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Preparation and mechanical characterization of a PNIPA hydrogel composite

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Abstract A poly (*N*-isopropylacrylamide) (PNIPA) hydrogel was synthesized by free radical polymerization and reinforced with a polyurethane foam to make a hydrogel composite. The temperature dependence of the elastic modulus of the PNIPA hydrogel and the composite due to volume phase transition was found using a uniaxial compression test, and the swelling property was investigated using an equilibrium swelling ratio experiment. The gel composite preserves the ability to undergo the volume phase transition and its elastic modulus has strong temperature dependence. The temperature dependence of the elastic modulus and swelling ratio of the gel composite were compared to the PNIPA hydrogel. Not surprisingly, the modulus and swelling ratio of the composite were less dramatic than in the gel.

1 Introduction

Gels are cross-linked networks of a polymer swollen with a liquid. From a structural standpoint, gels are containers of solvent made from a three-dimensional polymer mesh network [1]. Gels can change their volume due to changes in environmental factors. This is referred to as a "volume phase transition" phenomenon. It is a type of phase separation phenomenon which is very similar to a coil-globule transition [1]. The swelling and volume phase transition properties have made hydrogels very useful in biomedical and bioengineering applications such as tissue engineering [2], switches [3], micro/nonoactuators [4], artificial organs [5], and drug delivery [6–8].

Many studies have focused on the temperature sensitive poly (*N*-isopropylacrylamide) (PNIPA) gel and its volume phase transition phenomenon [3, 9–30]. PNIPA has a phase transition temperature or lower critical solution temperature (LCST) at about 32–35 °C [28, 30] below which it is hydrated and above which it is not hydrated. The volume phase transition of PNIPA gel was discovered by Hirokawa and Tanaka in 1984 [9]. The transformation is due to a change in hydrophilicity of the gel. PNIPA is hydrophilic and absorbs water at temperatures below the LCST to reach a swollen state. As the temperature increases up to and above the LCST, the gel becomes hydrophobic, releases its water, and shrinks. As the temperature increases even more above the LCST, the volume of the gel does not continue to change substantially and remains stable in the collapsed state.

Mechanical properties of hydrogel materials are of great interest in both basic studies of gels and in practical applications. The hyper-elastic theory or rubber elastic theory is a widely used theory to characterize the elastic behavior of hydrogels. Developed first by Flory, assuming the volume is constant and the polymer chain distribution is Gaussian, the theory gives the relationship between the applied stress and the stretch ratio as [31]:

$$\sigma = f/S_0 = E\left(\lambda - \lambda^{-2}\right), \quad (1)$$

where σ is the applied stress, f is the applied force, S_0 is the cross sectional area of the undeformed hydrogel sample, E is a constant which is often regarded as the elastic modulus, and λ is the stretch ratio, a measure of relative deformation defined as $\lambda = L/L_0$, where L is the current length and L_0 is the un-stretched length. Previous studies have shown that the elastic modulus of PNIPA gel, E, can change up to two or three orders of magnitude from the swollen state to the

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collapsed state [13, 19, 27, 32]. The gel deformation will typically be governed by this law until the stress reaches the strength of the material and it fails.

One drawback of PNIPA gel and other gels in practical applications is low strength and low modulus in the swollen state [11, 14, 24]. In fact, the strength is so low that care must be taken when handling the gel during experiments. The PNIPA gel can be easily broken by a small force applied by human hands, especially when a pre-crack exists. Furthermore, the swollen gels are so compliant that they cannot be used to support much load without significant deformation. Strong, stiff hydrogels with the same composition as PNIPA are highly desired for biomechanical applications and therefore it is desirable to increase the strength and stiffness of such gels.

There are several methods proposed to improve the mechanical properties, including semi-interpenetrating network (IPN) formation [11, 20, 21, 32, 33], fiber reinforcement [34], co-polymerization [13, 18, 35, 36], and increasing cross-linking density [27, 32]. Here, a new method is examined to make PNIPA gel composites (referred to here as a gel composite). A polyurethane open-cell foam is used as the matrix and the gel is formed directly inside the foam or matrix. To the best of the author's knowledge this is the first time such a gel composite has been reported in the open literature. Mansmann [37] referred to a similar idea in a patent without further development. Here a method is developed to make such a composite and the changes in mechanical properties that result for such an approach are reported.

