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CHARACTERIZATION OF AAm/MBA HYDROGELS PREPARED BY RADIATION INDUCED POLYMERIZATION

N. Mahmudi[1*] and S. Rendevski[2]

[1] *Faculty of Natural Science and Mathematics, State University of Tetovo, Bul. Ilinden bb, 1200 Tetovo, Republic of Macedonia*

[2] *Faculty of Electrical Engineering, University "Goce Delcev", Krste Misirkov, b.b., 2000 Stip, Republic of Macedonia*

Abstract. In this research the network structure of polyacrylamide hydrogels prepared by gamma radiation-induced polymerization has been investigated. The average molecular weight between cross-link junctions $\overline{M}_c$ and effective cross-link density of hydrogels were calculated from swelling data as well as shear modulus data. The mechanical tests showed that by increasing the amount of the crosslinker methylenebisacrylamide (MBA) into hydrogels, the value of shear modulus G and cross-link density ν_e increased, but the average molecular weight between cross-link junctions $\overline{M}_c$, decreased. The $\overline{M}_c$ and the effective cross-link density ν_e obtained from the mechanical characterization were significantly different than the values obtained from swelling experiments. These differences were attributed to the uncertainty on the value of the χ parameter used in the Flory-Rehner equations. The results have shown that simple compression analyses can be used for the determination of ν_e without any need of polymer-solvent interaction parameter for its calculations from the swelling analysis.

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INTRODUCTION

Cross-linked polymers are generally chemically prepared from AAm monomers in the presence of cross-linking agent and water. It is also well known that ionizing radiation that induces simultaneous polymerization and crosslinking has some advantages over chemical cross-linking and it is widely used in recent years for the synthesis of various hydrogels for biomedical applications. One of the basic parameters that describe the structure of a hydrogel network is the average molecular weight between cross-links or cross-link density of the network, $\overline{M}_c$. Several theories have been proposed to calculate the average molecular weight between cross-links. In the highly swollen state, the constrained junction theory indicates that a real network exhibits properties closer to those of the phantom network model. The following equation derived from the phantom network model has been used for nonionic polymeric networks known as Flory–Rehner equation [1,2]:

$$\overline{M}_c = -\frac{(1-2/\varphi)V_1 \nu_{2r}^{2/3} \nu_{2m}^{1/3}}{\overline{\nu}\left(\ln(1-\nu_{2m}) + \nu_{2m} + \chi \nu_{2m}^2\right)}, \quad (1)$$

where $\overline{\nu}$ - polymer specific volume; ν_{2m} – polymer volume fraction of crosslinked polymer at swelling equilibrium; ν_{2r} – polymer volume fraction in relaxed state; V_1 – molar volume of the swelling agent (water); ϕ - number of branches originating from the crosslinking sites.

The shear modulus values were calculated from the equation (2), where *f* is the force acting per unit cross-sectional area of the gel speciment, and λ is the deformation ratio:

$$f = G(\lambda - \lambda^{-2}). \quad (2)$$

When the equation (2) is applied to the initial stages of deformation, plots of f versus $\lambda - \lambda^{-2}$ yield straight lines (Fig. 2) where λ is the deformation ratio and equal to *L*/*L*o. *L*o and *L* are the lengths of the undeformed and deformed hydrogels during compression, respectively. The *G* values were calculated from the slope of the lines and are listed in Table 2. *G* is in connection to other parameters in the equation (3):

$$G = A\frac{\rho}{\overline{M}_c} RT \nu_{2r}^{2/3} \nu_{2m}^{1/3}, \quad (3)$$

where *A* is a prefactor and equals 1 for an infinite network and (1-2/ϕ) for a phantom network; ρ is polymer density [3]. The effective cross-link density, ν_e, of a cross-linked structure can be obtained from the results of compressive strain measurements using Eqs. (2)–(4)[4]:

$$\overline{M}_c = \frac{\rho}{\nu_e}. \quad (4)$$

By using *G* values and other relevant experimental parameters, $\overline{M}_c$ could be calculated from the mechanical analysis according to equation (3). ν_e usually is calculated from the corresponding relation, $\nu_e = \rho/\overline{M}_c$. The values of $\overline{M}_c$ and ν_e calculated from the mechanical properties are different from those obtained by using Eq.(1) and swelling experiments. Large difference between them was attributed to the uncertainty on the value of the χ parameter used in the modified Flory-Rehner equation (1),[5,6]. The χ_s parameter is calculated from the swelling analysis according to relation $\chi_s \cong 1/2 + \nu_{2m}/3$. The real χ_m parameter is calculated by using $\overline{M}_{c(m)}$ values from Eq(1). Recalculated χ_m by using $\overline{M}_c$ from Eq(3) in Eq(1) and the differences between χ_s and χ_m are also given in Table 2.

2. EXPERIMENTAL

In the research, three components were used in the preparation of acrylamide–methylenebisacrylamide (AAm//MBA/water) hydrogels, namely acrylamide as monomers and

methylenebisacrylamide as the cross-linking agents and water as dispersing medium. The mass proportion of the monomers in the initial mixtures is summarized in Table 1. The AAm/MBA/water solutions were placed in PVC straws of 3 mm diameter and irradiated at 15 kGy. This has been determined to be minimum dose corresponding to complete conversion. Fresh hydrogels obtained in long cylindrical shapes were cut into pieces 3–4 mm in length. Unreacted monomer and uncrosslinked polymers were removed by washing the gels for two days in distilled water. They were dried in vacuum oven on 315 K. Percentage gelation i.e. percentage conversion of monomers and cross-linking agent into insoluble networks, was based on the total weight of the cross-linking agent and monomer in the initial mixture. Washed and dried hydrogels were left to swell in distilled water at room temperature to determine the maximum swelling degree. Elastic properties and shear modulus of hydrogels were determined by using a Zwick Z010 model Universal Testing Instrument and uniaxial compression module. The crosshead speed was 5 mm/min.

Table 1: Mass of monomer, cross-linking agent and water into composition

Sample code	Mass of monomer (g)	Mass of cross-linking agent (mg)	Water (ml)
0.4g AAm / 1mgMBA/1ml H_2O	0.4	1	1
0.4g AAm / 2mgMBA/1ml H_2O	0.4	2	1
0.4g AAm / 4mgMBA/1ml H_2O	0.4	4	1
0.4g AAm / 6mgMBA/1ml H_2O	0.4	6	1
0.4g AAm / 8mgMBA/1ml H_2O	0.4	8	1
0.4g AAm /15mgMBA/1ml H_2O	0.4	15	1

3. RESULT AND DISCUSSION

For the characterization of the network structure and determination of effective cross-link density of prepared hydrogels their swelling behavior at pH 7 was first investigated. The percentage swelling of hydrogels was calculated by the following equation;

$$S\% = \left[\left(m_t - m_0 \right) / m_0 \right] \cdot 100 \,. \tag{5}$$

where m_t and m_o are the weights of the swollen and dry gels respectively.

The S% equilibrium swelling values of all prepared hydrogels were collected in Table 2. As can be seen from this table S% swelling of hydrogels is lower than 512%. The equilibrium value of swelling was used in each case to calculate the volume fraction of polymer (v_{2m}) by using Eq. (6) given below where ρ and ρ_w are the densities of dry gel and water. w is the weight fraction of polymer in swollen gel.

$$1 / v_{2m} = \left[1 + \rho / \rho_w \left(w^{-1} - 1 \right) \right]. \tag{6}$$

The χ parameter of hydrogels is generally calculated by using the following equation [7].

$$\chi \cong 1/2 + v_{2m}/3, \tag{7}$$

which is the result of an assumption as $\overline{M}_c$ goes to infinity which makes the denominator in Eq. (1) equal to zero i.e.

$$\ln(1-v_{2m}) + v_{2m} + \chi v_{2m}^2 = 0 \tag{8}$$

For small v_{2m} values the χ parameter approaches to 0.5. The $\overline{M}_{c(s)}$ values are calculated by using v_{2m} and values of χ obtained from Eq. (7) and other parameters from swelling experiments. The results collected in Table 2 derived from swelling experiments have "s" in the abbreviations.

