Permeation of sodium chloride and glucose through polydimethylsiloxane-poly(*N*-isopropylacrylamide) (PDMS-PNIPAAm) interpenetrating polymer networks (IPNs) of two different microstructures was investigated. We have successfully developed small-molecule permeable IPNs, by modifying PDMS film structure. A group of PDMS films was prepared using conventional solvent casting (SC) method and another group produced by introducing oil, followed by SC and leaching the oil out (SCOL method). Scanning electron microscopy (SEM) and attenuated total reflection fourier transformer infrared (ATR-FTIR) spectroscopy results confirmed the presence of PNIPAAm in the SC and SCOL IPNs. Results obtained from spectra of differential scanning calorimetry (DSC) showed that these IPNs had a phase transition temperature at about 32°C. Permeation measurements showed that the presence of PNIPAAm as the second phase in the IPN, improved the permeability of PDMS film. According to the results, maximum permeation coefficient was related to SCOL IPN containing 15.8% ± 0.3%PNIPAAm, at 23°C ( $5.98 \times 10^{-7} \pm 7.93 \times 10^{-9}$  cm<sup>2</sup>/s for sodium chloride and  $3.6 \times 10^{-7} \pm 7 \times 10^{-9}$  cm<sup>2</sup>/s for glucose). These results suggested that these PDMS-PNIPAAm IPNs with sodium chloride and glucose permeability may be further developed as ophthalmic biomaterials or corneal replacements. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** interpenetrating polymer networks; membranes; diffusion

Received 4 August 2011; accepted 11 March 2012; published online 00 Month 2012

DOI: 10.1002/app.37709

### INTRODUCTION

Permeability characteristic of biomaterials is a key important issue in biomedical devices, for example, diffusion of pharmaceuticals from drug eluting capsules, penetration of low molecular weight metabolites, which is critical for survival of cells present in the other side of biomembrane.<sup>1–5</sup> Transparent corneal endothelium balances corneal hydration and plays an important role in nourishing the epithelial cells of the cornea.<sup>6</sup> Therefore, water and small ions are able to transport through this membrane.

Because of low toxicity, nonadhesive properties, and physiological inertness, polydimethylsiloxane (PDMS) have been used in a wide range of biomedical applications such as, drug delivery systems, skin replacements, oxygenators, and contact lenses.<sup>7–11</sup> PDMS hydrophobicity and non-permeability to water-soluble solutes are disadvantages of this elastomer and thus, limit its application in cases that need permeability, like biomembranes, which are responsible for providing cell nutrients.<sup>1,12,13</sup>

According to previous studies, few attempts have been made with the goal of producing PDMS-based membranes with capa-

bility of small water-soluble molecule transport. Researchers have synthesized polydimethylsiloxane-poly(*N*-isopropylacrylamide) (PDMS-PNIPAAm) networks from a PDMS-OH matrix cured in the presence of solvent, onto the water.<sup>12–15</sup> These authors reported that glucose permeation occurred through the hydrophilic phase of the interpenetrating polymer network (IPN), at temperatures below the LCST (lower critical solution temperature) of the networks.<sup>12,13</sup> To improve permeability, there are few reports in the literatures of silicone rubber-hydrogel composite, containing fine particles of 2-hydroxyethyl methacrylate, acrylamide, or methacrylic acid.<sup>14–16</sup>

IPN can be defined as chemically distinct networks consist of two or more polymers, which at least one of them is crosslinked in the presence of the others. These networks link to each other by physical entanglements.<sup>17–25</sup> An IPN usually composed of a hydrophobic (such as PDMS) and a hydrophilic (such as PNIPAAm) polymer network. Because the permeation of water-soluble small molecules, primarily occurs through hydrophilic phase of the IPN, IPN hydration, and connectivity of hydrophilic domains are important parameters.<sup>14</sup> PDMS film

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structure (first phase) influences PNIPAAm dispersion (second phase) within the film, that affects hydration and transport properties of the produced IPN. Thus, in this report, novel oil-leached out PDMS films were prepared and modified with NIPAAm to produce PDMS-PNIPAAm IPNs and compared with solvent cast (SC) IPNs (IPNs produced from solvent cast PDMS films). Regarding to previous experiments, no attempts have been made to generate PDMS-PNIPAAm IPN from porous oil-leached out PDMS film. Permeation coefficients of these SC and SCOL IPNs were measured. In this case, sodium chloride and glucose were used as model solutes. The effect of temperature on permeation coefficients of the IPNs was also investigated.

## EXPERIMENTAL

### Materials

Silicone rubber and its curing agent used in this study was Silastic MDX4-4210 medical grade elastomer, made by Dow Corning Corp., Midland, MI. NIPAAm ( $M_w = 113.6$ , purity 97%), AIBN (azobisisobutyronitrile), ( $M_w = 164.21$ ) and MBAAm ( $N,N'$  methylenebisacrylamide), ( $M_w = 154.17$ ) were from Aldrich. Sodium chloride and glucose anhydrous were from Merck. Extra pure toluene purchased from Merck, was used as solvent. Food grade olive oil was from Gilavan Co.

