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Regular Article

Universality of elasticity on PAAM-NIPA copolymer gels

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Abstract. Polyacrylamide (PAAm)-N-isopropylacrylamide (NIPA) copolymers were prepared via free radical crosslinking copolymerization with different molar of NIPA varying in the range between 0 and 2 M. The mechanical properties of swollen PAAm-NIPA copolymers were characterized by the compressive testing technique. It is understood that the compressive elastic modulus was found to increase by increasing NIPA contents, keeping temperature constant at 30 °C. The critical exponent of elasticity, y above the critical NIPA concentration is found to be as 0.74, which is consistent with the suggestions of percolation for superelastic percolation network (SEPN) and the critical theory for PAAm-NIPA copolymers.

1 Introduction

There has been considerable interest in using percolation theory to model the static elasticity and vibrational dynamics of random systems over the past years. This is because of the relatively simple structure of a percolating network, which makes theoretical prediction and numerical simulation of the physical behavior feasible. The static elasticity of random percolating structures is of particular interest since the various different microscopic elasticity models predict vastly different critical exponents. A percolation system, being fractal at short systems which manifest similar behavior [1]. The first experimental system in which these predictions were tested consisted of sintered metal powders. Deptuck et al. performed measurements on beams of sintered, submicron, silver powder and found that the elasticity critical exponent was significantly greater than the conductivity critical exponent [2]. Relation between percolation theory and the elasticity of gels was performed by P.G. de Gennes theoretically [3]. The macroscopic conductance of a resistor network with a fraction p of conducting links, and the elastic modulus E of a gel was obtained by polymerization of z-functional units. Bond percolation on elastic networks involving nearest neighbor forces was studied by numerical simulations [4]. With purely central forces, the bulk and shear module go to zero, with exponent f and at a threshold p_{cen}. Elastic properties of random percolating systems in the critical region were studied by Kantor and Webman [5]. Hamiltonian was chosen to represent correctly the elastic behavior of continuous random composites made up rigid

regions and very soft regions near the percolation threshold. This result is relevant to experiments on such systems. Critical exponent and transitions in swollen polymer networks and in linear macromolecules were performed by Erman and Flory [6]. Critical behavior was found for the single chain and long chain limit. Imperfect duality, critical Poisson ratios and relations between microscopic models were described [7]. The connections between the elasticity and the superelasticity percolation problems were investigated in the case of the two dimensional granular model. Two superelastic percolation models were proposed to explain the observed behavior of the viscosity of gels near the gel point [8]. Critical properties of viscoelasticity of gels and elastic percolation networks were modeled on the Zimm limit. The scaling form for the correction dependence of viscosity in theta (θ) solvents and derivation the concentration dependences of the plateau modulus and longest relaxation time were explained by Colby and Rubinstein [9]. The two length scales depend on concentration differently in theta solvents. The viscosity and the modulus of near critical polyester gels were reported and modeled by Rouse model [10]. Scaling ideas were used to predict the modulus of the gels and equilibrium swelling of near critical gels. Bond and site percolation on two and three dimensional elastic and superelastic percolation networks with central forces were studied using large scale Monte Carlo simulations and finite size scaling analysis [11]. The critical exponents of the elastic modulus and correlation length of the system for the *bcc* network were determined. Elastic modulus and equilibrium swelling of near critical gels were performed theoretically [12]. The concentration dependence of the modulus when the gel was diluted in a good solvent was also calculated and

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used to predict the maximum swelling. The elastic properties of random networks of Hooke springs were examined under a tension supplied by a frame [13]. Although these networks were nonlinear, a harmonic approximation can be made that leaded to a very good effective medium theory of the phase boundary. Universality and specificity of polymer gels viewed by scattering methods were studied for various types of gels, including physical gels, and composite gels by a reviewer article [14]. The time correlation function of the scattering intensity entailed a power law behavior at the sol-gel transition.

The aim of the present study is to understand the effect of NIPA concentration on the swollen PAAm-NIPA copolymers elastic behavior and to determine the critical exponent of elasticity, experimentally. In this study, copolymer gel systems are produced by the inclusion of acrylamide and NIPA, which are capable of converting the system from hydrophilic to hydrophobic state when the amount of the addition exceeds a critical value known as the percolation threshold which the copolymer reached at 1 M NIPA. The observed elasticity is increased by increasing NIPA content with critical exponent around $y = 0.74$ which is indicative of superelastic percolation network (SEPN). The elastic percolation threshold agrees with the suggestions of percolation for SEPN and the critical theory for PAAm-NIPA copolymers.

