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Original Scientific Paper

Correlation between hardness and elastic properties of acrylamide based hydrogels prepared by radiation induced polymerization

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Abstract

In the present work, correlation between hardness and elastic properties of acrylamide-based hydrogels prepared by gamma-induced irradiation have been investigated. Poly(acrylamide/methacrylamide) P(AAm/MAAm) and poly(acrylamide/hydroxyethyl methacrylate) P(AAm/HEMA) hydrogels with various composition were prepared by gamma irradiation and used as model hydrogel systems. 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 uniaxial compression was applied to cylindrical gel samples in the swollen form at pH 7 by using the Universal Testing Instrument. The molecular weight between crosslinks $\overline{M}_c$ and the effective cross-link density of hydrogels ν_e were calculated from swelling, while shear modulus data were obtained from compression tests. 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. The hardness of polymer samples was determined by the Vickers method and correlation between these values and shear modulus was discussed.

Keywords: Polymers, swelling, mechanical test, crosslink density, hardness

1. Introduction

Highly cross-linked polymers are generally chemically prepared from their monomers. Cross-linking of polymers in order to create hydrogel can be achieved with radiation of linear polymers with gamma rays. Cross-linking 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 cross-linked with gamma radiation [1-6].

Cross-linked polymers are generally chemically prepared from AAm, MAAm and HEMA monomers in the presence of water. It is also well known that ionizing radiation that induces simultaneous polymerization and cross-linking 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. The basic parameter that describes the structure of a hydrogel network is the average molecular weight between cross-links or cross-link density of the network and elastic modulus G. 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 [7,8]:

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

$\bar{\nu}$ - polymer specific volume; ν_{2m} – polymer volume fraction of cross-linked 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 cross-linking 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:

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

When the equation (2) is applied to the initial stages of deformation, plots of *f* versus λ-λ^{-2} yield straight lines (Fig. 3). The *G* values of the gels were calculated from the slope of lines and are listed in Table 3. *G* is in connection to other parameters in the equation (3) [9]:

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

where *A* is a prefactor and equals 1 for an infinite network and (1-2/ϕ) for a phantom network; ρ is polymer density. By using *G* values and other relevant experimental parameters, $\overline{M}_c$ has been calculated from the mechanical analysis according to equation (3). ν_e was calculated from the corresponding relation, $\nu_e = \rho/\overline{M}_c$,[10]. In this study, we compared swelling and mechanical analyses for the determination of cross-link density of hydrogels prepared by ionizing radiation with relatively low degree of swelling and determined the correlation between these values and hardness obtained by the Vickers method.

2. Experimental

In this research three components were used in the preparation of acrylamide-methacrylamide P(AAm/MAAm/water) hydrogels, namely acrylamide and methacrylamide as a monomers and water as dispersing medium. Three components are used in the preparation of acrylamide-2-hydroxyethyl methacrylate P(AAm/HEMA/water) hydrogels, namely acrylamide and 2-hydroxyethyl methacrylate as monomers and water as dispersing medium. The mass/volume proportion of the monomers in the initial mixtures is summarized in the Table 1.

The AAm/MAAm/water and AAm/HEMA/water solutions were placed in PVC straws of 3 mm diameter and irradiated at 10 kGy and 6.4 kGy doses, respectively. They have been determined to be minimum doses 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 in 315K. Washed and dried hydrogels were left to swell in distilled water at a 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 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. Hardness measurements according to the Vickers method [11] were carried out by using a semi-automatic SIOMM HV-1000DT model hardness tester. For each specimen, a small load of 25 g and a dwelling time of 10 s were used. To estimate the hardness, three to five measurements were performed and the results were then averaged.

