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Temperature Effect on Elasticity of Swollen Composite Formed from Polyacrylamide (PAAm)-Multiwall Carbon Nanotubes (MWNTs)

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ABSTRACT

Composites formed from Polyacrylamide (PAAm)-Multiwalled carbon nanotubes (MWNTs) were prepared via free radical crosslinking copolymerization with different amounts of MWNTs varying in the range between 0.1 and 50 wt%. The temperature variations of the elastic modulus, *G* of the PAAm-MWNT composite due to volume phase transition were measured by using tensile testing technique. The composite preserves the ability to undergo the volume phase transition and its elastic modulus and toughness (*T*) are found strongly dependent on temperature. 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.

Keywords: Acrylamide; Multiwalled Carbon Nanotubes; Swelling; Mechanical Properties

1. Introduction

Carbon nanotubes (CNTs) can be described as long and slender fullerenes, in which the walls of the tubes are hexagonal carbon (graphite structure). These tubes can either be single (SWNT) or multiwalled (MWNT). They have high aspect ratios and unique, mechanical, thermal, and electrical properties. The CNTs have many interesting and unique properties potentially useful in a variety of biological and biomedical systems and devices including tissue engineering, biosensors, drug delivery, imaging, and cancer treatment [1]. The high mechanical strength makes them attractive materials for polymer reinforcement. Hydrogel-CNT composites were demonstrated for potential applications such as actuators with DC electric field as the stimulus and sensors for the detection of a variety of biomolecules including ethanol, glutamate, and glucose [1,2].

A novel hybrid gelatin hydrogel with carbon nanotubes was synthesized by a physical mixing method, characterized by SEM and swelling behavior was measured at 25°C and 37°C [3]. Synthesis and swelling of a novel gelatin-carbon nanotubes hybrid hydrogel were studied at different temperatures. This hydrogel could be used in biomedical field [4]. The mechanical properties of carbon nanotube-polymer composites were presented in a review article which includes properties of nanotubes, theory of fiber reinforced composite materials, and composite processing [5]. Swelling and mechanical behaviors of carbon nanotube/poly(vinyl alcohol) hybrid hydrogels were investigated and it was observed that tensile modulus, and tensile strength were increased at 0.5 wt% MWNT [6]. Electrical and rheological percolations in polystyrene/MWNT nanocomposites were reported [7]. Percolation threshold was found for these nanocomposites at 2 vol% MWNT. The experimental results indicated that the elastic load transfer and electrical conductivity were found to be sensitive to the onset of percolation than the viscous dissipation in the nanocomposites [7]. Nanohybrid hydrogels with micro or mesopores were designed and synthesized in the case of polyacrylamide and multiwalled carbon nanotube (MWNT) and hydroxyl functionalized MWNT.

Investigations indicated that the addition of carbon nanotubes can induce and/or improve swelling when the temperature increased from 25°C to 42°C [8]. The morphology, swelling behavior, and mechanical properties of the nanocomposites were characterized to evaluate the effect of adding different amounts of MWNT to the hydrogel. The mechanical properties of the nanocomposites were studied over a range of temperatures (25°C - 55°C) to characterize the effect of nanotube addition [1]. The temperature and pH sensitivity, on mechanical strength and the response rates of poly (N,N-diethylacrylamide-

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co-acrylic acid) composites were studied and found that the tensile strength of the composite hydrogel is as poor as that without modification [9]. The strong stretch of network strands and its effect on modulus and equilibrium swelling were observed by Rubinstein *et al.* [10]. Elastic and osmotic behavior and network imperfections of nonionic and weakly ionized acrylamide based on hydrogels were investigated as a function of swelling degree and initial total monomer concentration [11]. Physical mechanism for the mechanical reinforcement in nanotube-polymer composite materials was modeled by Frenkel-Kontorova model which was potentially capable of predicting the ideal combination of polymers and nanotube diameters [12]. A review of modeling techniques for predicting the mechanical behavior of polymer nanocomposites was presented where detailed discussion of computational chemistry and mechanics modeling techniques were given [13]. The mechanical properties of multiwalled carbon nanotubes(MWNT)/poly(methyl methacrylate) (PMMA) nanocomposites were studied as a function of nanotube orientation, length, concentration, and type [14]. A critical review on nanotube and nanotube/nanoclay related to polymer composite materials was introduced in detail [15]. The relation between the structure and the viscoelastic behavior of a model polymer nanocomposite system based on a mixture of titanium dioxide nanoparticles and polypropylene was investigated. Above a critical volume fraction, the elasticity of the hybrids increased dramatically, and the frequency dependence of the elastic and viscous module reflected the superposition of the independent responses of the suspending polymer melt and of an elastic particle network [16].