2 Theory

2.1 Mechanical properties

When a hydrogel is in the rubberlike region, the mechanical 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.

In order 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 [15]:

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

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 equation (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, equation (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 equation (3), integration and assuming no volume change upon deformation, the statistical thermodynamic equation of state for rubber elasticity is obtained below:

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

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 [16]. The quantity $\frac{\overline{r_0^2}}{r_f^2}$ 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 equation (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:

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

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

From constitutive relationship, the compressive elastic modulus S is then:

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

And the force per unit area is:

$$\tau = S\lambda, \tag{7}$$

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 compressive elastic 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 ($\lambda > 3$) [17]. On the other hand, toughness can be calculated from the area under the slope of strain and stress.

2.2 Percolation on elastic networks

Consider a percolation network whose bonds represent elastic springs that can be stretched and/or bent. The elastic energy of the system is given by [18]:

$$E = \frac{\alpha_1}{2} \sum_{\prec ij \succ} \left[(u_i - u_j) R_{ij} \right]^2 e_{ij} + \frac{\alpha^2}{2} \sum_{\prec jik \succ} (\delta\theta_{jik})^2 e_{ij}e_{ik}, \tag{8}$$

where the first term of the right side represents the contribution of the stretching or central forces (CFs), whereas the second term represents the contribution of angle-changing or bond bending (BB) force. Here $\propto_1$ and $\propto_2$ are the central and BB force constants, respectively, $u_i = (u_{ix}, u_{iy}, u_{iz})$ is the (infinitesimal) displacement of site i, R_{ij} is a unit vector from i to j, e_{ij} is the elastic constant of the (spring) between i and j, and $\prec jik \succ$ indicates that the sum is over all triplets in which the bonds j-i and i-k form an angle whose vertex is at i. The change of angle $\delta\theta_{jik}$ is given by:

see equation (9) *at the bottom of this page.*

where $u_{ij} = u_i - u_j$. We can now define the elastic properties of percolation networks. Suppose that the elastic constants e_{ij} can be chosen from a distribution.

As the model of disordered materials, each bond on disordered materials represents an elastic element, or a spring, with an elastic constant, e and the rest have an elastic constant b which can take on values from a probability density function $H(e)$. In most cases, the binary distribution:

$$H(e) = p\delta(e - a) + (1 - p)\delta(e - b), \tag{10}$$

e takes the values a and b with probability p and $1 - p$, respectively. If $b = 0$ and a is finite, system is called elastic percolation network (EPN) and defined S_e as the effective elastic module of the network. If $a = \infty$ and b is finite, a fraction p of the springs are totally rigid and the rest are soft, system is called a superelastic percolation

Table 1. Critical exponents for elastic and superelastic percolation networks for three dimensions and in the mean field approximation [18].

	x	y
$d = 3$	2.1	0.65
$d \geq 6$	3	0

network (SEPN) and defined S_s as the effective elastic module of a superelastic percolation network. As the percolation threshold p_c of an EPN is approached from above, all compressive elastic modulus S of the system vanish. Near the percolation threshold, p_c, the effective elastic module of the network, S_e obeys the following scaling law [18]:

$$S_e(p) \approx (p - p_c)^x, \tag{11}$$

where x is the critical exponent for EPN. Whereas, in a SEPN all elastic modulus diverge as p_c is approached from below according to:

$$S_s(p) \approx (p_c - p)^{-y}, \tag{12}$$

where y is the critical exponent for SEPN. x and y are given in Table 1 which includes critical exponents of elastic and superelastic percolation networks for three dimensions and in the mean field approximation [18].

3 Experimental

3.1 Preparation of copolymer

Copolymer gel was prepared with various molar percentages of monomers of PAAm and NIPA mixture in distilled water at room temperature by keeping the total molarities as 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 polymerization process starts [19].

