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Swelling and Mechanical Properties of Polyacrylamide Based Hydrogels Prepared by Radiation Induced Polymerization

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Abstract: The swelling and mechanical properties of Acrylamide/Methacrylamide (AAm/MAAm) and Acrylamide/Methacrylamide/Methylenebisacrylamide (AAm/MAAm/MBA) hydrogels prepared by radiation induced polymerization has been investigated in this study. The doses of irradiation have been determined to be optimum, corresponding to complete conversion or to control the swelling and mechanical properties of the obtained polymer networks. There was determined the swelling kinetics such as swelling ratio k_s, transport exponent n, diffusion coefficient d and diffusion constant k related to the structure of polymer crosslinked network. The study revealed that different crosslinked networks can be obtained by using different amount of crosslinker MBA which alters the swelling characteristics of the hydrogel. The molecular weight between crosslinks $\overline{Mc}$ and the effective cross-link density of hydrogels ν_e were calculated from swelling while shear modulus data were obtained from compression tests. Stress-strain curves of hydrogels were evaluated to calculate shear modulus values G, the average molecular weight between junctions $\overline{Mc}$ and the effective crosslink density ν_e. A comparative analysis between the cross-link density ν_e or average molecular weight of hydrogels by using swelling tests and mechanical measurements has been made. Results have shown that simple compression analyses can be used for the determination of the effective cross-link density of hydrogels ν_e without the need for some polymer-solvent based parameters as in the case of swelling based determinations.

Key words: Copolymers, gamma rays, hydrogels, swelling equilibrium, cross-link, mechanical test

INTRODUCTION

Cross-linked copolymers mainly are prepared from their monomers. Crosslinking of copolymers in order to create hydrogel can be achieved with radiation of linear polymers with gamma rays. Crosslinking comes under consideration through reaction between neighboring chains with the help of action of gamma rays. Polyacrylamides, polyacrylates and polyvinyl alcohol are some of hydrophilic polymers which can be crosslinked with gamma radiation (Philipp *et al*., 1989; Siyam, 1997; Wang *et al*., 2000; Guven and Sen, 1991; Kuo, 1999; Sperling, 2005).

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 and other applications. In order to evaluate the effect of composition and cross-linking agent on the properties of the copolymer systems in this research we prepare poly (AAm/MAAm) with different compositions and poly (AAAm/MAAm/MBA) hydrogels with different amount of cross-linking agent by γ-irradiation and characterize them in terms of swelling behavior and mechanical properties.

The mechanical test is important for the determination of the basic parameters that describe the structure of hydrogels, the average molecular weight between cross-links or cross-link density of the network and elastic modulus g of the polymer samples. 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

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model. The following equation derived from the phantom network model has been used for nonionic polymeric networks known as Flory-Rehner Eq. 1 (Mark and Erman, 1988; Sen *et al*., 1998):

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

Where:

$\bar{v}$ = Polymer specific volume
v_{2m} = Polymer volume fraction of crosslinked polymer at swelling equilibrium
v_{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 Eq. 2 where f is the force acting per unit cross-sectional area of the gel specimen and λ is the deformation ratio:

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

When, Eq. 2 is applied to the initial stages of deformation, plots of f versus $\lambda-\lambda^{-2}$ yield straight lines. The G values of the gels were calculated from the slope of lines and are listed in tables. G is in connection to other parameters in Eq. 3 (Okay and Durmaz, 2002):

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

Where:

A = A prefactor and equals 1 for an infinite network
$(1-2/\phi)$ = For a phantom network
ρ = Polymer density

By using g values and other relevant experimental parameters, $\overline{Mc}$ has been calculated from the mechanical analysis according to Eq. 3. v_e was calculated from the corresponding relation, $v_e = \rho/\overline{Mc}$ (Uzun *et al*., 2003). The network parameters derived from swelling and mechanical measurements are compared and discussed.

MATERIALS AND METHODS

Experimental: In this research, three components were used for the preparation of Acrylamide-Methacrylamide p (AAm/MAAm/water) hydrogels, namely acrylamide and methacrylamide as a monomers and water as dispersing medium. The mass/volume proportion of the monomers in the initial mixtures is summarized in Table 1. The

Table 1: Mass composition of monomers in the feed solutions and corresponding abbreviations used for the hydrogels

	Mass of monomers and water			
Gel codes	AAm (g)	MAAm (g)	MBA (mg)	Water (mL)
0.95 AAm 0.05 MAAm	0.95	0.05	-	1
0.9 AAm 0.1 MAAm	0.90	0.10	-	1
0.75 AAm 0.25 MAAm	0.75	0.25	-	1
0.2 AAm 0.2 MAAm2MBA	0.20	-0.20	2	1
0.2 AAm 0.2 MAAm4MBA	0.20	-0.20	4	1
0.2 AAm 0.2 MAAm6MBA	0.20	-0.20	6	1