In this work, the elastic modulus and toughness of the swollen PAAm-MWNT composites were measured to determine the effect of temperature on elasticity. Elasticity measurement was performed by tensile testing technique and modeled by the theory of rubber elasticity. Investigations indicated that the addition of carbon nanotubes can induce an improved elasticity by increasing the temperature from 30°C to 60°C. The temperature effect on the elastic modulus might be due to an electrostatic interaction between the amide groups of PAAm networks and the MWNT covered and/or the association/dissociation of hydrogen bonding between the free amino groups in PAAm network [10].

2. Theoretical Background

2.1. Network Elasticity

If a polymer network is in the rubberlike region, then the elastic behavior of the gel is dependent mainly on the architecture of the network. These gels lose their rubber elastic properties when the temperature is low enough

and exhibit viscoelastic behavior. It has been well known that 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.

A relationship can be derived from 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. The equation of state for rubber elasticity in classical thermodynamics may be expressed as [17]

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

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

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

Stress-strain analysis of the energetic and entropic contributes 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.

The refractive force of an ideal elastomer may be expressed as follows

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

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's 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

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

Here, τ is the shear stress per unit area, ρ is the den-

sity of the polymer, $\overline{M_c}$ is the number average molecular weight between cross-links, and λ is the extension/compression ratio. λ changes by different theories [18]. The quantity $\dfrac{\overline{r_0^2}}{\overline{r_f^2}}$ 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 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

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

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

From constitutive relationship, the elastic modulus G is then

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

And the force per unit area is

$$\tau = G\lambda \qquad (7)$$

where, $\lambda = \dfrac{\Delta l}{l_0}$, $\Delta l = l - l_0$; l, last distance and l_0, initial distance. Note the dependence of the 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 ($\lambda > 3$) [19].

3. Experimental

In this work MWNT which was analyzed by the Delta Nu Advantage 532 Raman Spectrometer with 100 - 3400 wave number spectral range (Cheap Tubes Inc., USA) with a length of 20 - 30 nm, and a diameter of 10 - 30 nm were used. The purity of the MWNT was >95 wt%.

Initially, the stock solution is composed of MWNT, PVP and water, in the proportions of 10 parts MWNTs: 1 - 2 parts PVP: 2000 parts distilled water at room temperature. The required dispersion time is approximately 5 or 6 minutes with an interruption of 10 seconds, every 30 seconds at full or high amplitude by using ALEX ultrasonic equipment.

Composite gels were prepared by using 2M AAm (Acrylamide, Merck) with various amounts 0.1 wt% - 50 wt% of MWNT content at room temperature. AAm, the monomer; BIS (N,N' methylenebisacrylamide, Merck), the crosslinker; APS (ammonium persulfate), the initiator; and TEMED (tetramethylethylenediamine, Merck), the accelerator were dissolved in distilled water. 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.

After gelation was completed, the composites were cut into discs with 10 mm in diameter and 4 mm in thickness from the injector. The composites were kept in water at 30°C to achieve swelling equilibrium before the compression measurements. A final wash of all samples was with deionized water for 1 week.