### PDMS Film Preparation

Two methods, SC and SCOL, were used for producing PDMS films of various structures. In SC method, silicone solution (20% wt) (containing curing agent in 100 : 10 ratio) was prepared in toluene. Then, the solution was poured into a glass Petridish, placed in an oven at 85°C for 1 h, followed by post curing process at 90°C for a period of 5 h to establish the required physical properties. In the second method (SCOL technique), oil was introduced into silicone-curing agent-toluene solution. First, oil in toluene solution (8% v/v) was prepared. After complete dissolution (5 min), silicone and then curing agent were added to the solution upon stirring. Dissolution takes place in 10 min. The final solution was poured into a glass Petridish. Curing process was performed at 85°C for 2 h. The films were postcured at 90°C for a period of 5 h. Toluene (at 60°C) used to leach the oil out for 1 h. Finally, the prepared PDMS films washed with distilled water and dried for further use. The PDMS films had thickness of 80  $\mu\text{m}$ .

### IPN Preparation

The PDMS films were immersed in monomeric solutions containing NIPAAm, AIBN (as initiator), MBAAm (as crosslinking agent), and toluene as solvent. The solutions were degassed at room temperature for 30 min. The films were allowed to swell in the presence of toluene for 3 h in a shaking incubator. Thus, NIPAAm monomers, AIBN and MBAAm diffused into the swollen films. After that, the solutions were kept at 85°C for 4 h and polymerization occurred. Finally, the IPNs were washed with distilled water and kept at 90°C for 4 h to complete the polymerization process. To remove unreacted monomers and homopolymers from the IPNs, Soxhlet extraction carried out for 24 h in toluene. Produced IPNs washed with distilled water and dried at 70°C for 2 h. PNIPAAm content (amount of second phase) of the IPN was calculated according to the following

equation:

$$\text{PNIPAAm (\% wt)} = \left( \frac{W_{\text{IPN}} - 0.96W_0}{W_{\text{IPN}}} \right) \times 100 \quad (1)$$

where  $W_{\text{IPN}}$  is the weight of the extracted IPN and  $W_0$  is the weight of the unmodified PDMS film.<sup>26</sup> The factor 0.96 is the correction factor for weight loss of PDMS film during swelling in monomer solution. The IPNs had thickness of 100  $\mu\text{m}$ .

### ATR-FTIR Spectroscopy

To confirm the presence of the two polymers in the network, attenuated total reflection Fourier transformer infrared (ATR-FTIR) spectrophotometer (Bruker EQUINOX 55) was employed, with the incidence angle of 45 degree. In this case, sample dimensions were 1 cm  $\times$  4 cm.

### Scanning Electron Microscopy

Morphology of the PDMS films and IPNs was studied using a (VEGA 2 TESCAN) scanning electron microscope (SEM) (operating at 10 kV). To assess the cross section, samples were fractured in liquid nitrogen. Before observation by SEM, the samples were gold coated by sputtering.

### Differential Scanning Calorimetry

To confirm the presence of PDMS and PNIPAAm in the network and LCST determination, differential scanning calorimetry (PL-DSC) was used for modified and unmodified PDMS film. DSC measurements were made over a temperature range of -50 to 80°C, with a heating rate of 10°C/min.

### Water Uptake Measurement

Swelling experiments were performed at different temperatures. IPNs with different amounts of PNIPAAm as the second phase were immersed in distilled water in a sealed reactor to prevent evaporation and placed in an incubator at required temperature. Then, the dry samples were weighed and resubmerged in fresh water and the test continued.<sup>11</sup> Water uptake percentage determined as:

$$\text{Water uptake (\%)} = \left( \frac{W_w - W_d}{W_d} \right) \times 100 \quad (2)$$

where  $W_w$  and  $W_d$  were the weight of swollen and dry IPN, respectively.<sup>26</sup>

### Permeation Measurement Cell

To carry out permeation measurement of the IPNs, a horizontal diffusion cell was used. The diffusion cell composed of two distinct chambers with equal volumes of 60 cm<sup>3</sup> and IPN could be placed and fixed between the chambers.<sup>5</sup> One chamber filled with NaCl or glucose aqueous solution (donor chamber) and the other chamber filled with deionized water (receiver chamber). The solution within the receiver chamber was analyzed (more details in permeation measurement section) at specific time interval and the concentration of permeated molecules calculated.

### Permeation Measurement: Sodium Chloride

To investigate the permeation of NaCl molecules through the produced IPN, dry IPN was pre-equilibrated in 6 % wt/v NaCl

aqueous solution at room temperature for 1 day.<sup>16</sup> Permeation of NaCl molecules was measured at 23°C and 37°C using the two compartment diffusion cell, in which the donor chamber contained NaCl aqueous solution (6% wt/v) and the acceptor chamber contained deionized water.<sup>16–18</sup> To eliminate boundary layer resistance and to control temperature, the diffusion cell was kept in a shaking incubator. The molecules could pass by diffusion from the donor cell, which had higher concentration of NaCl, into the receiver cell.<sup>17</sup> To measure sodium chloride permeation coefficient, solution within the receiver chamber was analyzed by conductimeter (Crison GLP 32 Conductimeter). In addition, calibration curve of conductivity of the known concentration solutions was plotted. The permeation coefficient,  $P$ , was calculated from the following equation:

$$P = \frac{m \times d}{\Delta c \times s \times t} \quad (3)$$

where  $m$  is the amount of the compound passed after time  $t$ , through the membrane having an area  $s$ , and thickness  $d$ , at the concentration difference on both sides of the membrane,  $\Delta c$ .<sup>15</sup>

#### Permeation Measurement: Glucose

Similar to NaCl permeation measurement, dry IPN was pre-equilibrated in a 6% wt/v glucose aqueous solution for 1 day. The IPN was placed between the donor and receiver chambers of the diffusion cell, as described earlier. The donor chamber was filled with glucose aqueous solution (6% wt/v) and the other chamber was filled with deionized water. After specific period, the solution within the receiver chamber analyzed using an autoanalyzer (TECHNICON RA-XT) and glucose concentration determined.