AAm/MAAm and Aam/MAAm/MBA hydrogels in the rod form were prepared without crosslinker and in the presence of crosslinker MBA, respectively and water by gamma rays at ambient temperature. Unreacted monomers and uncrosslinked polymers were removed by washing the gels for two days in distilled water. They were dried in vacuum oven in 315 k. Washed and dried hydrogels were left to swell in distilled water at room temperature to determine the parameters of swelling. Swollen gels removed from the water bath at regular intervals were dried superficially with filter paper, weighed and immediately placed in the same bath still in equilibrium swelling state.

Elastic properties of hydrogels were determined by using a Zwick Z010 model Universal testing instrument and uniaxial compression module. The crosshead speed was 5 mm/min.

RESULTS 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 Eq. 4:

$$S\%(m) = \left[(m_t-m_o)/m_o\right]/100 \quad (4)$$

where m_t and m_o are the weights of the swollen and dry gels, respectively. The % equilibrium swelling values, the coefficient of swelling kinetics k_s, equilibrium swelling degree S_{eq}, the coefficient of water sorption rate k, the diffusional exponent n and the coefficient of water diffusion in the hyfrogel at sorption D for AAm/MAAm hydrogels at corresponding doses of 10 kGy are determined and listed in Table 2. The same swelling parameters for AAm/MAAm/MBA hydrogels at corresponding doses of 10 kGy are determined and listed at Table 3. As can be seen from the tables, the equilibrium swelling degree can be controlled by changing the amount of the used monomers Aam and MAAm from 720-1070% into AAm/MAAm or from

Table 2: Hydrogel names of AAm/MBA hydrogels, the percentage equilibrium swelling values, the coefficient of swelling kinetics k_s, the coefficient of water sorption rate k, equilibrium swelling degree S_{eq} the diffusional exponent n and the coefficient of water diffusion in the hyfrogel at sorption D

Samples	S (%)	k_s	$k\times10^{-2}$	S_{eq}	n	$D\times10^{-6}$ (cm^2/sec)
0.95 AAm 0.05 MAAm	720	0.0418	2.80	7.93	0.76	7.360
0.9 AAm 0.1 MAAm	800	0.036	2.81	8.84	0.79	6.609
0.75 AAm 0.25 MAAm	1070	0.018	2.52	12.30	0.85	6.300

Table 3: Hydrogel names of AAm/MAAm/MBA hydrogels, the percentage equilibrium swelling values, the coefficient of swelling kinetics k_s, the coefficient of water sorption rate k, equilibrium swelling degree Seq, the diffusional exponent n and the coefficient of water diffusion in the hyfrogel at sorption D

Samples	S (%)	$k_s\,10^2$	$k\times10^{-2}$	S_{eq}	n	$D\times10^{-6}$(cm^2/sec)
0.2 Aam 0.2 MAAm2 MBA	541	2.13	3.28	5.61	0.497	0.0195
0.2 Aam 0.2 MAAm4 MBA	364	0.87	3.12	3.77	0.422	0.0561
0.2 Aam 0.2 MAAm6 MBA	302	0.59	2.95	3.11	0.365	0.0748

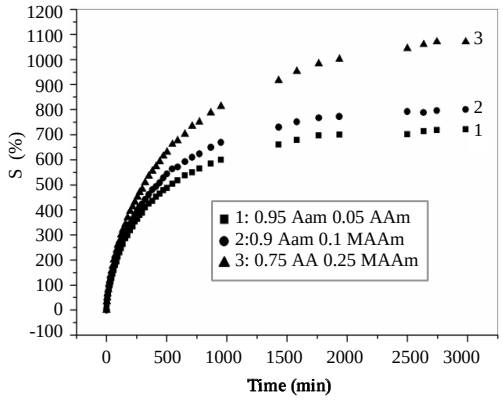

Fig. 1: Swelling curves of AAm/MAAm hydrogels

541-302% into AAm/MAAm/MBA copolymers. The equilibrium value of swelling was used to calculate the volume fraction of polymer (v_{2m}) by using Eq. 5 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:

$$1/v2_m = (1+\rho/\rho_m)(w^{-1}-1) \quad (5)$$

For the investigation of the mechanical properties of AAm/MAAm and AAm/MAAm/MBA copolymers, the mechanical test were made. The stress-strain curves obtained for AAm/MAAm copolymers are shown in Fig. 1 and 2 whereas $\lambda-\lambda^{-2}$ versus stress curves of AAm/MAAm copolymers are shown in Fig. 3. Here, 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.