In this work, the elastic moduli of the PNIPA gel and gel composite were measured at a range of temperatures above and below the LCST, using the uniaxial compression test and the constitutive law given above. The results are compared to the equilibrium swelling properties of the non-reinforced gel. The phase separation/swelling properties and LCST may be obtained from measurements of the swelling ratio as a function of temperature. Various techniques have been applied to measure the LCST of the PNIPA hydrogel including the cloud point method [38, 39], differential scanning calorimetry (DSC) [18, 30, 39], light scattering [39, 40], and direct measurement of volume/geometric factor/weight of the sample [9, 10, 29, 30, 41]. Here, the weight method was chosen to investigate the swelling properties and LCST of synthesized PNIPA samples.

2 Materials and methods

2.1 Synthesis of PNIPA hydrogel and gel composite

The PNIPA hydrogel was prepared by free radical polymerization. The NIPA monomer (Aldrich, Milwaukee, MI) was dissolved in 1,4-dioxane with ethylene glycol dimethacrylate (EGDMA, Aldrich) as the cross-linker and 2,2′-azobisisobutyronitrile (AIBN, Aldrich) as the initiator. The concentration of PNIPA in the pregel solution is 1.0 mol/L, that of EGDMA is 0.1 mol/L, and that of AIBN is 0.036 mol/L. Once the solution is prepared, nitrogen gas is bubbled into the solvent for 10 min to remove dissolved oxygen. A glass mold consisting of two plates and a spacer having dimensions 80 × 80 × 5 mm was used to make rectangular hydrogel sheets with dimensions of 63 × 38 mm and a thickness of 6 mm. The polymerization was carried out at 55–60 °C for 4 h. The PNIPA hydrogels produced were then immersed in distilled water for at least 48 h at room temperature for storage.

The matrix of the gel composites is open-cell polyurethane foam (McMaster-Carr Supply, Chicago) with a thickness of 6.4 mm (0.25 inch). Selected material properties of this foam are listed in Table 1. Polyurethane foams were used because they are biocompatible and easy to obtain [42]. The open-cell feature is necessary for the foam to absorb the pre-gel solution. Various types of open-cell foams were tested. The Aquazone Super-Absorbent polyurethane foam is the best among several open cell polyurethane foams tested with PNIPA.

The PNIPA gel composite was synthesized by free radical polymerization of the pure PNIPA gel within the foam. The same pre-gel solution described above was used in synthesis of the gel composite. A glass mold consisting of two plates and a spacer with dimensions of 80 × 80 × 5 mm was used to make rectangular gel composite sheets (the synthesized PNIPA gel composite had dimensions of 83 × 53 × 6.5 mm since the gel composite sheets swelled more in water than in dioxane). The pregel solution was poured directly into the matrix in the glass mold. The pregel solution was completely absorbed by the polyurethane foam. The volume fraction of the gel was 0.77 (vacancy percentage calculated from density of the foam over density of solid polymer, assuming the gel occupies all pores). The polymerization was carried out at 55–60 °C for 4 h, and the PNIPA gel composite samples produced were then immersed in distilled water at room temperature for at least 48 h for storage.

Table 1 Material properties of polyurethane foam used as the matrix for gel composites (values obtained from McMaster-Carr Supply, Chicago)

Material	Density (lbs./cu. ft./ kg m^{-3})	Firmness rating	Type	Compression at 25% deflection (psi/kPa)
Polyurethane	1.8/28.8	2	Plain back	30/206.8

The structure of the gel composite was studied under an optical microscope (Eclipse ME 600L, Nikon Instruments, Inc, Melville, NJ) at room temperature.

2.2 Swelling properties of PNIPA hydrogel and gel composite

Swelling properties of the PNIPA hydrogel and gel composite were studied by the equilibrium swelling ratio method. To insure that the material reached equilibrium, the samples were immersed in distilled water for at least 60 h at various temperatures from 15 °C to 42 °C. The water temperature was controlled to ±0.5 °C by a circulating bath machine (VWR 1165, VWR, Niles, MI). The swelling ratio was measured by the weight method [29, 30, 41]. First, the gel sample was dried in a vacuum oven at room temperature and a vacuum level of 10 in-Hg until fully dried (indicated by no weight change) and weighed to first determine the weight in the dry state. At a particular temperature after equilibrium had been reached, the hydrogel sample was taken out and the excess water on the surface was removed by wiping with filter papers. At each temperature, the gel sample was allowed to swell for over 75 h to reach equilibrium. The method used to determine equilibrium was simple. The sample was removed and weighed several times throughout the equilibrating process. When its weight remained constant, the gel sample could be assumed to be in an equilibrium state. Then the sample was weighed. The swelling ratio was defined as:

$$s.w. = W_s/W_d = \left(W_g - W_d\right)/W_d, \tag{2}$$

where W_s and W_g are the weight of water and gel network in the hydrogel at a particular temperature respectively, and W_d is the weight of the hydrogel in the dried state. Different temperatures from around 15–41 °C were examined (temperature levels vary slightly from gel to gel-composite). One sample was used for all the temperatures in the measurement. From the plot of swelling ratio versus temperature, the LCST was determined as the temperature point at which the swelling ratio curve reaches the plateau.