#### Statistical Analysis

The samples used in all experiments were in three replicates and the results were given as “mean  $\pm$  standard deviation”.

## RESULTS AND DISCUSSION

### PNIPAAm Content of the IPNs

As described in IPN preparation section, to produce IPNs, monomeric NIPAAm solutions with different concentrations were prepared (Table I). Each SC and SCOL film was immersed in separate monomeric solution and IPNs with different PNIPAAm contents were prepared. According to Table I, IPN produced by immersing SCOL film in monomeric NIPAAm solution (10% wt) had 19.1%  $\pm$  0.2% PNIPAAm in its final structure. However, IPN produced by SC film which was immersed in monomeric NIPAAm solution (10% wt), had 15.5%  $\pm$  0.5% PNIPAAm in its final structure. The IPNs contained different amounts of PNIPAAm, which depended on the concentration of monomeric NIPAAm solution and the method of PDMS film preparation (SC or SCOL). Regarding to different morphology of SC and SCOL films, absorption of NIPAAm monomers into these films was different. Compared with SC film, the porous structure of SCOL film (more details in SEM micrograph section), facilitated NIPAAm absorption from immersing solution. Thus, PNIPAAm content of the SCOL IPN was more than the SC IPN, at a same concentration of NIPAAm monomeric solution.

**Table I.** Concentrations of NIPAAm Solutions, Concentrations, and Densities of the IPNs

PDMS film	NIPAAm monomeric solution (% wt)	PNIPAAm content of IPN (% wt)	Density of IPN (g/cm <sup>3</sup> )
SC	3	5.44 $\pm$ 0.1	2.36 $\pm$ 0.01
	5	11.29 $\pm$ 0.2	2.3 $\pm$ 0.05
	10	15.5 $\pm$ 0.5	2.4 $\pm$ 0.04
	12	18.47 $\pm$ 0.44	2.49 $\pm$ 0.01
	15	29.15 $\pm$ 0.25	2.82 $\pm$ 0.01
SCOL	3	11.65 $\pm$ 0.2	2 $\pm$ 0.01
	5	15.8 $\pm$ 0.3	2 $\pm$ 0.02
	10	19.1 $\pm$ 0.2	2.24 $\pm$ 0.02
	12	29.5 $\pm$ 0.15	2.56 $\pm$ 0.01
	15	30.1 $\pm$ 0.1	2.63 $\pm$ 0.02

As shown in Table I, the densities of SCOL IPNs were slightly lower than SC IPNs. The pores of the SCOL films were filled with PNIPAAm during the process of IPN formation. Thus, densities of the IPN domains and PNIPAAm domains present in the pores were different.

### ATR-FTIR Spectra

The presence of the PNIPAAm in the PDMS film was confirmed by comparing the ATR-FTIR spectra of unmodified and modified PDMS (Figure 1). Peaks at 1100 and 2970 cm<sup>-1</sup> were characteristics of PDMS (indicated Si—O—Si and C—H stretching in CH<sub>3</sub>) [Figure 1(a)], while peaks at 1647 and 3310 cm<sup>-1</sup> were observed due to carbonyl stretching vibration at 1647 cm<sup>-1</sup> and N—H stretching at 3340 cm<sup>-1</sup>, which were present in the PNIPAAm [Figure 1(b,c)].<sup>12,21</sup>

### SEM Micrographs

The SEM micrographs of unmodified PDMS and SC IPNs are shown in Figure 2. Unmodified PDMS film had a smooth surface without any contrast [Figure 2(a)]. SEM micrograph of the SCOL film, before leaching the oil out, is shown in Figure 3(a). After leaching the oil out, pores were formed in PDMS film [Figure 3(b)]. Therefore, at IPN preparation step, by immersing the porous SCOL film in NIPAAm monomeric solution, monomers could diffuse and aggregate into these pores and form connected PNIPAAm domains [Figure 3(c)]. Thus, SEM demonstrated that the PNIPAAm domains of SCOL IPN showed greater connectivity than PNIPAAm domains of SC IPN [Figures 2(b) and 3(c)].