3.2 Mechanical measurements

After gelation, the gels prepared with various monomer contents were cut into disks with 10 mm in diameter and 4 mm in thickness. Before the compression measurements, the copolymers were maintained in water at different

$$\delta\theta_{jik} = \{(u_{ij} \times R_{ij} - u_{ik} \times R_{ik}) \cdot (R_{ik} \times R_{ik}) / |R_{ij} \times R_{ik}| \quad R_{ij} \text{ not parallel to } R_{ik}$$

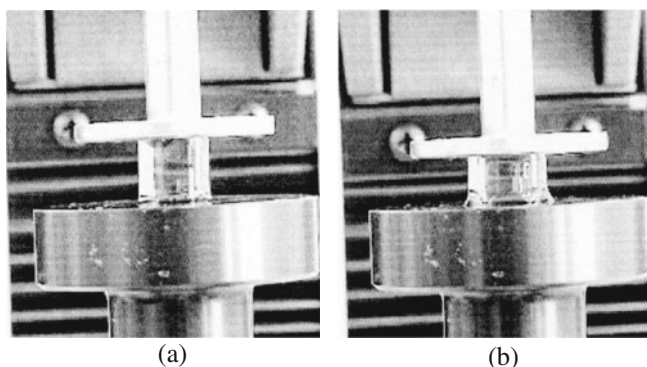$$\delta\theta_{jik} = \{|(u_{ij} + u_{ik}) \times R_{ij}| \quad R_{ij} \text{ parallel to } R_{ik} \tag{9}$$

Fig. 1. Compression process of 0.2 M 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 0.5 and 1.5 M NIPA content at 30 °C.

Fig. 3. Stress and strain curves for 0.5 and 1.5 M NIPA content at 30 °C.

temperatures to achieve swelling equilibrium. A final wash of all samples was with deionized water for 1 week. The mechanical experiments of PAAm-NIPA gels were performed at 30 °C. Hounsfield H5K-S model tensile testing machine, settled a crosshead speed of 1.0 cm/min and a load capacity of 5N was used to perform uniaxial compression experiments on the samples of each type of composite gels. Figure 1 shows the behaviors of PAAm-NIPA copolymers before and after applying the uniaxial compression. Figure 1a corresponds to initial state, i.e., zero loads and, Figure 1b presents the gel under 5N, respectively. Any loss of water and changing in temperature during the measurements was not observed because of the compression period being less than 1 min. There is no deswelling during the compressive deformation stage: which means that our experiment corresponds to the case where we can assume the compressive elastic modulus, S is uniform, which of each composite was determined from the slope of the linear portions of compression stress-strain curves, using equation (7).

4 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 0.5 M and 1.5 M NIPA at 30 °C are shown in Figure 2. The repulsive force between monomers increases rapidly when the bond length is shorten from the equilibrium position. For low NIPA content gel, repulsive force increased more rapidly when compression is increased. The reason can be thermodynamically explained that a decrease in length brings about an increase in entropy because of changes in the end-to-end distances of the network chains of PAAm-NIPA copolymer gels.

Stress (Pa)-strain plots in Figure 3 for low and high NIPA content gels were drawn by using the data obtained from the linear region observed in the plots of F (N) and compression curves for 0.5 M and 1.5 M NIPA in
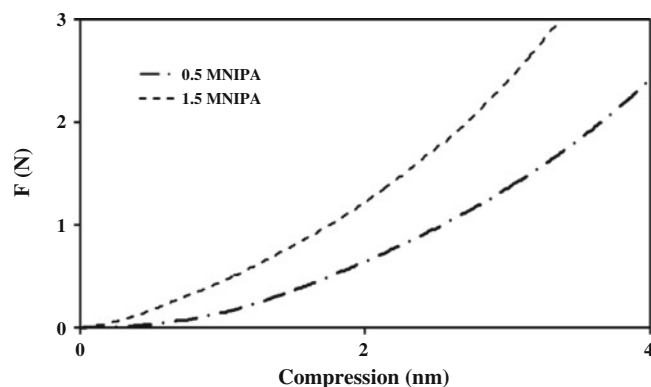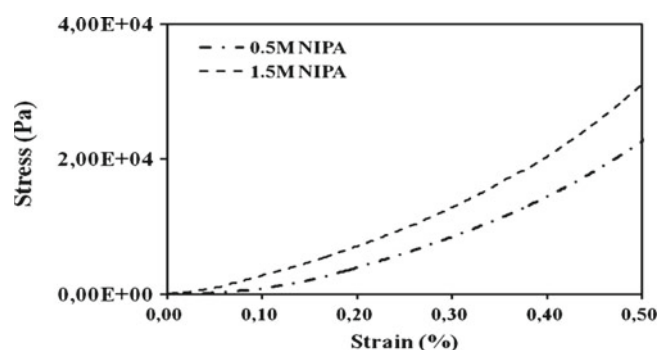
the copolymer at 30 °C. The stress-strain curves display a good linear relationship at 30 °C, which agrees with equation (7).