Hounsfield H5K-S model tensile testing machine, settled a crosshead speed of 1.0 cm/min and a load capacity of 5 N was used to perform uniaxial compression experiments on the samples of each type of composite gels. No water loss was observed during the measurements because of the compression period being less than 1 min. There is no deswelling during the compressive deformation stage: this means that our experiment corresponds to the case where we can assume that the uniform elastic modulus, G is infinite. Elastic modulus and toughness were measured at 30°C, 40°C, 50°C and 60°C temperatures. The elastic modulus of each composite was determined by the slope of the linear portions of compression stress-strain curves, using Equation (7). Toughness is measured by the underneath area of linear portions of compression stress- strain curves.

4. Result 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 at 30°C and 40°C for 0.3 wt% MWNT are shown in **Figure 1(a)**.

The repulsive force between atoms increases slowly when the bond length is shorten from the equilibrium position. If temperature increases for this MWNT content composite, then repulsive force increases, presenting larger numbers [20].

On the other hand, **Figure 1(b)** presented force, F(N) versus compression (mm) curves at 30 and 60°C for 5 wt% MWNT samples, presenting the reverse behavior compared to the low MWNT composite. If temperature increases for this high MWNT content composite, repulsive force presents smaller values as shown in **Figure 1(b)**.

Stress (Pa)-Strain plots of 0.3 and 5 wt% MWNTs contents composites were drawn by using the data observed in the plots of F(N) versus compression curves at 30°C, 40°C and 30°C, 60°C in **Figures 2(a)** and **(b)**, re-
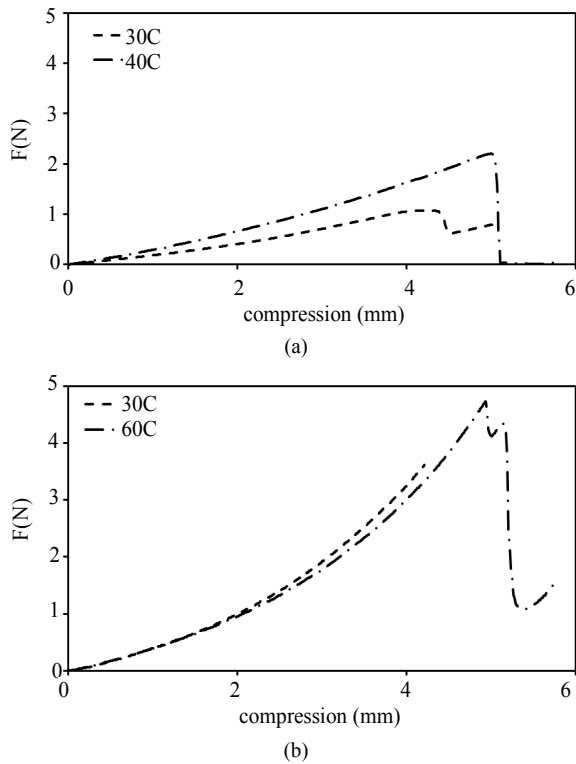
Figure 1. The Force F(N) and compression (mm) curves for (a) 0.3 wt% low MWNT content at 30°C and 40°C; and (b) 5 wt% high MWNT content at 30°C and 60°C, respectively.
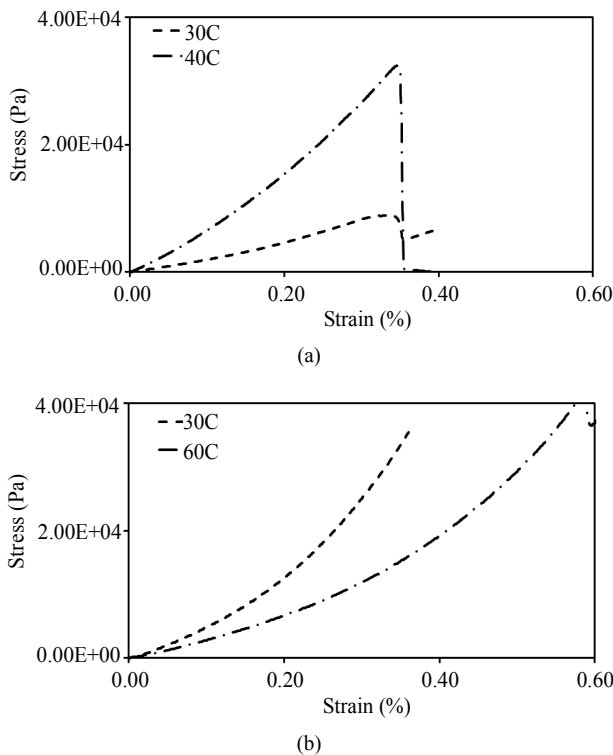