### DSC Results

DSC spectra provided further evidence for the presence of PNIPAAm in the IPNs, particularly in the case of SCOL IPNs. DSC spectra of SC and SCOL PDMS-PNIPAAm IPNs (Figure 4), showed a transition temperature at about 32°C. This phase transition may be due to the fact that, hydrogen bonds between PNIPAAm and water weakened at LCST, so that, hydrophobic interactions became dominant above the LCST. This phase transition phenomenon resulted in an endothermic peak in DSC curve. In other words, at lower temperatures, hydrogen bonding

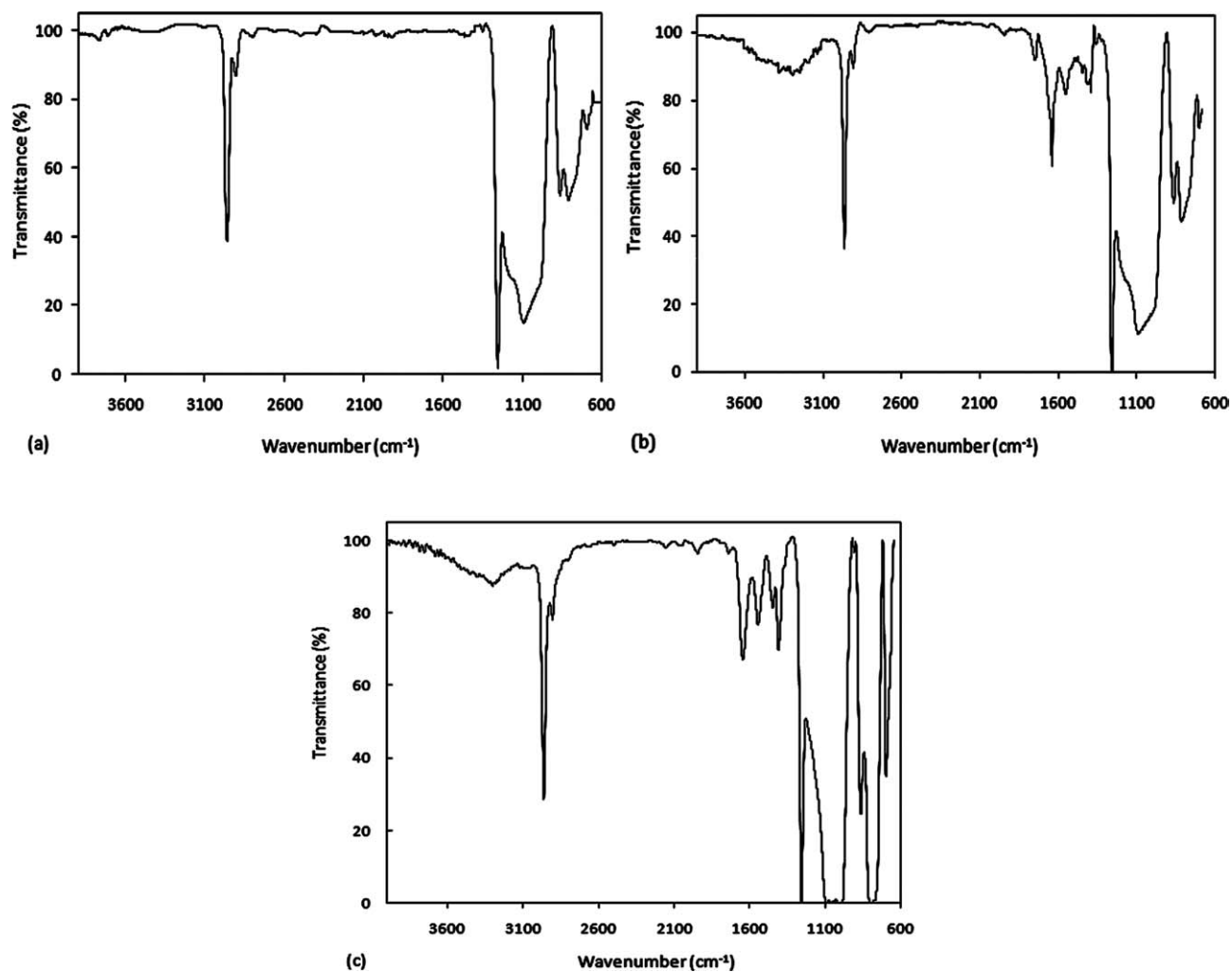


Figure 1. ATR-FTIR spectra of (a) unmodified PDMS film, (b) SC PDMS-PNIPAAm IPN, (c) SCOL PDMS-PNIPAAm IPN.