2.3 Uniaxial compression test

The prepared gel and gel composite sheets were swelled in water at room temperature for over 1 week to reach equilibrium. Rectangular samples were cut from the sheets with dimensions of 8 × 8 × 6 mm. Using an EnduraTec ELF 3300 material test machine, uniaxial compression experiments were performed in a water bath with temperature control accurate to 0.5 °C. The elastic modulus was measured at temperatures of 23, 25, 27.5, 30, 32.5, 35, and 40.0 °C. The sample was immersed in water at the specified temperature for over 48 h prior to each test to reach equilibrium. Three samples were tested at each temperature. The crosshead speed was 0.1 mm/s and a 25 lb. (111.2 Newton) Interface 1500ASK-25 load cell (Interface, Scottsdale, Arizona) with a high sensitivity of 0.03% was used. The elastic modulus E was calculated from the hyperelasticity stress-elongation relationship [14, 20, 31, 33, 43] by a least-squares fit of the following relationship to the linear region using Eq. 1.

3 Results and discussion

3.1 Swelling ratio

The pure PNIPA gel has a light transparent appearance (Fig. 1a), whereas the PNIPA gel composite has a white appearance due to the white color of the polyurethane foam (Fig. 1b). The PNIPA gel particles can be seen within the polyurethane matrix. The structure of the polyurethane foam was not destroyed during the polymerization at elevated temperature. Its operating temperature can reach 88 °C. The structure of the gel composite is shown in Fig. 2 through an optical microscope. The matrix appears to be a three-dimensional cellular structure. The gel particles fill in the porous structure.

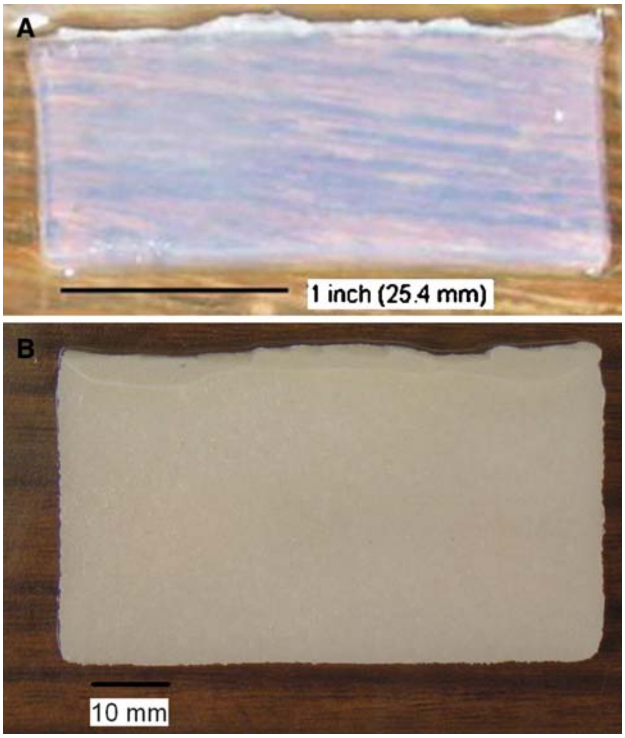

Fig. 1 (**a**) Photo of the PNIPA gel at room temperature. (**b**) Photograph of PNIPA gel composites with polyurethane foam matrix

