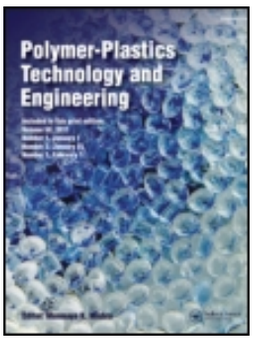

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Elastic Properties of a Swollen PAAm-NIPA Copolymer with Various NIPA Contents

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Copolymer based on cross-linked polyacrylamide (PAAm) having N-isopropylacrylamide (NIPA) was prepared and their elastic properties were studied as a function of NIPA contents. NIPA content dependency of the shear modulus, *S* of the PAAm-NIPA copolymers due to volume phase transition was measured using tensile testing technique at 30°C. It was observed that its shear modulus and toughness were found to be strongly dependent on NIPA content. It is understood that the shear modulus was found to increase with NIPA contents, keeping constant temperature at 30°C. Elastic properties of the PAAm-NIPA copolymers show compositional dependence.

Keywords Acrylamide; Elasticity; NIPA; Swelling; Toughness

INTRODUCTION

The polyacrylamide (PAAm)- N-isopropylacrylamide (NIPA) copolymers may have useful applications in various areas of biophysics and medicine such as in thermal switches, drug-release systems, micro/nanoactuators, or microvalves/pumps. The mechanical properties of poly (N-isopropylacrylamide) and poly (acrylamide) were known separately[1,2]. Mechanical properties of polyacrylamide gels covering a wide range of polymer concentrations have been studied[1]. The elastic modulus was found to increase exponentially with total comonomer concentration, keeping constant the percentage of bisacrylamide comonomers. The swelling characteristics and mechanical properties of gelatin-polyacrylamide interpenetrating networks were reported[3].

A temperature-sensitive poly((*N*-isopropylacryamide-co-acrylamide)/montmorillonite (P(NIPAAm-co-Am)/MMT) nanocomposite hydrogel with enhanced mechanical properties and thermodynamic stability based on chitosan and nanoparticle MMT was studied[4]. The temperature-sensitive behavior, mechanical property, thermodynamic stability, and enzymatic degradation of the nanocomposite hydrogels were investigated in detail. The PVC/Polyhedral oligomeric silsesquioxanes containing octyl groups (O-POSS) nanocomposites were prepared[5]. Plastic behavior and dynamic rheology of nanocomposites were investigated. Influences of composition on storage modulus, loss modulus and complex viscosity were discussed. The mechanical properties and morphology were determined.

The elastic and osmotic behavior and network imperfections of nonionic and weakly ionized acrylamide-based hydrogels were studied as a function of swelling degree *Q* and initial total monomer concentration[6]. Compressive elastic modulus of polyacrylamide hydrogels and semi-IPNs with poly(N-isopropylacrylamide) were studied at several temperatures[7]. The semi-IPN presented a greater elastic modulus when compared to the cross-linked PAAm hydrogel. The values of apparent cross-linking density were determined from the mechanical compression measurements at temperatures from 25 to 40°C.

The equilibrium swelling and the plateau elastic modulus of a family of hydrogels made by the polymerization of acrylamide with itaconic acid or some of its esters were investigated as a function of composition and cross-linking degree to find materials with satisfactory swelling and elastic properties[8]. Elastic properties of poly (N-isopropylacrylamide) and poly (acrylamide) hydrogels were studied by Scanning Force Microscopy[2]. Young's modulus was found to be slightly dependent on the temperature however the cross-linker concentration presented a strong influence. Semi-interpenetrating polymer networks were synthesized to improve the mechanical properties of NIPA gels[9]. These networks reinforced with cationic and nonionic PAAm exhibited higher tensile strength and elongations at break than NIPA hydrogels, whereas the presence of anionic PAAm caused a reduction in the mechanical properties. Polyacrylamide gels with glucose oxidase were used to designed a biosensor with proper viscoelastic and swelling properties[10]. The swelling and viscoelastic properties of the hydrogels were evaluated as a function of the cross-linker content of the polymer chains and enzyme concentration. Polymer-clay nanocomposite hydrogels were prepared by free radical polymerization of the

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monomers acrylamide, N, N′-dimethyacrylamide (DMA), and N-isopropylacrylamide in aqueous clay dispersions[11].