Figure 2. Stress versus strain curves (a) 0.3 wt% low MWNT content at 30°C and 40°C; and (b) 5 wt% high MWNT content at 30°C and 60°C, respectively.

spectively. It is seen in **Figure 2(a)** that 0.3 wt% MWNT composite at 30°C has smaller initial slope than at 40°C. In this case, it appears that the alignment effect of MWNT plays an unimportant role at this temperature [8]. The stress of the 0.3 wt% MWNT composite at 40°C increases dramatically when the strain exceeds 0.4%, where most probably the considerable amount of alignment is taking place in the composite. On the other hand, for high MWNT content, the composites are highly hydrated at lower temperatures and have more mechanical strength and hence increasing temperature leads to poor elastic properties.

Elastic modulus, G and toughness, T of low MWNTs contents composites for different temperatures are plotted by using the data produced from the linear regions observed in the plots of stress-strain curves **Figures 3(a)** and **(b)**, respectively. There can be seen an increase in elastic modulus and a decrease in toughness for low MWNT content composites, as the temperature increased.

Similarly, **Figures 4(a)** and **(b)** present elastic modulus and toughness for high MWNTs content composites against temperatures, respectively. It is seen in **Figure 4** that high content MWNT composites show an increase in elastic modulus and decrease in the toughness, presenting the similar behavior with the low MWNT composites. When elastic modulus increases, then toughness decreases by increasing temperatures due to the electrostatic interaction between the amide groups of PAAm networks and the MWNTs covered and the associa-
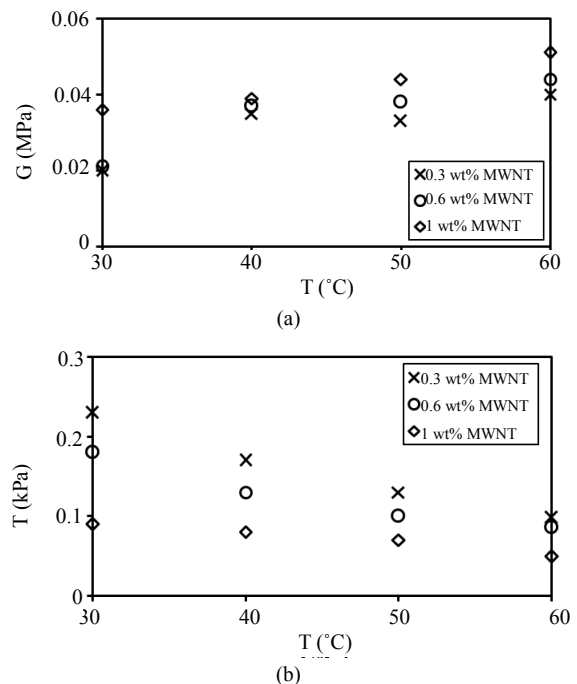