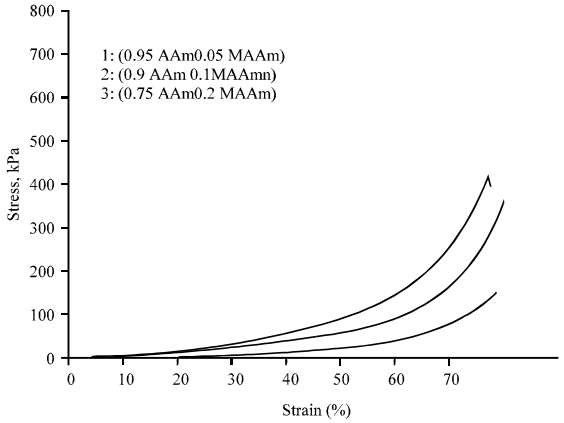

Fig. 2: Strain versus stress curves of AAm/MAAm hydrogels

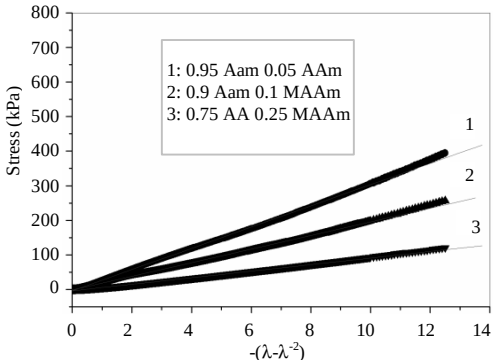

Fig. 3: $\lambda-\lambda^{-2}$ versus stress curves of AAm/MAAm hydrogels

Into the crosslinked AAm/MAAm/MBA hydrogels by gamma rays, the water transport is Fickian in nature while in the case of crosslinked AAm/MAAm hydrogels the water transport mechanism is anomalous indicating major change in the relaxation mechanism due to the nature of crosslinks in the absence of the crosslinker. The increased content of hydrophobic MAAm monomer into AAm/MAAm compositions caused the increase of maximum swelling degree because of the weakened network structure of these polymers. The value of transport exponent is in the range of 0.49-0.36 for AAm/MAAm/MBA hydrogels and 0.76-0.85 for AAm/MAAm, respectively. Results also indicate that the swelling ratio depends on hydrophilic AAm and hydrophobic MAAm ratio into AAm/MAAm compositions as well as the crosslinker MBA percentage into AAm/MAAm/MBA compositions. The diffusion coefficients of these hydrogels were calculated by the short time approximation. These results indicate that the value of the diffusion coefficient is in the

Table 4: The swelling and mechanical parameters of AAm/MAAm 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

Samples	χ_s	$\overline{Mc}_{(s)}$ (g/moL)	$\overline{Mc}_{(m)}$ (g/moL)	χ_m	$ve_{(s)}$ (moL/cm^3)	$ve_{(m)}$ (moL/cm^3)	χ_s-χ_m	G, kPa
0.95 AAm 0.05 MAAm	0.5325	98420	10725	0.5113	1.32E-05	1.22E-04	0.0211	30.60
0.9 AAm0.1 MAAm	0.5321	1102610	16510	0.5190	1.28E-05	7.95E-05	0.0131	19.60
0.75 Aam 0.25 MAAm	0.5217	4401239	27202	0.5063	3.25E-06	4.79E-05	0.0153	9.48

Table 5: The swelling and mechanical parameters of AAm/MAAm/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

Samples	χ_s	$\overline{Mc}_{(s)}$ (g/moL)	$\overline{Mc}_{(m)}$ (g/moL)	χ_m	$ve_{(s)}$ (moL/cm^3)	$ve_{(m)}$ (moL/cm^3)	χ_s-χ_m	G, kPa
0.2 AAm 0.2 MAAm2 MBA	0.54	39600	6790	0.52	3.29E-05	1.92E-04	0.02	29.0
0.2 AAm 0.2 MAAm4 MBA	0.55	19750	2970	0.54	1.32E-04	1.32E-04	0.01	77.1
0.2 Aam 0.2 MAAm6 MBA	0.56	46230	2880	0.55	2.09E-04	2.09E-04	0.01	87.3

of range 0.019-0.074×10^{-6} cm^2/sec and 6-7.3×10^{-6} cm^2/sec for AAm/MAAm/MBA hydrogels and AAm/MAAm, respectively. The diffusion of water into hydrogels was examined by analyzing the water absorption kinetics. As can be seen from the previous Table 2 and 3, the different network structures affect on the diffusion type and on the value of their coefficients.