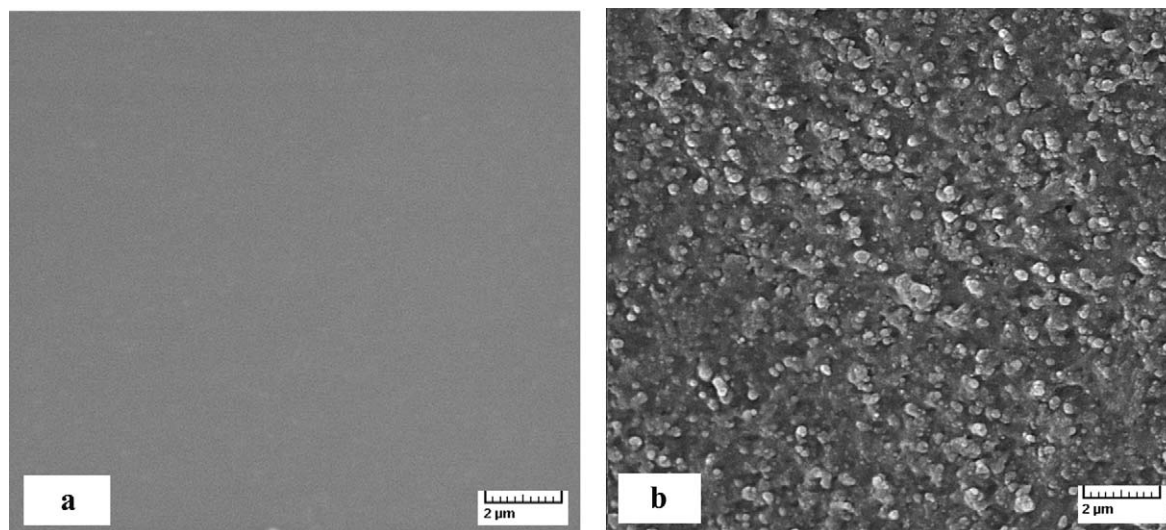
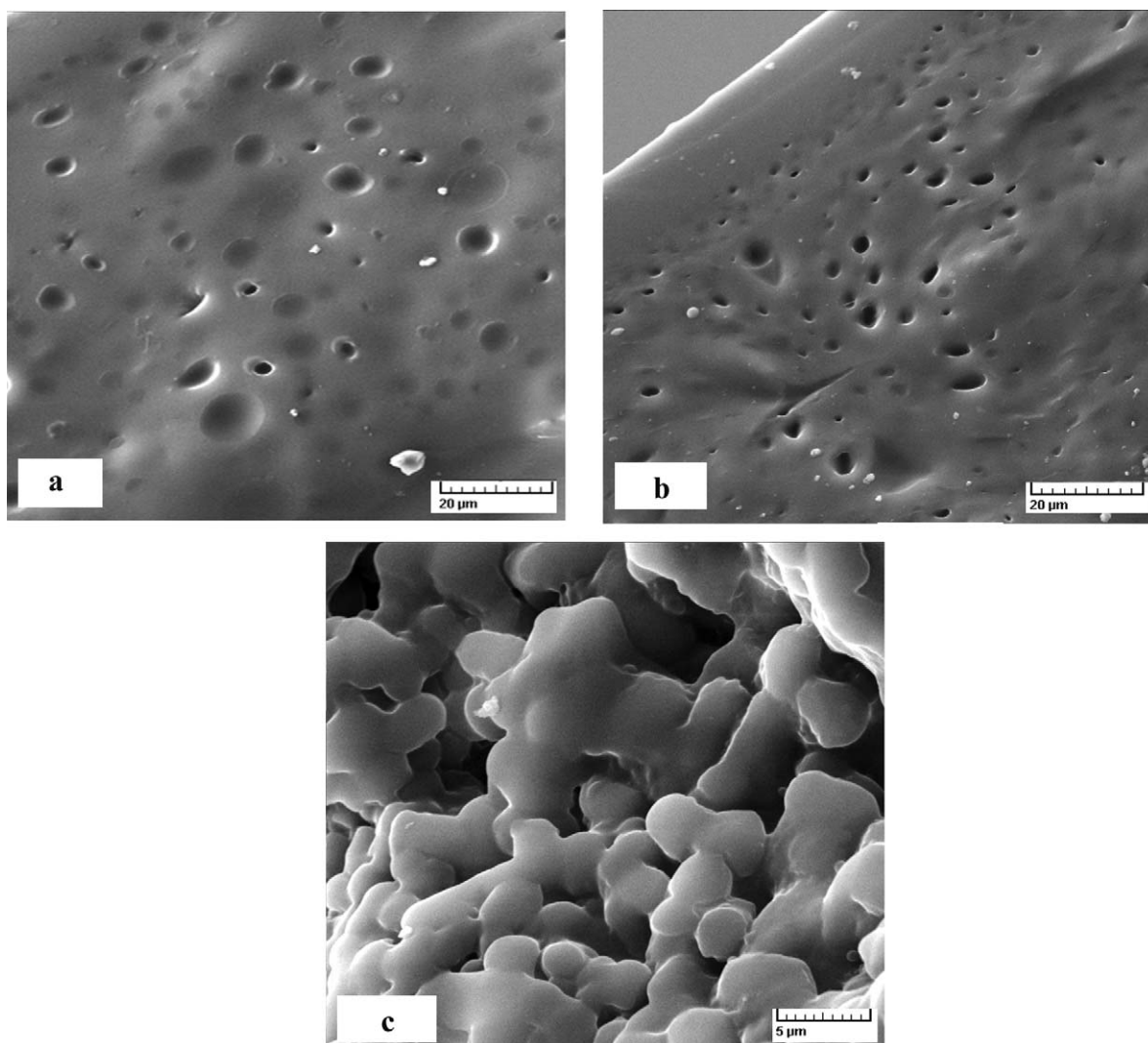
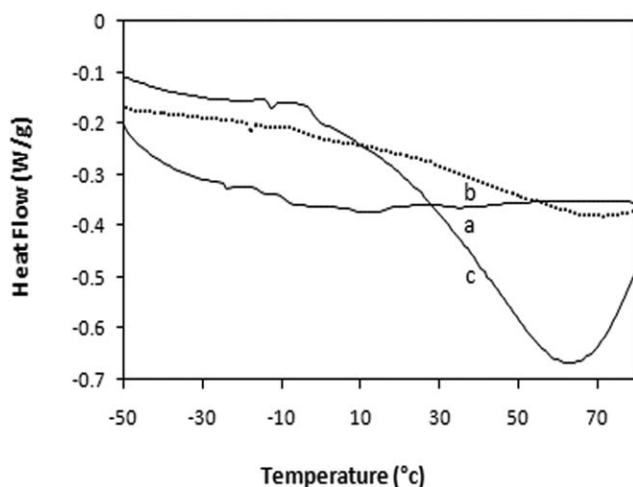


Figure 2. SEM cross sectional micrographs of (magnification  $\times 10,000$ ) (a) SC PDMS film, (b) SC PDMS-PNIPAAm IPN (15.5% wt second phase).