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

Gel code	Mass of monomers and water			
	AAm (g)	MAAm (g)	HEMA (ml)	Water (ml)
0.95AAm0.05MAAm	0.95	0.05	-	1
0.9AAm0.1MAAm	0.9	0.1	-	1
0.75AAm0.25MAAm	0.75	0.25	-	1
1AAm0.5HEMA	1	-	0.5	2
1AAm1HEMA	1	-	1	2
1AAm1.5HEMA	1	-	1.5	2
1AAm2HEMA	1	-	2	2
1AAm2.5HEMA	1	-	2.5	2

3. Result and discussions

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:

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

where m_t and m_o are the weights of the swollen and dry gels respectively. The coefficient of swelling kinetics k_s, equilibrium swelling degree *S*eq, the coefficient of water sorption rate *k*, the diffusion exponent *n*, and the coefficient of water diffusion in the hydrogel at sorption D for AAm/MAAm hydrogels are determined and listed in Table 2. The % equilibrium swelling values of all prepared AAm/MAAm hydrogels at corresponding doses of 10 kGy were collected in Table 3. As can be seen from the table, the equilibrium swelling degree can be controlled by changing the amount of the used monomers AAm and MAAm from 720% to 1070% into AAm/MAAm compositions and changing the monomer HEMA, namely from 794% to 246% by changing the amount of HEMA from 0.6 ml to 2.5 ml into AAm/HEMA compositions. (Table 4)The equilibrium value of swelling was used to calculate the volume fraction of polymer (ν_{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.

$$1/\nu_{2m}=(1+\rho/\rho_m)\,(w^{-1}-1) \quad (5)$$

For the investigation of the mechanical properties of AAm/MAAm and AAm/HEMA polymers, the mechanical test were made. The stress-strain curves obtained for AAm/MAAm polymers are shown in Figure 2 whereas $\lambda-\lambda^{-2}$ versus stress curves of AAm/MAAm hydrogels are shown in Figure 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.

Table 2. Hydrogel names, 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*.

Gel name	*k*s	*S*eq	k x10^{-2}	*n*	D x 10^{-6} cm^2/s
0.95AAm0.05MAAm	0.0418	7.93	2.8	0.76	7.36
0.9AAm0.1MAAm	0.036	8.84	2.81	0.79	6.609
0.75Aam0.25MAAm	0.018	12.3	2.52	0.85	6.3

Table 3. 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 $\nu e_{(s)}$, $\nu e_{(m)}$, all obtained from the swelling and mechanical analysis, shear modulus values *G* and hardness values.

Sample	S(%)	χ_s	$\overline{M}_{c\,(s)}$	$\overline{M}_{c\,(m)}$	χ_m	$\nu e_{(s)}$	$\nu e_{(m)}$	$\chi_s - \chi_m$	*G*, kPa	*Hardness*
0.95AAm0.05MAAm	720	0.5325	98420	10725	0.5113	1.32E-05	1.22E-04	0.0211	30.6	22.70
0.9AAm0.1MAAm	800	0.5321	102610	16510	0.5190	1.28E-05	7.95E-05	0.0131	19.6	25.31
0.75Aam0.25MAAm	1070	0.5217	401239	27202	0.5063	3.25E-06	4.79E-05	0.0153	9.48	26.17

Table 4. The swelling and mechanical parameters of AAm/HEMA 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 $\nu e_{(s)}$, $\nu e_{(m)}$, all obtained from the swelling and mechanical analysis, shear modulus values *G* and hardness values.

Sample	S(%)	χ_s	$\overline{M}_{c\,(s)}$ (g/mol)	$\overline{M}_{c\,(m)}$ (g/mol)	χ_m	$\nu_{e(s)}$	$\nu_{e(m)}$	$\chi_s - \chi_m$	*G* (kPa)	$\rho(kg/m^3)$	*Hardness*
1gAAm/ 0.6ml HEMA/2ml H_2O	794	0.5279	142012	15327	0.5123	9.08E-06	8.42E-05	00.00333	16.7	1289.9	17.59
1gAAm/ 1ml HEMA/2ml H_2O	544	0.5405	38440	12170	0.5316	3.35E-05	0.000106	00.00515	25.8	1285.9	15.55
1gAAm/ 1.5ml HEMA/2ml H_2O	380	0.5555	12785	12575	0.5554	0.0001	0.000102	00.00573	30.6	1284.8	14.78
1gAAm/ 2ml HEMA/2ml H_2O	301	0.5674	6299	13908	0.5741	0,000203	9.17E-05	00.00456	34.6	1276.1	14.63
1gAAm/ 2.5ml HEMA/2ml H_2O	246	0.5783	3694	12239	0.5902	0,000346	0.000104	0000511	38.4	1277.4	14.39