The properties of the hydrogels varied depending on the type of the monomer used in their preparation. Poly (N-isopropylacrylamide) gels were prepared by UV polymerization with different degree of cross-linking in different solvents[12]. The free volume fraction and hole size distribution in the dry gels were measured using positron annihilation lifetime spectroscopy. The free volume fractions in the gels were found to be inversely correlated to the extent of equilibrium swelling for similar chemical compositions. Mechanical characterization of poly (N-isopropylacrylamide) gels were performed for a use in smart actuators[13].

Mechanical properties were obtained at different hydration levels and for the different cross-linking density and the effects of these parameters were studied statistically. The elastic properties of the PAAm-NIPA copolymers are quite important for a number of practical applications. Several techniques such as dynamic light scattering, viscoelastic measurements, stress relaxation, and swelling equilibrium have been used in order to determine the compressive elastic modulus. In addition, we studied the elastic percolation of the swollen polyacrylamide (PAAm)-multiwall carbon nanotube (MWNTs) composite[14], which shows that compressive elastic modulus increases dramatically up to 1 wt.% MWNT by increasing the nanotube content and then decrease presenting a critical MWNT value indicating that there is a sudden change in the material elasticity. The effect of κC content on the elastic behavior of the swollen PAAm-κC composites was determined experimentally to decide the critical exponent of elasticity[15].

The elastic properties of the PAAm-κC composites are highly dependent on κC content, which directly influences the interactions between PAAm and κC monomers in the composites. Such monomer interactions will play a critical role in the load transfer and interfacial bonding that determine the elastic properties of the composites. Last, composites formed from the polyacrylamide (PAAm)-multiwalled carbon nanotubes (MWNTs) were prepared via free radical cross-linking copolymerization with different amounts of MWNTs varying in the range between 0.1 and 50 wt.%[16]. It is observed that elastic modulus increased when temperature is increased from 30°C to 60°C. Toughness, however presented the reversed behavior versus temperature compare to the elastic modulus.

In this article, the elastic behavior of the swollen PAAm-NIPA copolymers was determined by using tensile testing technique. The PAAm-NIPA copolymers[17] were prepared by adding different molar % of the NIPA and modeled by using the theory of rubber elasticity. It was observed that elasticity increased by increasing the NIPA content for a given temperature. However, toughness, T of the copolymer presented a reverse behavior as molar % NIPA content is increased.

THEORY

If a hydrogel is in the rubberlike region then, the elastic behavior of the gel is dependent mainly on the architecture of the polymer network. At low enough temperatures, these gels can lose their rubber elastic properties and exhibit viscoelastic behavior. General characteristics of rubber elastic behavior include high extensibility generated by low mechanical stress, complete recovery after removal of the deformation, and high extensibility and recovery that are driven by entropic rather than enthalpic changes.

To derive relationship between the network characteristics and the mechanical stress-strain behavior, classical thermodynamics, statistical thermodynamics, and phenomenological approaches have been used to develop an equation of state for rubber elasticity. From classical thermodynamics the equation of state for rubber elasticity may be expressed as[7]

$$f = \left(\frac{\partial U}{\partial L}\right)_{T,V} + T\left(\frac{\partial f}{\partial T}\right)_{L,V} \tag{1}$$

where f is the refractive force of the elastomer in response to a tensile force, U is the internal energy, L is the length, V is the volume, and T is the temperature. For ideal rubber elastic behavior, the first term in Eq. (1) is zero where changes in length cause internal energy driven refractive forces. For elastomeric materials, an increase in length brings about a decrease in entropy because of changes in the end- to- end distances of the network chains. The refractive force and entropy are related through the following Maxwell equation

$$-\left(\frac{\partial S}{\partial L}\right)_{T,V} = \left(\frac{\partial f}{\partial T}\right)_{L,V} \tag{2}$$

Stress-strain analysis of the energetic and entropic contributions to the refractive force, Eq. (1) indicates that entropy accounts for more than 90% of the stress. Thus, the entropic model for rubbery elasticity is a reasonable approximation.