**Figure 3.** SEM cross sectional micrographs of (a) oil-unleached out PDMS film, magnification  $\times 1500$ , (b) SCOL PDMS film, magnification  $\times 1500$ , (C) SCOL PDMS-PNIPAAm IPN (15.8% wt second phase), magnification  $\times 5000$ .



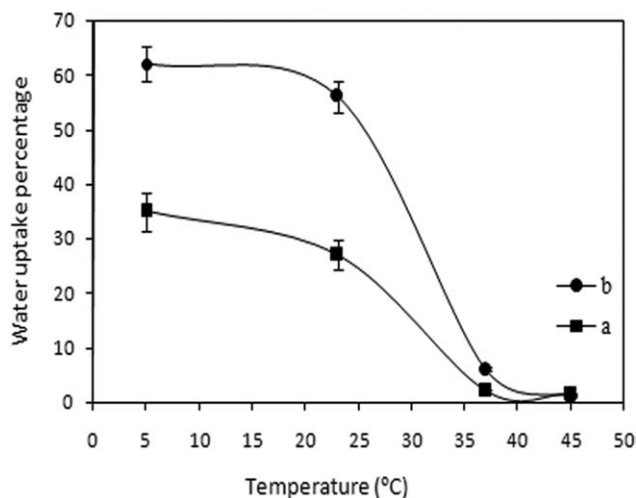
**Figure 4.** DSC spectra of (a) PDMS film, (b) SC PDMS-PNIPAAm IPN (15.5% wt second phase), (c) SCOL PDMS-PNIPAAm IPN (15.8% wt second phase).

between hydrophilic segments of PNIPAAm chains and water molecules was dominated and enhanced water uptake of IPN. However, above the LCST the hydrophobic interactions were strengthened, while hydrogen bonding became weaker. Thus, the net result was shrinking of IPN. This phenomenon affected the permeability of the IPN, which is discussed in effect of temperature section.<sup>27</sup>

As described in SEM micrograph section, there were two phase with different distributions and concentrations of PNIPAAm in the structure of SCOL IPNs, thus, at sampling step for DSC analysis, it may cause a little difference in the sharpness of LCST point for different samples of a determined IPN.

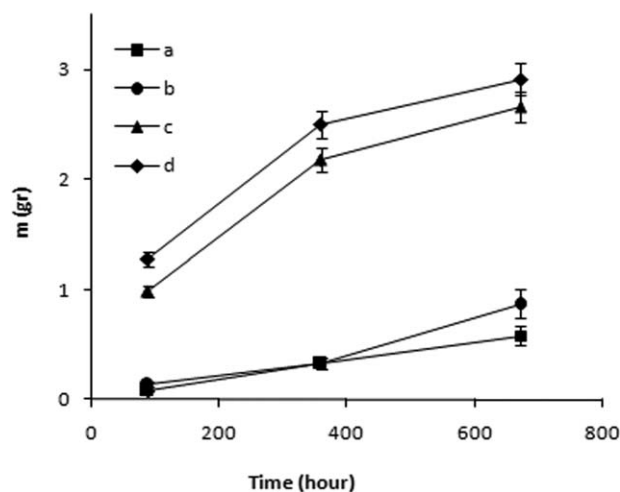
#### Water Uptake Measurement

Effect of temperature on water uptake percentage of SC and SCOL IPNs is shown in Figure 5. At 23°C, equilibrium water uptake percentages of SC and SCOL IPNs containing 15.5%  $\pm$  0.5% wt and 15.8%  $\pm$  0.3% wt second phase, were 27% and 56%, respectively. Higher water uptake percentage of SCOL



**Figure 5.** Water uptake percentage vs. temperature for (a) SC PDMS-PNIPAAm IPN ( $15.5\% \pm 0.5\%$  wt second phase) and (b) SCOL PDMS-PNIPAAm IPN ( $15.8\% \pm 0.3\%$  wt second phase).

than SC IPNs may be related to higher connectivity of PNIPAAm domains in SCOL IPNs (as resulted from SEM micrographs). Moreover, at  $23^{\circ}\text{C}$  which was below the phase transition temperature of the IPNs (as resulted from DSC), maximum water uptake percentage observed for SCOL IPNs ( $56\% \pm 0.05\%$ ). Nevertheless, at  $37^{\circ}\text{C}$  that was above the phase transition temperature of the IPN, water uptake percentage was at its minimum level ( $5\% \pm 0.07\%$ ). As could be seen, water uptake percentage of the samples was changed by temperature changing. The IPNs showed a significant decrease in water uptake percentage at LCST, which is attributed to the hydrophobicity of PNIPAAm domains at this temperature (as DSC results showed). At lower temperatures ( $5^{\circ}\text{C}$ ,  $23^{\circ}\text{C}$ ), hydrogen bonds between amide groups of PNIPAAm network and water molecules were formed but destabilized at higher temperatures, probably because of the presence of the hydrophobic isopropyl groups presented in the IPNs. Thus, when the temperature reached the LCST of PNIPAAm network, the hydrophobic interactions were dominant, resulted in the lower water uptake. Swelling percentage of IPNs decreases by further increase in temperature.<sup>27</sup>



**Figure 6.** Total amounts of permeated sodium chloride molecules with time for (a,b) SC IPNs containing  $11.29\% \pm 0.2\%$  and  $15.5\% \pm 0.5\%$  wt PNIPAAm, (c,d) SCOL IPNs containing  $11.65\% \pm 0.2\%$  and  $15.8\% \pm 0.3\%$  wt PNIPAAm.