The molecular weight between crosslinks $\overline{Mc}$ and the effective cross-link density of hydrogels ν_e were calculated from swelling while shear modulus data were obtained from compression tests. Mechanical tests indicated that by increasing the amount of the crosslinker MBA into AAm/MAAm/MBA compositions, the value of shear modulus g and crosslink density ν_e increased but the average molecular weight between junctions $\overline{Mc}$ decreased. In the meantime, the value of shear modulus g and crosslink density ν_e decreased by increasing the amount of hydrophobic monomer MAAm into AAm/MAAm compositions. Stress-strain curves of hydrogels were evaluated to calculate shear modulus values g, the average molecular weight between junctions $\overline{Mc}_{(m)}$ and the effective crosslink density $ve_{(m)}$

The values of $\overline{Mc}$ and ν_e of radiation synthesized AAm/MAAm and AAm/MAAm/MBA hydrogels calculated from the mechanical properties are different from those obtained by using swelling experiments (Table 4 and 5). The results from the swelling analysis are briefly presented on Fig. 1 for AAm/MAAm copolymers through the swelling degree dependence on the time of swelling. Values of $\overline{Mc}$ calculated from mechanical tests were found to be quite different from those obtained by using swelling experiments. Large difference was attributed to the uncertainty on the value of the χ parameter used in the modified Flory-Rehner Eq. 1. The χ_s parameters were calculated from the swelling analysis according to relation $\chi_S \cong 1/2+\nu_{2m}/3$. The real χ_m parameters were calculated by using $\overline{Mc}_{(m)}$ values from Eq. 1. Recalculated χ_m by using $\overline{Mc}$ from Eq. 3 in Eq. 1 and the differences between χ_s and χ_m are also given in

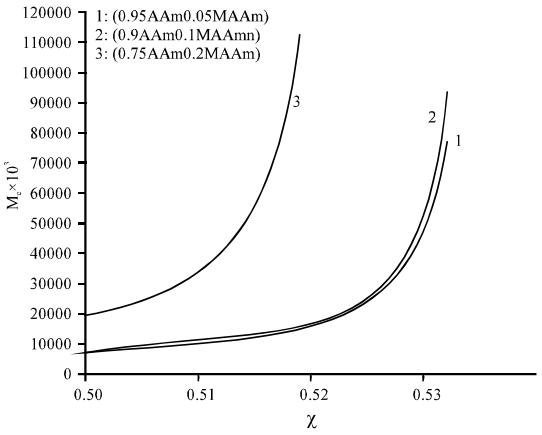

Fig. 4: The effect of χ on the $\overline{Mc}$ value of Am/MAAm hydrogels

Table 4 and 5 for AAm/MAAm and AAm/MAAm/MBA copolymers, respectively. For the investigation of the effect of χ parameter on the $\overline{Mc}$ values the theoretical $\overline{Mc}$ values were obtained (Fig. 4) for AAm/MAAm polymers by using χ_m and experimentally obtained polymer based parameter. As can be seen from Fig. 4 and Table 4 for first sample of AAm/MAAm composition, only 0.0211 changes in χ parameter caused 9.17 fold increase in the $\overline{Mc}$ value. For the second sample, 0.0131 difference in the χ parameter caused 6.21 fold increase in $\overline{Mc}$. For the third sample, 0.0153 difference in the χ parameter caused 14.75 fold increase in $\overline{Mc}$. The same analysis is made for AAm/MAAm/MBA compositions and results are collected in Table 5. 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.

As can be seen from Table 4, the presence of hydrophobic MAAm monomer into AAm/MAAm compositions contribute to weakening of polymer. network of these hydrogels. The higher amount of

hydrophobic MAAm monomer into AAm/MAAm compositions. Results to the lower G values. For the same amount of monomers into AAm/MAAm/MBA compositions, the higher values of cross-linking agent MBA contribute to higher values of G modulus (Table 5).

CONCLUSION

A comparative analysis to determine the cross-link density ν_e of hydrogels or average molecular weight between junction zones $\overline{M_c}$ by using swelling tests and mechanical measurements has been made. Large differences between these values obtained from swelling tests and mechanical measurements were attributed to the uncertainty of the value of the χ parameter used in the Flory-Rehner equations. It was found that only 1% change of this parameter doubled or reduced the $\overline{M_c}$ value of the hydrogel to a half value or even more. For the reliable determination of cross-link density of hydrogels by swelling experiment the χ parameter must be determined experimentally.

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