From statistical thermodynamics, the refractive force of an ideal elastomer may be expressed as

$$f = -\left(\frac{\partial S}{\partial L}\right)_{T,V} = -kT\left(\frac{\partial \ln \Omega(r,T)}{\partial r}\right)_{L,V} \tag{3}$$

where, k is the Boltzmann constant, r is a certain end-to-end distance, and $\Omega(r, T)$ is the probability that the polymer chain with an end to end distance r at temperature T will adopt a certain conformation. Equation (3) assumes that the internal energy contribution to the refractive force is constant or zero. Only entropy contributions to the refractive force are considered. After evaluation of Eq. (3), integration and assuming no volume change upon deformation,

the statistical thermodynamic equation of state for rubber elasticity is obtained as

$$\tau = \left(\frac{\partial A}{\partial \lambda}\right)_{T,V} = \frac{\rho RT}{\overline{M}_c}\frac{\overline{r_0^2}}{\overline{r_f^2}}\left(\lambda - \frac{1}{\lambda^2}\right) \tag{4}$$

Here, τ is the shear stress per unit area, ρ is the density of the polymer, $\overline{M_c}$ is the number average molecular weight between cross-links, and λ is the extension/compression ratio. Extension/compression ratio, λ changes by different theory[18]. The quantity $\frac{\overline{r_0^2}}{\overline{r_f^2}}$ is the front factor and is the ratio of the end to end distance in a real network versus the end to end distance of isolated chains. In the absence of knowledge concerning these values, the front factor is often approximated as 1. From Eq. (4), the elastic stress of a rubber under uniaxial extension/compression is directly proportional to the number of network chains per unit volume. This equation assumes that the network is ideal in that all chains are elastically active and contribute to the elastic stress. Network imperfections such as cycles, chain entanglements, and chain ends are not taken into account. To correct for chain ends

$$\tau = \frac{\rho RT}{\overline{M}_c}\frac{\overline{r_0^2}}{\overline{r_f^2}}\left(1 - \frac{2\overline{M_c}}{\overline{M_n}}\right)\left(\lambda - \frac{1}{\lambda^2}\right) \tag{5}$$

where $\overline{M_n}$ is the number average molecular weight of the linear polymer chains before cross-linking. This correction becomes negligible when $\overline{M_n} \rangle\rangle \overline{M_c}$.

From a constitutive relationship, the shear modulus S is then given by the following relation

$$S = \frac{\rho RT}{\overline{M}_c}\frac{\overline{r_0^2}}{\overline{r_f^2}}\left(1 - \frac{2\overline{M_c}}{\overline{M_n}}\right) \tag{6}$$

Here the force per unit area is taken as

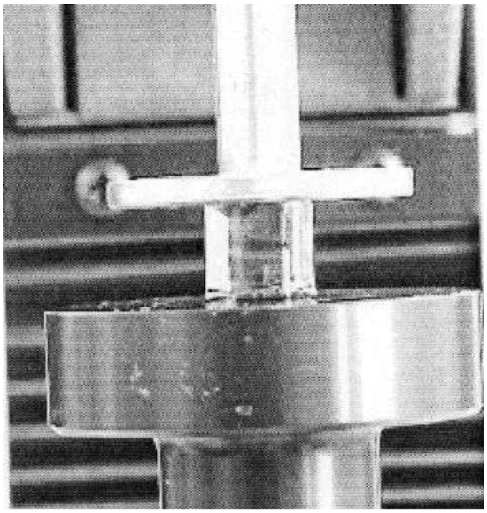
$$\tau = S\left(\lambda - \frac{1}{\lambda^2}\right) \tag{7}$$

where $\lambda = \frac{\Delta l}{l_0}$, $\Delta l = l - l_0$; l, last distance and l_0, initial distance. Note the dependence of the shear modulus on $\overline{M_c}$. Also, the stress-strain behavior of rubbery elastic materials is nonlinear. The equations are less applicable and invalid at higher elongations ($\lambda > 3$)[19]. On the other hand, toughness is determined by the underside area of linear portions of compression stress-strain curves.