The compressive elastic modulus was obtained by a least square fit analysis to the linear region observed. The values of compressive elastic modulus and dimensions of the copolymers were placed in Table 2. For pure PAAm gels, the value of the compressive elastic modulus was found 0.0358 MPa at 30 °C. The addition of NIPA has increased the modulus of the copolymer as expected. In 2 M NIPA, the measured compressive elastic modulus is 0.1154 MPa. Thus, pure NIPA is found to possess one and half times higher modulus than pure PAAm. It is seen in Figure 3 that, 0.5 M NIPA copolymer has smaller initial stress-strain slope than 1.5 M NIPA copolymer. In this case, it appears that the hydrophobic interactions between PAAm and NIPA monomers play an important role for producing the different onset behavior. The stress of the PAAm-NIPA copolymer increases dramatically when the strain exceeds about 0.6% strain, where the NIPA monomers are taking responsibility in the copolymer gel. In Figure 3, the increase in mechanical (parameter the slope of stress and strain curve at higher NIPA content) can be explained that increasing NIPA forms a hydrophobic network which significantly improves the stress relaxation of copolymer.

Table 2. Some experimental and calculated parameters of PAAm-NIPA copolymers at 30 °C.

PAAm (M)	NIPA (M)	R (mm)	h (mm)	S (MPa)
2	0	8.06	5.84	0.0358
1.8	0.2	11.6	11.1	0.0457
1.5	0.5	11.5	7.9	0.0567
1.6	0.6	11.0	7.5	0.0758
1	1	11.6	7.2	0.0758
0.8	1.2	11.1	7.3	0.077
0.5	1.5	11.2	6.8	0.0781
0.2	1.8	10.6	7.1	0.0941
0	2	8.0	5.0	0.1154

Figure 4 shows that compressive elastic modulus depend on the content of NIPA in the copolymer gel, where compressive elastic modulus increases progressively by increasing NIPA content, indicating that there is a change in the copolymer's structure. This change in S predicts that the copolymers have reached a super elastic percolation network. To determine the percolation threshold, the derivative of compressive elastic modulus with respect to NIPA content was taken by using the Matlab programme of moving derivative. The percolation threshold was found as 1 M NIPA where the monomers form hydrophilic and hydrophobic equilibrium, exhibiting a high degree of NIPA and PAAm monomers interactions and/or entanglement. The effect of increasing NIPA content in reducing the swelling and in increasing compressive elastic modulus was an expected result for copolymers having NIPA.

The reason can be thermodynamically explained by a decrease in length brings about an increase in entropy because of changes in the end-to-end distances of the network chains of PAAm-NIPA copolymer gels. Thus, the entropic model for copolymer elasticity is a reasonable approximation. In other words, the effect of increasing NIPA content in increasing the modulus was an expected result.

The increase in compressive elastic modulus can be explained by the collapsed phase which has a network structure with flexible polymer chains just as in 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 crosslinks and swelling induced relaxation. On the other hand, the modulus increases because the swelling and hence the osmotic (bulk) modulus decreases as NIPA is added to the copolymer. Another explanation; the compressive elastic modulus increases as NIPA is added because the free chain size decreases [20].