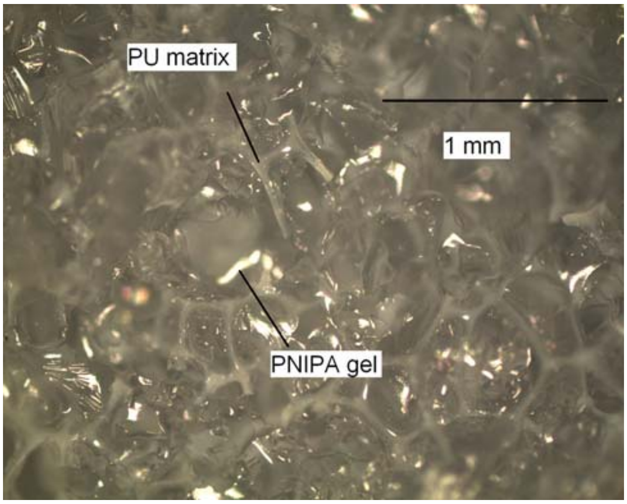

Fig. 2 The structure of the gel composite under an optical microscope. PNIPA gel particles filled in the pores of polyurethane (PU) matrix

The results of equilibrium swelling ratio experiments are shown in Fig. 3. The swelling ratio was higher at the lower temperatures. It decreases with increasing temperature. The LCST was determined as the temperature at which the swelling ratio no longer changes substantially. This is a difficult definition to apply, since the swelling ratio exhibits a continuously crossover and gradually reaches a plateau about the LCST as can be seen in Fig. 3. Nonetheless, the LCST determined was approximately 34.7 °C where the first derivative of the curve equals to 0.1, in agreement with other investigations [30]. During the transformation the weight percent of water decreases from 94.5% at 15 °C to 23.3% at 41.5 °C. At temperatures below 25 °C, the gel sample was transparent. It turned cloudy at 27 °C (see Fig. 1), and completely opaque at 32 °C. This observation agreed with cloud point measurements in the literature [38].

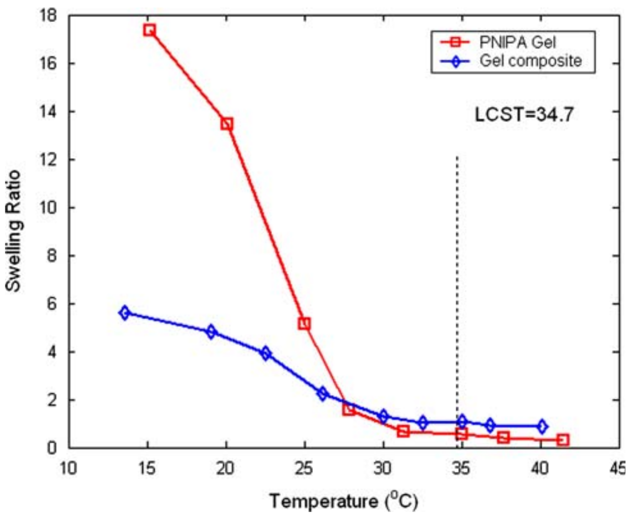

Fig. 3 Results of the swelling ratio experiments for the gel composite

The data shown in Fig. 3 was from the heating test (increasing temperature). Further results showed that during cooling, the swelling and de-swelling speed of the PNIPA gel varied somewhat. During a cooling swelling experiment, it took about 300 h for the gel to reach equilibrium, significantly longer. The conclusion is that the speed of de-swelling (losing water) is higher for the gel than that of swelling (gaining water). Clearly, the uptake of water is much slower than its release from the gel. This agrees with earlier observations reported in the literature [30].

Figure 3 also shows data from the swelling ratio experiments for the gel composite. The gel composite preserved its capability for a volume phase transition, however its swelling ability was lower than the pure PNIPA gel in the swollen state. In the collapsed state, the gel composite contains more weight percent of water, since the swelling ability of the open-cell foam is lower than the PNIPA gel in the swollen state and higher in the collapsed state. Thus, for temperatures above the LCST, the foam retains the water in the gel composite, and at low temperature the foam prevents water from entering.

3.2 Mechanical behavior

Figure 4 shows the measured stress-deformation curve for PNIPA gel at 25 °C. The stress and the deformations $(\lambda - \lambda^{-2})$ are both negative (compression) but are plotted as absolute values. The stress and deformation display a good linear relationship at 25 °C, which agrees with Eq. 1. At higher temperatures, the stress-deformation curve has toe region (Fig. 5). The elastic modulus was obtained by a least-squares fit to the linear region observed in the plots. It was reported that hydrogels are elastic under the LCST and