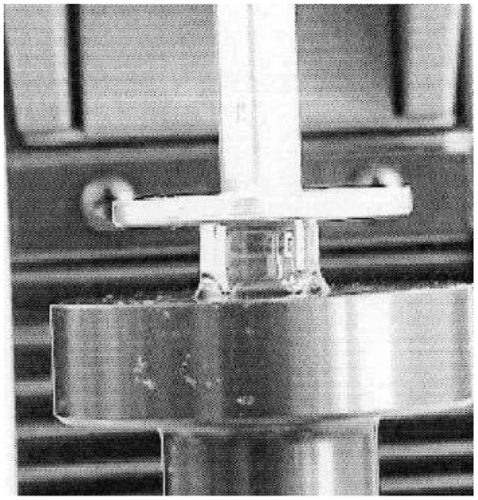
EXPERIMENT

Copolymer gels were prepared with various molar percentages of monomers of PAAm and NIPA in distilled water at room temperature by keeping total amount of 2 M. 0.01 g of BIS (N, N′-methylenebisacrylamide, Merck), 0.008 g of APS (ammonium persulfate, Merck) and 2 µl of TEMED (tetramethylethylenediamine, Merck) were dissolved in 5 ml distilled water (pH 6.5). The solution was stirred (200 rpm) for 15 min to achieve a homogenous solution. All samples were deoxygenated by bubbling nitrogen for 10 min just before the polymerization process[17].

After gelation, copolymers prepared with various molar AAm and NIPA contents were cut into discs with a 10 mm diameter and 4 mm thickness. Before the compression measurements, the copolymers were maintained in distilled water at different temperatures to achieve swelling equilibrium. A final wash of all samples with distilled water was carried out for 1 week at a desired temperature to remove unreacted repeated units and to allow the gel to



(a)



(b)

FIG. 1. Compression process of 10 molar % NIPA (a) initial (F = 0.0 N) and (b) final states (F = 5.0 N).

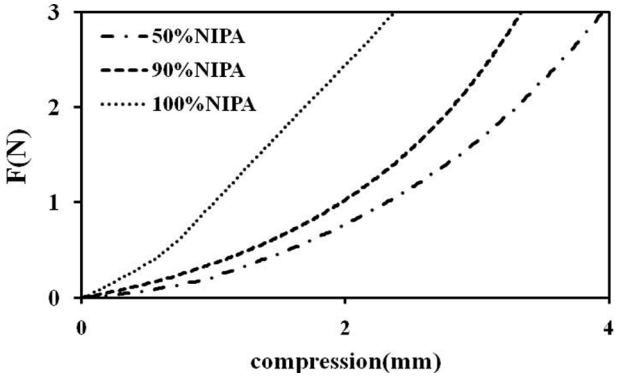


FIG. 2. The force F (N) and compression (mm) curves for 50, 90, and 100 molar % NIPA contents at 30°C, respectively.

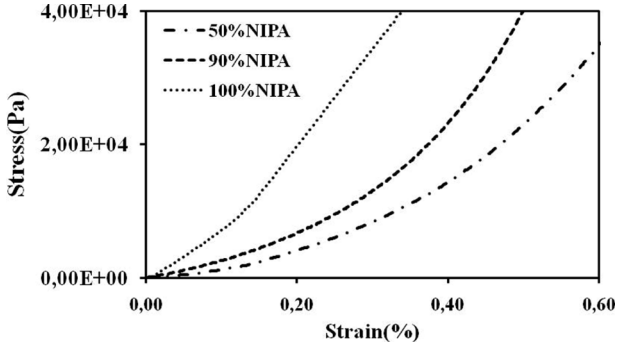


FIG. 3. Stress and strain curves 50, 90, and 100 molar % NIPA contents at 30°C.

achieve swelling equilibrium. The mechanical experiments of PAAm-NIPA copolymers were performed at 30°C. A Hounsfield H5K-S model tensile testing machine, set at crosshead speed of 1.0 cm/min, probe size of 2 cm and load cell of 5N sensibility were used to perform uniaxial compression.