The values of $\overline{M}_c$ and ν_e of radiation synthesized AAm/MAAm and AAm/HEMA hydrogels calculated from the mechanical properties are different from those obtained by using swelling experiments (Table 3 and Table 4). The results from the swelling analysis are briefly presented on Fig.1 for AAm/MAAm polymers through the swelling degree dependence on the time of swelling. Values of $\overline{M}_c$ 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 equation (1). The χ_s parameters were calculated from the swelling analysis according to relation $\chi_s \cong 1/2 + v_{2m}/3$. The real χ_m parameters were 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 3 and Table 4 for AAm/MAAm and AAm/HEMA polymers, respectively. For the investigation of the effect of χ parameter on the $\overline{M}_c$ values the theoretical $\overline{M}_c$ 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 3, for first sample of AAm/MAAm composition, only 0.0211 changes in χ parameter caused 9.17 fold increase in the $\overline{M}_c$ value. For the second sample, 0.0131 difference in the χ parameter caused 6.21 fold increase in $\overline{M}_c$. For the third sample, 0.0153 difference in the χ parameter caused 14.75 fold increase in $\overline{M}_c$. The same analysis is made for AAm/HEMA and results are collected in Table 4. 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 [12]. The correlation between G modulus and hardness for AAm/MAAm polymers and AAm/HEMA is presented in Figure 5 and Figure 6, respectively. The decreasing rate is different, namely around 28(…/kPa) and 19.73(…./kPa) for AAm/MAAm polymers and AAm/HEMA, respectively. The higher decrease rate for AAm/MAAm is due to hydrophobic nature of MAAm monomer used into AAm/MAAm compositions. 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 then AAm/HEMA compositions where greater amount of hydrophilic HEMA monomer contribute to not higher decrease of G modulus, as can seen in the Table 3

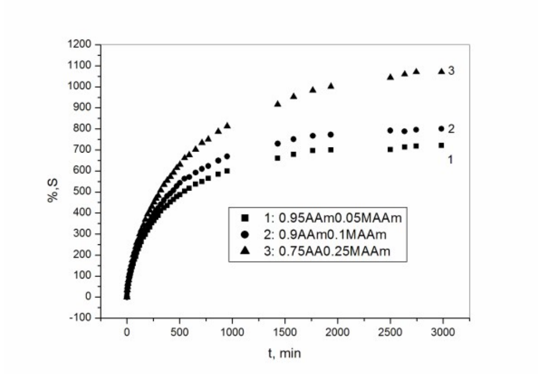

Fig. 1. Swelling curves of AAm/MAAm hydrogels

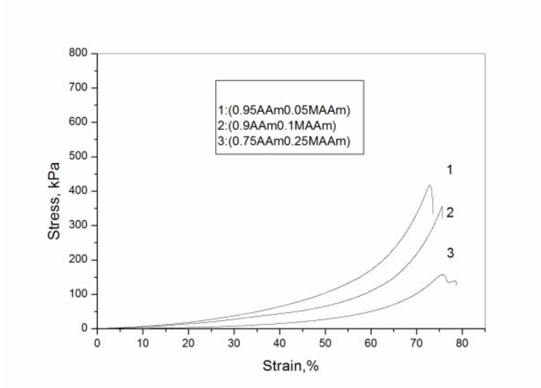

Fig. 2. Strain versus stress curves of AAm/MAAm hydrogels.

