

Ultrasonic degradation of hydrogels in aqueous solutions

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ABSTRACT

Continuous exposure to high-energy ultrasonic waves depolymerises macromolecules in solutions and produces a permanent reduction in viscosity. Different factors affect the efficiency of this ultrasonic depolymerisation. In this work ultrasonic degradation of one commercially important hydrogel based on acrylic acid and acrylamide was carried out in aqueous solution at room temperature (25°C). Also, the effect of sonication parameters (power and cycle) on the rate of degradation was investigated. A method of viscometry was used to study the degradation behaviour of the hydrogel and a first order kinetic equation was developed to calculate the degradation rate constants. The experimental results indicated that the rate of ultrasonic degradation increased with increasing ultrasonic power and pulse. FT-IR spectrometry measurements confirmed that the degradation proceeds by mechanical forces. Finally a mechanism was proposed according to the experimental data.

KEYWORDS

Hydrogel, Sonication, Degradation, Viscosity, Kinetics.

1. INTRODUCTION

Depending on the application, polymers and gels may need to be degraded. For certain applications, polymers of lower molecular mass have been selected advantages over the high molecular mass candidates due to their improved diffusion into biological tissues. Shortening of the macromolecular chains can be achieved by various methods. Different methods of degradation are available such as thermal, photo and catalytic degradation [1,2]. The methods like UV [3], microwave[4], and ultrasonic degradation [2] are also important. Polymers can be degraded thermally by pyrolysis or in solution. Alternative energy reducing techniques required for degradation process are important. Ultrasound, photo and chemical methods are less

energy-intensive polymer degradation. Further, the mechanism by which they interact with the polymeric systems can help get insight into the degradation pathways or mechanisms [5]. Polymers undergo degradation when they are subjected to ultrasound irradiation of high intensity. Several Scientists have investigated the ultrasound degradation of polymers, which has been summarized by Price [6]. The effect of various parameters like temperature, pressure, ultrasound intensity, dissolved gases and polymer concentration on the ultrasonic degradation of polymers has been investigated [1-8]. The sound waves do not directly interact with the polymer but they act on the solvent causing the growth and rapid collapse of micro-bubbles resulting in high shear gradient. It has been shown that this shear force is sufficient to break chemical bonds

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in polymers [7,8]. In the degradation of polymers in solution, the generated heat could be of minor importance as hot spots are highly localized and quenched in a very short time [9]. Another unique feature of ultrasonic degradation is the fact that, in contrast to all chemical and thermal decomposition reactions, the ultrasound depolymerization is a non-random process which produces fragmentation at the mid-point of the chain [10]. The existence of certain and limiting molecular weight, below which degradation by ultrasound does not take place, has the additional effect in that the molecular weight distribution initially broadens before narrowing during degradation [11].

Ultrasonic waves were also used for gelation of polymers. For example, the time of ultrasonic velocity evolution and attenuation has been investigated during the gelation process of polyacrylamide (PAAm) hydrogels[12]. The cross-linker concentration dependence was further examined in order to investigate the gelation process accompanied by phase separation. Also, the ultrasonic degradation of poly(acrylic acid), a water-soluble polymer has been investigated in the presence of different oxidizing agents (KPS, APS, and SPS), at different temperatures, and in various methanol/water binary solvent mixtures[13]. Continuous distribution kinetics has been applied to model the experimental data and the degradation rate coefficients were determined. The ultrasonic degradation of polyacrylamide and poly(ethylene oxide) in solution was studied at different temperatures[14]. The degradation rate coefficient decreased with increasing temperature and was attributed to lower viscosity at higher temperatures. They showed that cavitation collapse in viscous liquids is stronger than collapse in less viscous liquid. According to cavitation mechanism for the ultrasonic degradation of the polymer solutions, the degradation of a polymer is hardly carried out when the viscosity of solution is about 2.0 mPaS due to the disappearance of cavitation [5].

In this work the effect of some sonication parameters (Ultrasonic cycle and power) on degradation of the hydrogels was studied. The hydrogel based on acrylic acid and acrylamide is an important commercial polymeric gel, however sonochemical depolymerization of it has not been

reported [15]. The purpose of this study is to present new experimental data for the ultrasonic degradation of these hydrogels. This study investigates the effect of the ultrasonic irradiation on the degradation of the hydrogel in water. This is conducted by correlating viscosity measurements at different sonication times. It is shown that the rate of ultrasonic degradation of the hydrogels follow a linear dependence of the logarithm of the viscosity with irradiation time. The effects of other parameters such as concentration, external pressure, temperature and solvent will be carried on the next work.

2. EXPERIMENTS

2.1. MATERIALS

Acrylic acid (AA, Merck) was used after vacuum distillation. Acrylamide (AAm, Fluka), ammonium persulfate (APs, Fluka) and methylene bisacrylamide (MBAAm, Fluka) were analytical grade and used without further purification.

2.2. HYDROGEL PREPARATION

The hydrogel was prepared according to early works in optimum conditions [16]. In Brief, Certain amounts of water (40ml), Acrylamide (AAm, 2.4g) and acrylic acid (AA, 1.6g) were added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021), while stirring (rpm 300). The reactor was placed in a thermostated water bath preset at a desired temperature (80°C) for 5 min. After homogenizing the mixture, the crosslinker (MBA, 0.1g) and initiator (APS, 0.1g) was simultaneously added and the reaction mixture was stirred. After 1hour, the mixture was treated with 1M sodium hydroxide (16.2ml) for partial neutralization (75%) of the carboxylic groups of the acrylic acid. Finally, the produced gel was added to 200ml of ethanol for 12hour and then scissored to small pieces (diameter 5mm). The non-solvent ethanol was then decanted and 200ml fresh ethanol was added. Having been remained the particles for 24hour, they were solidified completely. The dehydrated gel particles were filtered and dried in oven at 50oC for 10hour. After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat and light.