Figure 1 shows to the behaviors of 10 molar % NIPA in the copolymer before and after applying the uniaxial compression. Figure 1(a) corresponds to initial state, i.e., zero loads and, Figure 1(b) presents the gel under 5N, respectively. Loss of water and changes in temperature during the measurements were not observed because the compression period was less than 1 min. Just before starting the experiment, we made a correction indicating that the curve in Figure 2 is smaller at low deformations because of the nominal surface. All samples presented this behavior. The experimental data in all compression experiments, which obtained up to about 5% deformation were rejected as given in Muniz and Geuskens[7].

RESULTS AND DISCUSSION

Forces (F) or loads corresponding to compression (mm) were obtained from the original curves of uniaxial compression experiments. The force, F (N) versus compression (mm) curves for 50, 90, and 100 molar % NIPA content gels at 30°C are shown in Figure 2, where it is seen that the repulsive force between monomers increases rapidly when the bond length is shortened with respect to the equilibrium position. When NIPA content is increased then the repulsive force increased as shown in Figure 2. The reason for this can thermodynamically be explained in that a decrease in length brings about an increase in entropy because of changes of the end to end distances of the network chains in PAAm-NIPA copolymers.

Stress (Pa)–strain plots of PAAm-NIPA gels were drawn in Figure 3 by using the data obtained from the plots of F (N) versus compression curves for 50, 90, and 100 molar % NIPA content at 30°C. The stress versus strain displays a good linear relationship at low strains, which agrees with Eq. (3). The shear modulus and toughness were obtained by using a least square fit analysis to the linear region of stress (Pa) - strain plots and are listed in Table 1.

The addition of NIPA into PAAm caused an increase in compressive elastic modulus for all NIPA content gels. Thus, pure NIPA content copolymer is found to possess approximately 1.5 times higher modulus than pure PAAm sample. It is seen in Figure 3 that 50 molar % NIPA content gel has smaller initial slope than 90 molar % NIPA content gel. In this case, it appears that the hydrophobic interactions between PAAm and NIPA monomers play an important role for obtaining the varying onset behavior. The stress of 50, 90, and 100 molar % NIPA content copolymers increases dramatically when the strain exceeds 0.6%, where the NIPA monomers have taken the responsibility in the copolymer.

Figures 4(a) and (b) show the plot of shear modulus, S and toughness, T versus molar % NIPA content in the copolymer, respectively. Shear modulus increases progressively by increasing NIPA content, indicating that there is a change in the material elasticity. Most probably the sudden

TABLE 1
Shear modulus and toughness for various molar % NIPA contents at 30°C

Sample		T = 30°C	
PAAm (%)	NIPA Molar (%)	S (MPa)	T (kPa)
100	0	0.0358 ± 0.0018	3.74 ± 0.16
90	10	0.0457 ± 0.0004	2.33 ± 0.07
75	25	0.0567 ± 0.0022	2.10 ± 0.05
50	50	0.0758 ± 0.0025	1.84 ± 0.06
25	75	0.0781 ± 0.0009	1.79 ± 0.06
10	90	0.0941 ± 0.0019	1.76 ± 0.06
0	100	0.1154 ± 0.0046	1.12 ± 0.08