### Permeation Measurement

Permeability of the SC and SCOL PDMS-PNIPAAm IPNs to sodium chloride and glucose was determined. As Figure 6 showed, the total amounts of sodium chloride molecules permeated through the IPNs were increased by time. Effect of temperature, method of PDMS film production (SC or SCOL) and PNIPAAm content of the IPNs, on permeability was investigated.

### Effect of Temperature

According to permeation results (Table II), for SC IPNs, containing  $15.5\% \pm 0.5\%$  wt PNIPAAm, sodium chloride permeation coefficient was  $4.45 \times 10^{-8} \pm 1.41 \times 10^{-9} \text{ cm}^2/\text{s}$  at  $23^{\circ}\text{C}$  and  $7.2 \times 10^{-10} \pm 3.18 \times 10^{-11} \text{ cm}^2/\text{s}$  at  $37^{\circ}\text{C}$ . Glucose permeation coefficient was  $1.63 \times 10^{-8} \pm 1.12 \times 10^{-9} \text{ cm}^2/\text{s}$  at  $23^{\circ}\text{C}$  and  $2.03 \times 10^{-10} \pm 1.32 \times 10^{-11} \text{ cm}^2/\text{s}$  at  $37^{\circ}\text{C}$  (Table III). This temperature-sensitivity provided additional evidence that small molecules transport in these membranes via the PNIPAAm domains. As aforementioned, because at temperatures below the LCST ( $23^{\circ}\text{C}$ ), IPN could absorb water and PNIPAAm chains were swollen, the solutes (sodium chloride or glucose molecules) could permeate through these moieties.<sup>28</sup> However,

**Table II.** Sodium Chloride Permeation Coefficients for the SC and SCOL IPNs

PDMS film	PNIPAAm (% wt)	Permeation coefficient ( $\text{cm}^2/\text{s}$ )			
		$23^{\circ}\text{C}$	$P \leq$	$37^{\circ}\text{C}$	$P \leq$
SC	$11.29 \pm 0.2$	$2.7 \times 10^{-8} \pm 1.15 \times 10^{-9}$	0.002	$1.62 \times 10^{-10} \pm 2.5 \times 10^{-12}$	0.004
	$15.5 \pm 0.5$	$4.45 \times 10^{-8} \pm 1.41 \times 10^{-9}$	0.002	$7.2 \times 10^{-10} \pm 3.18 \times 10^{-11}$	0.001
	$18.47 \pm 0.44$	$3.08 \times 10^{-9} \pm 3.86 \times 10^{-10}$	0.004	$4.24 \times 10^{-10} \pm 1.6 \times 10^{-11}$	0.002
	$29.15 \pm 0.25$	$5.63 \times 10^{-10} \pm 9.71 \times 10^{-12}$	0.002	$3 \times 10^{-11} \pm 1 \times 10^{-12}$	0.002
SCOL	$11.65 \pm 0.2$	$4 \times 10^{-7} \pm 5.03 \times 10^{-9}$	0.003	$4.6 \times 10^{-9} \pm 2.06 \times 10^{-10}$	0.008
	$15.8 \pm 0.3$	$5.98 \times 10^{-7} \pm 7.93 \times 10^{-9}$	0.002	$5.8 \times 10^{-9} \pm 1.21 \times 10^{-10}$	0.001
	$19.1 \pm 0.2$	$3.6 \times 10^{-7} \pm 1.5 \times 10^{-8}$	0.005	$4.5 \times 10^{-9} \pm 1.65 \times 10^{-10}$	0.002
	$29.5 \pm 0.15$	$2.3 \times 10^{-7} \pm 8.5 \times 10^{-9}$	0.005	$7.2 \times 10^{-9} \pm 1.45 \times 10^{-10}$	0.002