For the investigation of the effect of MBA on the mechanical properties of AAm hydrogels and for the determination of true $\overline{M}_c$ ($\overline{M}_{c(m)}$) and χ parameter, uniaxial compression was applied by using the Universal Testing Instrument. The subscript ''m'' was used to indicate that these parameters are calculated from mechanical measurements. Typical stress–strain curves of hydrogels were given in Fig.1. As can be seen from the figure, the magnitude of stress increased with increasing MBA content in the hydrogel for a given strain. Shear modulus values of hydrogels were calculated by using elastic deformation theory and Eq. (2). [1]. By using *G* values and other relevant experimental parameters, $\overline{M}_c$ and ν_e were calculated from Eqs. (3) and (4) and collected in Table 2. As can be seen from Table 2, the magnitudes of $\overline{M}_c$ calculated from mechanical properties are different from those obtained by using swelling experiments. Large difference was attributed to using incorrect χ parameter in the modified Flory–Rehner equation. The actual χ parameters were calculated by using $\overline{M}_{c(m)}$ values and Eq. (1). Recalculated χ parameters (χ_m) and the differences between χ_s and χ_m are also given in Table 2.

For the investigation of the effect of χ parameter on the $\overline{M}_c$ values, the theoretical $\overline{M}_c$ values were obtained (Fig. 3) by using χ and experimentally obtained polymer based parameter. As can be seen from Fig. 3 and Table 2, for first sample of AAm/MBA composition, only 0.034428 changes in χ parameter caused 8.48 fold increase in the $\overline{M}_c$ value. For the second sample changes in χ parameter by 0.050436 caused 10.4 fold increase in $\overline{M}_c$. For the third sample, 0.047788 difference in the χ parameter caused 8.04 fold increase in $\overline{M}_c$. For the fourth sample, 0.044212 difference in the χ parameter caused 6.45 fold increase in $\overline{M}_c$. For the fifth sample, 0.034103 difference in the χ parameter caused 4.24 fold increase in $\overline{M}_c$. For the sixth sample, 0.039008 difference in the χ parameter caused 4.05 fold increase in $\overline{M}_c$. These results clearly show that for the precisely determination of crosslink density of low degree swelling hydrogels, the χ parameter must be calculated (measured) more precisely [5,6].

In this study we also showed the effect of higher concentration of the cross-linking agent MBA on the increasing of mechanical properties of AAm/MBA hydrogels which is

shown on Table 2. The increasing of cross-linking agent from 1mg in the first sample to 15 mg in the sixth sample causes the increasing of G value from 87.1 kPa to 298.5 kPa.

As can be seen from Table 2, the increasing of amount of cross-linking agent from 1mg to 2mg caused the decreasing of $\overline{M}_c$ calculated by swelling method and compress test for 1.34 and 1.64 fold, respectively; the increase from 2mg to 4mg caused the decreasing of $\overline{M}_c$ calculated by swelling method and compress test for 1.49 and 1.16 fold, respectively; the increase from 4mg to 8mg caused the decreasing of $\overline{M}_c$ calculated by swelling method and compress test for 1.33 and 1.065 fold, respectively and the increase from 8mg to 15mg caused the decreasing of $\overline{M}_c$ calculated by swelling method and compress test for 1.55 and 1.48 fold, respectively.