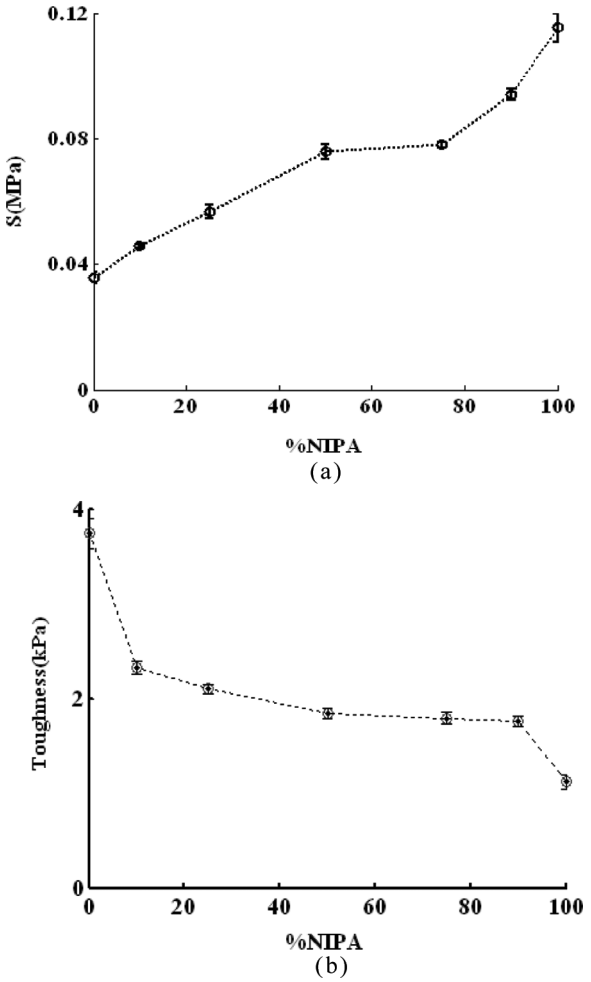


FIG. 4. Effect of various molar % NIPA on the (a) shear modulus (S) and (b) toughness (T) of PAAm-NIPA copolymer at 30°C.

change in S predicts that the copolymers have reached a super elastic percolation network in the gel. Further increase in NIPA content produce an infinite network, which results in an increase in the elasticity and decrease in toughness as was expected for the copolymer gels at high NIPA content. This can be explained for the reason that an increase shear modulus, S or decreasing toughness, T as shown in Figure 4 can be explained by increasing NIPA content in the gel, which forms a hydrophobic network that significantly improves the stress relaxation of copolymer.

Due to the high hydrophobic ability of NIPA network, the elastic properties of the gel composite can be influenced substantially. This must suggest that the collapsed phase has a network structure with flexible polymer chains just as swollen phase. It was identified that whole stress relaxation of PAAm-NIPA copolymers is composed of three contributions: relaxation observed commonly for elastomer, breakdown of physical cross-links, and swelling induced relaxations[20].

Lastly, we believe in that the elastic properties of PAAm-NIPA copolymers are highly dependent on the molar % NIPA content, which directly influences the repeated units' interactions between PAAm and NIPA in the copolymers. Such the repeated units' interactions will play a critical role in the load transfer and interfacial bonding that determines the elastic properties of the copolymers. The variations in the NIPA content in the resultant copolymer could be the major reason for this phenomenon.

CONCLUSION

In this work tensile testing technique was used to determine elastic behavior of PAAm-NIPA copolymer for various molar percentages of NIPA content. This technique was employed to measure force versus compression, strain and yield for the copolymers. The behavior of compressive elastic modulus was explained by the theory of rubber elasticity. It is important to note that compressive elastic modulus of the copolymers is larger in the high NIPA content region of the copolymer than in the low NIPA content, less elastic region.

Here, experiments were done with dynamical compression technique with a piston velocity of (1 cm/min), which can be considered as the nonequilibrium case. We applied equilibrium statistical theory to produce our results. This application seems to contradict the experimental method. However, since we are dealing with the cross-linked network, whose relaxation time is so slow compared to the compression time, then at the first approximation, this situation can be considered as an equilibrium state of the system under consideration. On the other hand we may argue that if the compression experiments were done using a static compression technique, the produced curves might be slightly steeper than the produced ones, which may result in slightly larger slopes and larger shear modulus compared to the modules given in Table 1.

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