Figure 3. Effect of temperature on the (a) Elasticity and (b) Toughness of PAAm-MWNT composite for low MWNT content, respectively.
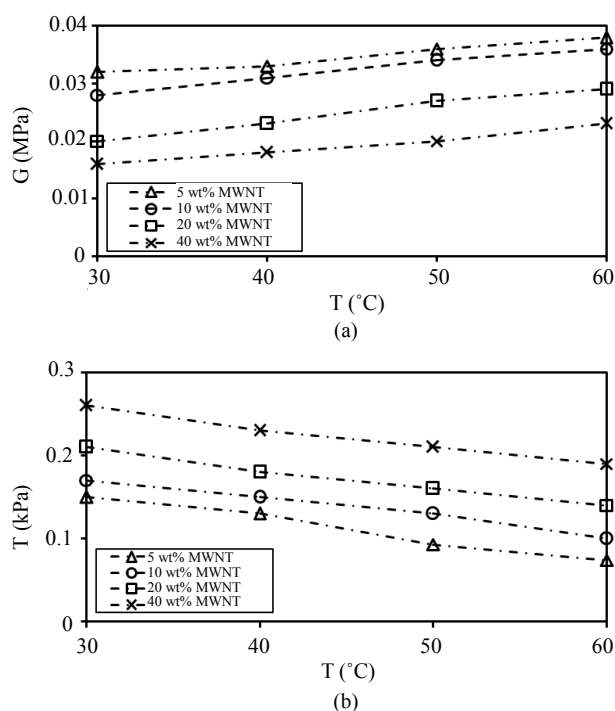
Figure 4. Effect of temperature on the (a) Elasticity and (b) Toughness of PAAm-MWNT composite for high MWNT content, respectively.

tion/dissociation of hydrogen bonding between the free amino groups in PAAm network [10].

5. Conclusion

Tensile testing technique can be used to study elastic behavior of PAAm-MWNT composite for various MWNT content and temperatures. This technique was employed to measure force versus compression, strain and yield for the composites. The behavior of elastic modulus was explained by the theory of rubber elasticity. Investigations indicated that elastic modulus can be improved between the temperatures of 30˚C and 60˚C. In other words increasing the temperature above the glass transition temperature of PAAm, composite's toughness decreases, which results in an increase in elastic modulus of the composite. It is also seen that increase in MWNT content in the composite produces a high toughness and naturally low elasticity in the PAAm-MWNT composites at high MWNT content samples. However, at low MWNT content samples the picture is quite different *i.e*. Elastic modulus and toughness behave almost similar at high temperature region, but at low temperature results are distinguishable, and low MWNT content sample presents high toughness and low elasticity.

REFERENCES

[1] N. S. Satarkar, D. Johnson, B. Marrs, R. Andrews, C. Poh,

B. Gharaibeh, K. Saito, K. W. Anderson and J. Z. Hilt, "Hydrogel-MWNT Nanocomposites: Synthesis, Characterization, and Heating with Radiofrequency Fields," *Journal of Applied Polymer Science*, Vol. 117, 2010, pp. 1813-1819.

[2] E. Fernandez, D. Lopez, E. L. Cabarcos and C. Mijangos, "Viscoelastic and Swelling Properties of Glucose Oxidase Loaded Polyacrylamide Hydrogels and the Evalution of Their Properties as Glucose Sensors," *Polymer*, Vol. 46, No. 7, 2005, pp. 2211-2217. doi:10.1016/j.polymer.2004.12.039

[3] H. Li, D. Q. Wang, H. L. Chen, B. L. Liu and L. Z. Gao, "A Novel Gelatin-Carbon Nanotubes Hybrid Hydrogel," *Macromolecular Biosciences*, Vol. 3, No. 12, 2003, pp. 720-724. doi:10.1002/mabi.200300034

[4] H. Li, D. Q. Wang, H. L. Chen, B. L. Liu and L. Z. Gao, "Synthesis of a Novel Gelatin-Carbon Nanotubes Hybrid Hydrogel," *Colloids and Surfaces B*: *Biointerfaces*, Vol. 33, No. 2, 2003, pp. 85-88. doi:10.1016/j.colsurfb.2003.08.014

[5] J. N. Coleman, U. Khan, W. J. Blau and Y. K. Gun'ko, "Small But Strong: A Review of the Mechanical Properties of Carbon Nanotube-Polymer Composites," *Carbon*, Vol. 44, No. 9, 2006, pp. 1624-1652. doi:10.1016/j.carbon.2006.02.038

[6] X. Tong, J. Zheng, Y. Lu, Z. Zhang and H. Cheng, "Swelling and Mechanical Behaviors of Carbon Nanotube/Poly(Vinyl Alcohol) Hybrid Hydrogels," *Materials Letters*, Vol. 61, No. 8-9, 2007, pp. 1704-1706. doi:10.1016/j.matlet.2006.07.115