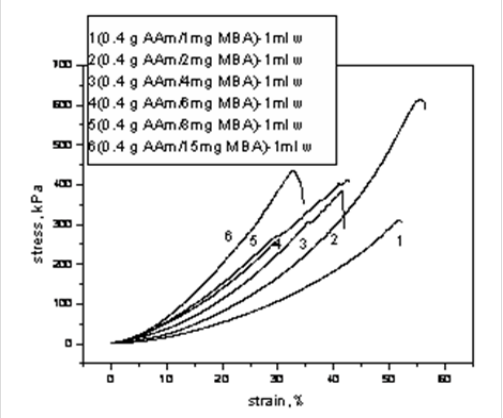

Fig. 1: Strain versus stress curves of AAm/MBA hydrogels

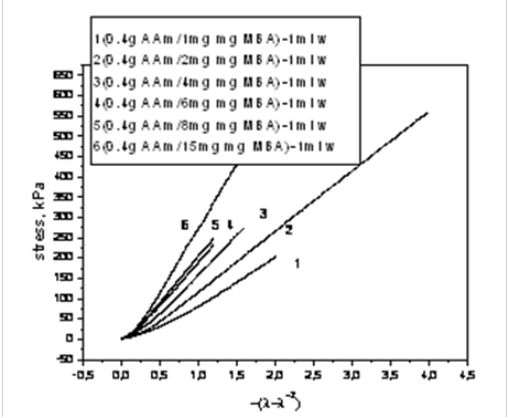

Fig. 2: $-(\lambda-\lambda^{-2})$ versus stress curves of AAm/MBA hydrogel.

Table 2: The swelling and mechanical parameters of AAm/MBA hydrogels: Flory polymer interaction parameters χ_s, χ_m; average molecular weight between hydrogel junction zones $\overline{M}_{c\,(s)}$, $\overline{M}_{c\,(m)}$; effective crosslink density $ve_{(s)}$, $ve_{(m)}$, all obtained from the swelling and mechanical analysis, and shear modulus values *G*.

Sample	S,%	χ_s	$\overline{M}_{c\,(s)}$	$\overline{M}_{c\,(m)}$	χ_m	$ve_{(s)}$	$ve_{(m)}$	$\chi_s - \chi_m$	*G* (kPa)
0.4g AAm / 1mgMBA/1ml H_2O	512	0.54282	21028	2478	0.508392	6.29E-05	0.000534	0.034428	87.1
0.4g AAm / 2mgMBA/1ml H_2O	476	0.546041	15665	1506	0.495606	8.36E-05	0.000869	0.050436	143.9
0.4g AAm / 4mgMBA/1ml H_2O	410	0.551385	10445	1298	0.503597	0.000128	0.00103	0.047788	175.3
0.4g AAm / 6mgMBA/1ml H_2O	376	0.555835	7844	1215	0.511622	0.000168	0.001087	0.044212	198.5
0.4g AAm / 8mgMBA/1ml H_2O	337	0.562963	4998	1178	0.52886	0.000254	0.001078	0.034103	215.3
0.4g AAm /15mgMBA/1ml H_2O	318	0.568819	3224	795	0,529812	0.000375	0.001519	0.039008	298.5

4. CONCLUSION

The aim of this study was to control the mechanical properties of radiation synthesized hydrogels by using different amounts of cross-linker into feed solution.

The decreasing of percentage swelling of hydrogels, the decreasing of the average molecular weight between junctions $\overline{M}_c$ and increasing of *G* modulus is caused by increasing of the amount of cross-linking agent into feed solution. The characterization of the network structure of hydrogels was done by determination of molecular weight between cross-links and effective cross-link density of radiation synthesized AAm/MBA hydrogels by using data from swelling analyses and compression tests. Values calculated from mechanical tests were found to be quite different from those obtained by using swelling experiments. Large difference was attributed to the incorrect value of the χ parameter used in the modified Flory–Rehner equation. These results clearly show that for reliable determination of cross-link density of hydrogels the χ parameter must be precisely determined experimentally from swelling experiments.

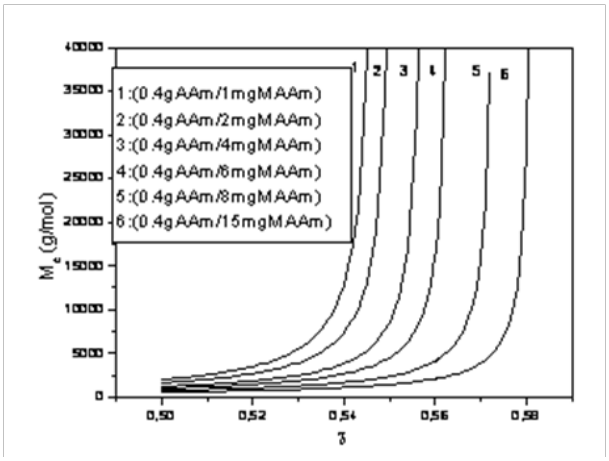

Fig. 3: The change of $\overline{M}_C$ with χ value of AAm/MBA hydrogels.

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