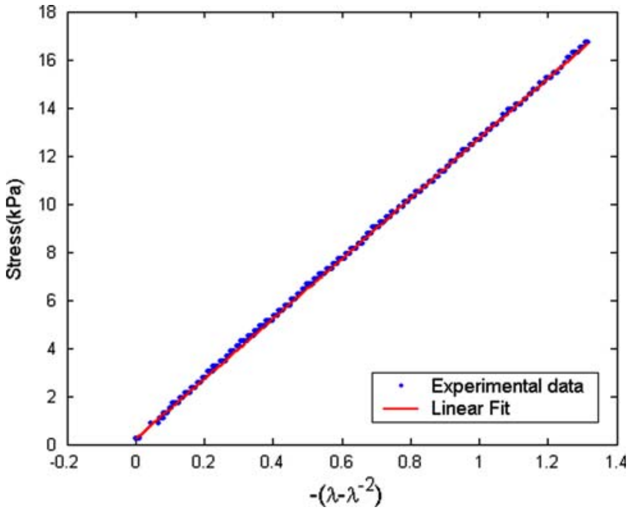

Fig. 4 Stress-deformation curve of pure PNIPA gel specimen at 25 °C

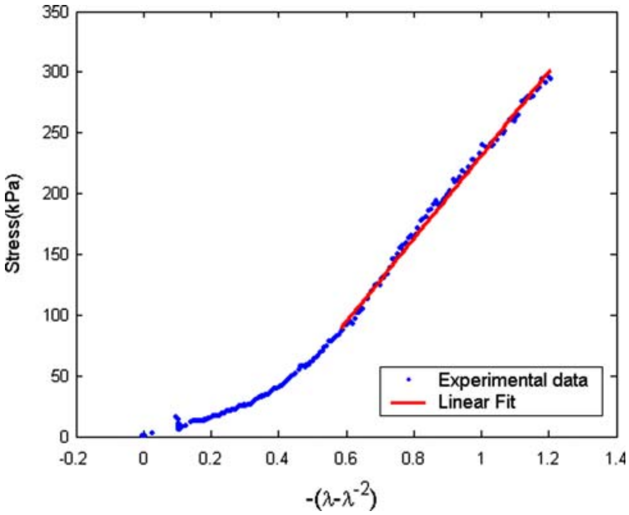

Fig. 5 Stress-deformation curve of pure PNIPA gel specimen at 35 °C

viscoelastic above the LCST [24]. Thus, for higher temperatures, the initial elastic modulus is often taken as the modulus at the given temperature [26]. The initial toe region is either due to non-flatness of the specimen, as reported by Muniz and Geuskens [20], or due to viscoelasticity of the material. Considering the time scale of the test (this is a quasi-static test completed in 14 s) and the fact that perfectly flat samples are difficult to produce, it is our opinion that non-flatness of the samples is the dominant effect. The measured values of elastic moduli are different, however, 6.9 kPa at 25 °C and 1,847 kPa at 40 °C. The elastic modulus increases about 267 times from 25 °C to 40 °C.

The measured elastic modulus also depends on the loading speed. In the limit of extremely low strain rates, the water can move in or out of the gel network, thus at very low rates the measured modulus occurs under conditions of constant osmotic pressure [14]. With relatively high strain rates, the modulus measured occurs under conditions of constant volume [14]. To determine which conditions exist in a particular test, the strain rate should be compared with the swelling speed of the gel sample, which is proportional to the square of the characteristic length of the sample [1]. In these experiments, a relatively high strain rate was used and the measured modulus corresponds to constant volume conditions.

Normally there are two environments that can be employed when performing a compression test on hydrogels: water or air. In the latter case, the water may release from the hydrogel sample [44] though some researchers claim that when the loading time needed to finish the test is less than 1 min, one can avoid the loss of water [20]. In this work, the compression test was performed in a water bath to avoid such issues altogether.

Selected values of elastic modulus of a pure gel reported in the literature are shown in Table 2. In those results, it is seen that the elastic modulus increases with increasing temperature. The results here agree. The value of *E* for the pure gel at 25 °C agrees with the values reported in other studies [19, 27]. The value of *E* for the pure gel at 40 °C is higher than some literature results (Table 2). However, Harmon reported *E* as high as 1,540 kPa [13]. One explanation for the higher value seen here is that the crosslink density in our sample is different than the materials reported in the literature; crosslink density has a significant effect on the elastic modulus.

A typical stress–strain curve for the compression tests of the PNIPA gel composites is shown in Fig. 6. The elastic modulus calculated by a linear fit to the initial region was taken as the elastic modulus at that temperature. The elastic modulus of the gel composite shows temperature dependence similar to the pure PNIPA gel. The measured values of elastic moduli are different however, 12.8 kPa at 25 °C and 458 kPa at 40 °C (Fig. 7). The elastic modulus increases about 40 times from 25 °C to 40 °C.