**Table III.** Glucose Permeation Coefficients for the SC and SCOL IPNs

PDMS film	PNIPAA m (%wt)	Permeation coefficient (cm <sup>2</sup> /s)			
		23°C	P ≤	37°C	P ≤
SC	11.29 ± 0.2	1.07 × 10 <sup>-9</sup> ± 1.45 × 10 <sup>-10</sup>	0.004	1.12 × 10 <sup>-9</sup> ± 1.2 × 10 <sup>-10</sup>	0.0002
	15.5 ± 0.5	1.63 × 10 <sup>-8</sup> ± 1.12 × 10 <sup>-9</sup>	0.001	2.03 × 10 <sup>-10</sup> ± 1.32 × 10 <sup>-11</sup>	0.001
	18.47 ± 0.44	3.52 × 10 <sup>-9</sup> ± 1 × 10 <sup>-10</sup>	0.0002	5 × 10 <sup>-12</sup> ± 1.8 × 10 <sup>-13</sup>	0.0004
	29.15 ± 0.25	1.67 × 10 <sup>-9</sup> ± 1.3 × 10 <sup>-10</sup>	0.002	2.15 × 10 <sup>-12</sup> ± 6.02 × 10 <sup>-14</sup>	0.0002
SCOL	11.65 ± 0.2	2.2 × 10 <sup>-7</sup> ± 8.5 × 10 <sup>-9</sup>	0.002	3 × 10 <sup>-9</sup> ± 7.37 × 10 <sup>-10</sup>	0.002
	15.8 ± 0.3	3.6 × 10 <sup>-7</sup> ± 7 × 10 <sup>-9</sup>	0.003	1.21 × 10 <sup>-9</sup> ± 1.09 × 10 <sup>-10</sup>	0.006
	19.1 ± 0.2	2.6 × 10 <sup>-7</sup> ± 6.5 × 10 <sup>-9</sup>	0.003	1.02 × 10 <sup>-9</sup> ± 7.5 × 10 <sup>-11</sup>	0.001
	29.5 ± 0.15	1.16 × 10 <sup>-7</sup> ± 1 × 10 <sup>-8</sup>	0.002	1.13 × 10 <sup>-9</sup> ± 4.72 × 10 <sup>-11</sup>	0.002

as concluded from water uptake measurements, swelling of the IPN decreased by increasing temperature above the LCST of the IPN. Thus, by increasing permeation temperature to 37°C, PNIPAAm domains were dehydrated and collapsed and thus, there was a great decrease in permeability. However, it should be noted that a measurable permeability remained in the IPNs, even at temperatures above the LCST.

#### Effect of PDMS Film Structure

Sodium chloride permeation coefficients for SC IPNs, containing 15.5% ± 0.5% wt PNIPAAm, was 4.45 × 10<sup>-8</sup> ± 1.41 × 10<sup>-9</sup> cm<sup>2</sup>/s and for SCOL IPNs containing 15.8% ± 0.3% wt PNIPAAm was 5.98 × 10<sup>-7</sup> ± 7.93 × 10<sup>-9</sup> cm<sup>2</sup>/s, respectively (Table II). Similarly, glucose permeation coefficients were 1.63 × 10<sup>-8</sup> ± 1.12 × 10<sup>-9</sup> cm<sup>2</sup>/s and 3.6 × 10<sup>-7</sup> ± 7 × 10<sup>-9</sup> cm<sup>2</sup>/s, respectively (Table III). As could be seen, there was little measurable sodium chloride and glucose permeation through the SC IPNs, while, similar PNIPAAm content in the SCOL IPNs resulted in higher permeability. The difference between permeation coefficients of SC and SCOL IPNs may be related to PNIPAAm network. Herein, connectivity of PNIPAAm networks plays a key role in transporting the solutes. In the SCOL IPNs, as SEM results showed, PNIPAAm regions were in the form of connective structures. Therefore, in the case of SCOL IPNs, connectivity of PNIPAAm chains increased the probability of solute transport throughout the IPN.

#### Effect of PNIPAAm Concentration

As described earlier, water molecules could hydrate the hydrophilic chains of IPN and made free water paths, which were suitable for transporting water-soluble molecules across the membrane. Thus, solutes could easily solve in water and pass through the IPN. However, according to the results (Table II), it is important to note that by increasing the hydrophilic secondary phase of the IPN up to 15.8% ± 0.3% wt for SCOL IPNs, NaCl permeation coefficient was also increased and reached to 5.98 × 10<sup>-7</sup> ± 7.93 × 10<sup>-9</sup> cm<sup>2</sup>/s, and then gradually decreased to 2.3 × 10<sup>-7</sup> ± 8.5 × 10<sup>-9</sup> cm<sup>2</sup>/s, by increasing the second phase concentration to 29.5% ± 0.15% wt. The results suggested that PNIPAAm concentration affected the permeability of the IPN. PNIPAAm regions played an important role in permeation. Therefore, permeation coefficient increased by increasing PNIPAAm content of the IPN. Although at higher concentra-

tions of PNIPAAm, these networks maybe had compact structures, so that, swelling did not allow the solute molecules to diffuse to these domains.

#### CONCLUSIONS

While PDMS film is impermeable to small water-soluble molecules, PDMS-PNIPAAm IPNs permeable to sodium chloride and glucose were successfully synthesized from SC and porous SCOL PDMS films. In these IPNs, as confirmed by SEM micrographs, PNIPAAm regions were presented as connective domains in PDMS film. As concluded from DSC results and water uptake measurements, the IPNs had a phase transition temperature (LCST) at 32°C. Thus, permeation coefficient decreased by increasing temperature above 32°C. Below this temperature, the IPNs were hydrophilic, so that, NaCl or glucose molecules could easily pass through the hydrated connective PNIPAAm chains. The results suggested that permeability of the IPN changed, depending on the PDMS film fabrication method, PNIPAAm content of the IPN and permeation temperature. Maximum permeation coefficient was observed in SCOL IPNs containing 15.8% ± 0.3% wt PNIPAAm at 23°C. In future, to improve the transparency and permeability of these IPNs and make them more suitable for ophthalmic biomaterials, the IPNs can be modified by copolymerizing PNIPAAm with other hydrophilic polymers.

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