[7] A. K. Kota, B. H. Cipriano, M. K. Duesterberg, A. L. Gershon, D. Powell, S. R. Raghavan and H. A. Bruck, "Electrical and Rheological Percolation in Polystyrene/ MWNT Nanocomposites," *Macromolecules*, Vol. 40, No. 20, 2007, pp. 7400-7406. doi:10.1021/ma0711792

[8] Y. L. Luo, C. H. Zhang, Y. S. Chen and W. Yang, "Preparation and Characterisation of Polyacrylamide/ MWNTs Nanohybrid Hydrogels with Microporous Structures," *Materials Research Innovations*, Vol. 13, No. 1, 2009, pp. 18-27. doi:10.1179/143307509X402138

[9] H. Liu, M. Liu, L. Zhang, L. Ma, J. Chen and Y. Wang, "Dual-Stimuli Sensitive Composites Based on Multi-Walled Carbon Nanotubes and Poly(N, N-Diethylacrylamide-co-Acrylic Acid) Hydrogels," *Reactive and Functional Polymers*, Vol. 70, No. 5, 2010, pp. 294-300. doi:10.1016/j.reactfunctpolym.2010.02.002

[10] M. Rubinstein, R. H. Colby and A. V. Dobrynin, "Elastic Modulus and Equilibrium Swelling of Polyelectrolyte Gels," *Macromolecules*, Vol. 29, No. 1, 1996, pp. 398-406. doi:10.1021/ma9511917

[11] S. A. Dubrovskii and G. Rakova, "Elastic and Osmotic Behavior and Network Imperfections of Nonionic and Weakly Ionized Acrylamide Based Hydrogels," *Macromolecules*, Vol. 30, No. 24, 1997, pp. 7478-7486. doi:10.1021/ma970788e

[12] A. Wall, J. N. Coleman and M. S. Ferreira, "Physical Mechanism for the Mechanical Reinforcement in Nanotube-Polymer Composite Materials," *Physical Review B*, Vol. 71, 2005, Article ID: 125421.

[13] P. K. Valavala and G. M. Odegard, "Modeling Techniques for Determination of Mechanical Properties of Polymer Nanocomposites," *Review Advances in Materials Science*, Vol. 9, 2005, pp. 34-44.

[14] R. E. Gorga and R. E. Cohen, "Toughness Enhancements in Poly(Methyl Methacrylate) by Addition of Oriented Multiwalled Carbon nanotubes," *Journal of Polymer Science*, *Part B*, *Polymer Physics*, Vol. 42, No. 14, 2004, pp. 2690-2702. doi:10.1002/polb.20126

[15] K. Lau, C. Gu and D. Hui, "A Critical Review on Nanotube and Nanotube/Nanoclay Related Polymer Composite Materials," *Composites Part B*, Vol. 37, No. 6, 2006, pp. 425-436. doi:10.1016/j.compositesb.2006.02.020

[16] G. Romeo, G. Filippone, A. Fernandez-Nieves, P. Russo and D. Acierno, "Elasticity and Dynamics of Particle Gels in Non-Newtonian Melts," *Rheologica Acta*, Vol. 47, No.

9, 2008, pp. 989-997. doi:10.1007/s00397-008-0291-2

[17] L. R. G. Treloar, "The Physics of Rubber Elasticity," Clarendon Press, Oxford, 1975.

[18] L. E. Nielsen and R. F. Landel, "Mechanical Properties of Polymers and Composites," Marcel Dekker, New York, 1994.

[19] K. S. Anseth, C. N. Bowman and L. B. Peppas, "Mechanical Properties of Hydrogels and Their Experimental Determination," *Biomaterials*, Vol. 17, No. 17, 1996, pp. 1647-1657. doi:10.1016/0142-9612(96)87644-7

[20] T. Natsuki and M. Endo, "Stress Simulation of Carbon Nanotubes in Tension and Compression," *Carbon*, Vol. 42, No. 11, 2004, pp. 2147-2151. doi:10.1016/j.carbon.2004.04.022