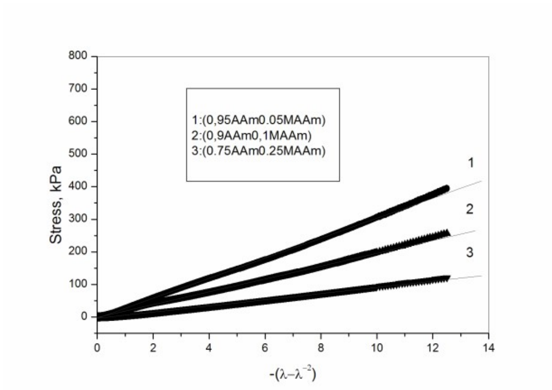

Fig. 3. λ-λ^{-2} versus stress curves of AAm/MAAm hydrogels

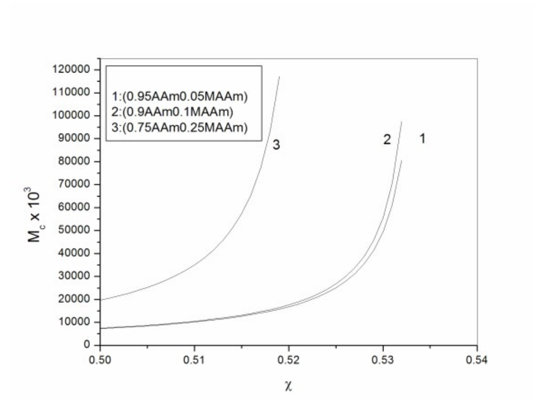

Fig. 4. The effect of χ on the $\overline{M}_c$ value of Am/MAAm hydrogels.

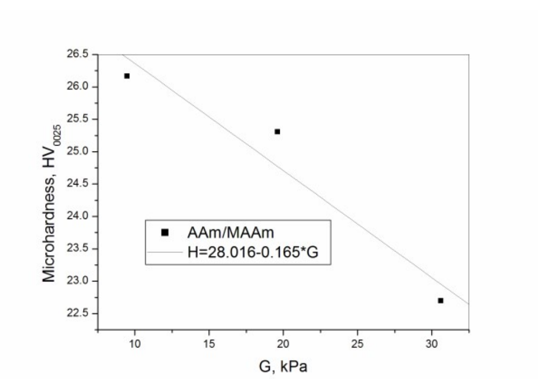

Fig. 5. The correlation between hardness and G modulus for AAm/MAAm hydrogels

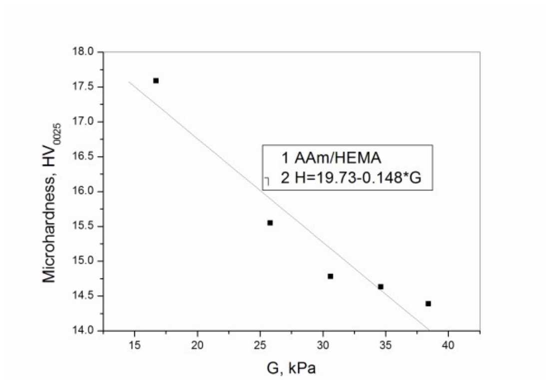

Fig. 6. The correlation between hardness and G modulus for AAm/HEMA hydrogels

4. Conclusions

The aim of this study was to determine the mechanical properties such as average molecular weight between cross-links or cross-link density of the network, elastic modulus *G* of the polymer samples and to find the correlation between these values and hardness of polymers. The determination of elastic properties was made by two methods, the swelling method and mechanical test. Comparison of values obtained by these two methods showed large difference between them which is attributed to the incorrect value of the χ parameter used in the modified Flory-Rehner equation. For the reliable determination of cross-link density of hydrogels by swelling experiment the χ parameter must be determined experimentally. The correlation between G values and hardness values of acrylamide based hydrogels clearly showed that by inceasing of G values, the hardness values are decreasing.

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