Lastly, we believe that the elastic properties of copolymer gel are highly dependent on NIPA content, which directly influences PAAm-NIPA monomers interactions in the copolymers. The monomer's interactions will play a critical role in load transfer and interfacial bonding that determines elastic properties of the copolymers. The variations in the NIPA content in the resultant copolymer could be the major reason for this phenomenon.
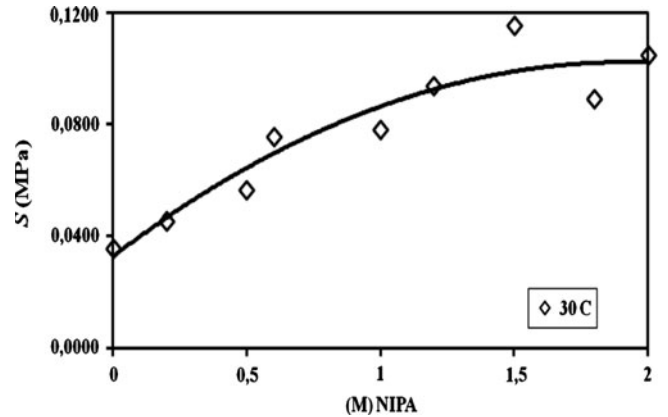
Fig. 4. Compressive elastic modulus dependence on concentration of molar NIPA in the copolymer.
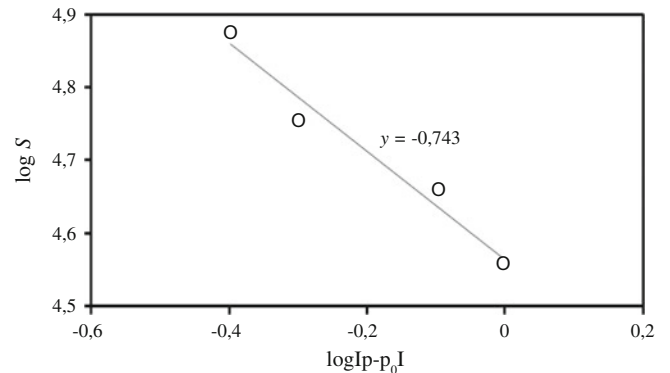
Fig. 5. Logarithmic plot of the compressive elastic modulus versus NIPA contents curves for $p < p_c$. The y exponent ($y = 0.743$) was determined from the slope of the straight line.

The value of the fitting exponent y in equation 12 was estimated from the slope of the linear relation in $\log S - \log |p - p_c|$ at $p < p_c$ as shown in Figure 5. At $p > p_c$, nonuniversal behavior might be explained by the samples corresponding to different areas of the static crossover between the mean field and the critical percolation [10]. Elastic percolation occurs at 1 M NIPA (as shown in Fig. 4) with a critical exponent around $y \approx 0.74$ which is close to the theoretical prediction of this value in the 3D percolated system known as a superelastic percolation network (SEPN). The observed critical exponent, y agrees with literature [10,18]. On the other hand, the elasticity of the polyacrylamide (PAAm)-kappa carrageenan (κC) composite was previously studied by us, as a function of (w/v-%) kappa carrageenan (κC) content at 40 °C [21]. In PAAm-κC system, the elastic percolation threshold occurred at 1.0 (w/v-%) of κC content in the percolation region with a critical exponent around $y \approx 0.68$ which is in good agreement with superelastic percolation network (SEPN). Besides PAAm-κC system, elastic percolation study on the polyacrylamide (PAAm)-multiwalled carbon nanotubes (MWNTs) composites were also reported [22], where compressive elastic modulus increased dramatically up to 1 (wt.%) MWNT by increasing nanotube content, and then decreased presenting a

critical MWNT value indicating that there is a sudden change in the material elasticity. The critical exponent, y of elasticity, below the critical MWNT content, 1 (wt.%) was found to be 0.58 which is consistent with the suggestions of the model for the superelastic percolation network (SEPN) for PAAm-MWNT composite. When the results of the work for PAAm-NIPA system, reported in this article were compared with the results of PAAm-κC and PAAm-MWNTs composite systems, it is seen that both results are in good agreement with the superelastic percolation network (SEPN), and are close to the theoretical prediction of the critical parameters in 3D percolated system.

5 Conclusions

The mechanical measurement by the compressive testing machine used to characterize PAAm-NIPA copolymer gel. The behavior of compressive elastic modulus explained that a decrease in length brings about an increase in entropy because of changes in the end-to-end distances of the network chains of PAAm-NIPA copolymer gel. Thus, the entropic model for copolymer elasticity is a reasonable approximation.

The elastic percolation occurs above 1 M NIPA with the critical exponent of $y = 0.74$ which is close to the theoretical prediction of this value in a 3D percolated system ($y = 0.65$) and $y = 0.88$ in the critical theory [10,18]. The produced critical exponent y is consistent with the suggestions for the percolation for superelastic percolation network (SEPN) (see Tab. 1) and the critical theory for PAAm-NIPA copolymers.

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