Table 2 Selected results of measured elastic modulus from compression test for pure PNIPA gel

T (°C)	25	30	35	40
Measured elastic modulus (kPa)	6.9 (2.83 [19]; 9.8 [27])	77.5 (18.5 [16])	314.5 (183 [19])	1847.1 (170 [27]; 1540 [13])
E of gel composite (kPa)	12.8	99.7	143.3	458.3

Values in parentheses are literature values

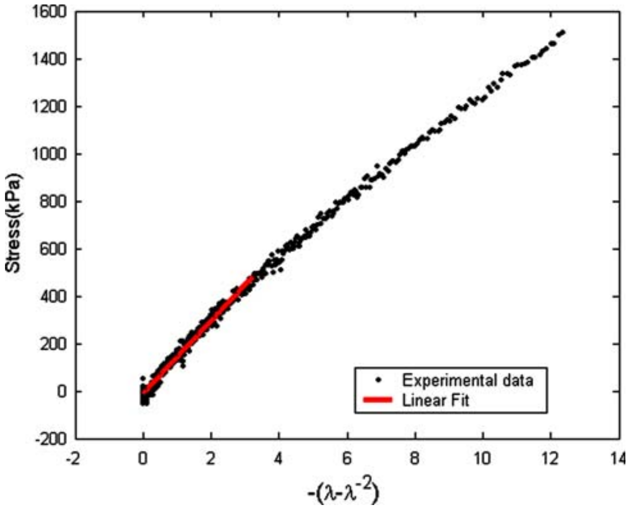

Fig. 6 Stress-deformation curve of PNIPA gel composite specimen at 32.5 °C

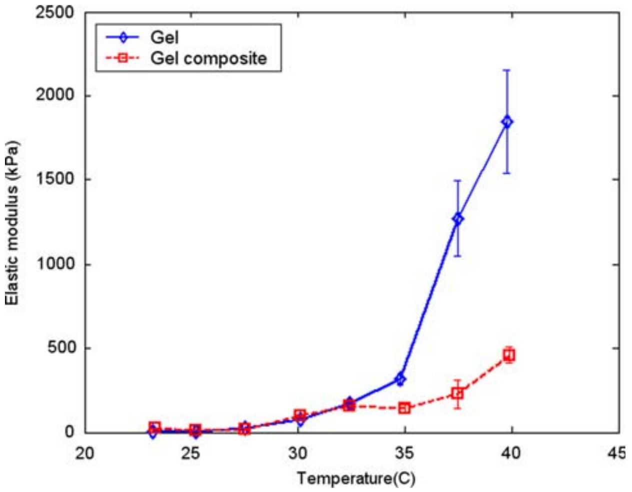

Fig. 7 Comparison of the temperature dependence between the gel and gel composite

The modulus of the composite is much lower than the pure gel at high temperatures and higher than the pure gel at low temperatures (Fig. 7). The desired result of increasing stiffness in the swelled state is achieved through this reinforcement strategy. Also, while the value of elastic modulus of the pure gel changes dramatically from swollen to collapsed states, the modulus changes less for the gel composite during the same transition. It seems clear that the modulus of the matrix, which has no temperature dependence within the tested range, dominates the response of the composite. During handling, it is also observed that, unlike the pure PNIPA gel which can be easily broken, the composite is much stronger.

There are some factors limiting the precision of the experimental results. First, the surface of the sample is not totally flat, which may have resulted in an initially-low slope in the curve, resulting in underestimation of the modulus. Second, the theory requires zero friction at both contact surfaces. This is not completely true, even though the samples were submerged in water. The possible consequence of this latter effect is the overestimation of the stiffness [45].

4 Conclusions

To improve the mechanical properties of PNIPA gels, a new gel composite was developed with polyurethane foam as the matrix. Results of swelling ratio experiments showed that the gel composite preserves the ability to undergo a volume phase transition. Temperature dependence of the swelling ratio and the elastic modulus occurred in both the PNIPA gel and the gel composite. The modulus of the composite is much lower than the pure gel at high temperatures and higher than the pure gel at low temperatures. This is a direct result of the matrix having a higher modulus than the swelled PNIPA gels and a lower modulus than the dehydrated PNIPA gels. The composite properties are an average of the gel and matrix. Overall, the mechanical properties of the gel composite are improved in the swollen state as a result of the introduction of the matrix, as compared to a pure PNIPA gel.

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