2.3. SWELLING MEASUREMENTS

The hydrogel sample (0.5 g) was put into a weighed tea bag and immersed in 100ml distilled water and allowed to soak for 2h at room temperature[17]. The equilibrated swollen gel was allowed to drain by removing the tea bag from water and hanging until no drop drained (10min). The bag was then weighed to determine the weight of the swollen gel. The equilibrium swelling was calculated using the following equation 1:

$$\text{Water Absorbance} = \frac{(W_S - W_D)}{W_D} \quad (1)$$

Where W_S and W_D are the weights of the swollen gel and the dry sample, respectively. So, absorbency was calculated as grams of water per gram of dry hydrogel (g/g). Swelling power of all degraded samples and undegraded hydrogel were measured. All degraded samples were filtered and their swelling were measured.

2.4. ULTRASONIC DEGRADATION

The reaction was carried out in a 250-ml beaker and distilled water was used as solvent. Hydrogel solution(1g/140ml H₂O) was taken each time and the beaker was held in a constant temperature(25°C) circulator water bath(±1°C). The range of probe homogenizer treatment and spindle type and rpm of the viscometer were adapted with this beginning concentration [11]. Ultrasound was coupled directly to the reaction system by a horn type homogenizer (Sonopuls HD 2070, Bandelin, Germany) with HF-power and frequency of 70 W and 20 KHz, respectively. The diameter of the horn tip was 2 mm. In order to eliminate the effect of the ultrasonic action distance on the degradation process, the probe was immersed 15 mm below the liquid surface (center of the solution). The beaker was put in a sound proof box with clear acrylic glass door. At a certain irradiation time, the degraded samples were picked out at regular intervals (5 or 10 min) to measure their viscosities and then returned to continue irradiation (without sampling). A mechanical stirring for achieving homogeneous irradiation of ultrasound was applied to the sample.

2.5. VISCOSITY MEASUREMENTS

The dynamic viscosity of the hydrogel solutions before and after sonication was measured at room temperature (25°C) using a rotational viscometer (DV-II + Pro RV, Brookfield, USA). The viscometer was a spindle type (#2) with a spring of 10-100% torque of unit (Viscosity 40 to 400 cP or mPa.s) and was rotated at 100 rpm. The result was a direct reading of the viscosity value in mPa.s. Samples were withdrawn for viscosity analysis at every 5min to 60min and every 10min to 180min. The reproducibility of the ultrasonic degradation was also determined (section 3.2).

2.6. SPECTROSCOPY MEASUREMENTS

FTIR analysis of undegraded and degraded hydrogel (intensity 85% and pulse 8) was conducted with a Perkin – Elmer RX1 spectrometer at the wavelength region between 4000 and 400cm⁻¹. Samples were prepared as a thin film of the hydrogel mixed with KBr at gel/KBr ratio of 1/50. Obtained spectra were the result of 24 scans at the spectrophotometer with 2cm⁻¹ resolution.

UV absorption spectra were obtained using Hp- Agilent 8452A spectrophotometer at the range of 190–600nm from undegraded and all degraded hydrogel solutions.

3. RESULTS AND DISCUSSION

3.1. EFFECT OF ULTRASONIC WAVES ON THE VISCOSITY

The ultrasonic degradation is a fluid mechanical process, thus viscosity of the solvent plays an important role in determining the degradation rate. The extent of degradation decreases with a decrease in solution concentration. It is important to emphasize that there was no optimization on such reaction. We studied ways to improve experimental conditions such as power, pulse, time, volume and probe distance. Fig. 1 shows the typical changes in viscosity η_r which have been observed by sonicating (intensity 85% and pulse 8) of the hydrogel solution after gelatinization. It can be observed that there is a drastic decrease in viscosity of these solutions at first and after about 30min in this case.

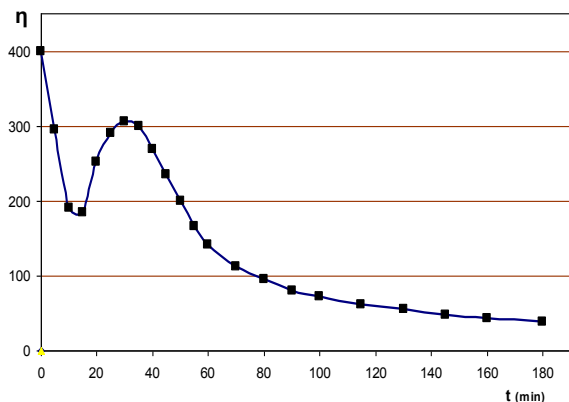
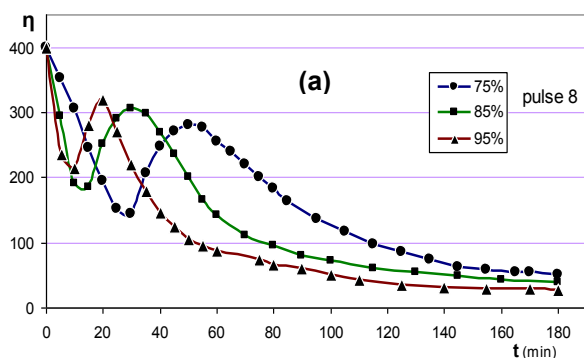


Fig. 1: Typical changes in viscosity by sonicating (intensity 85% and pulse 8) of the hydrogel solution after gelatinization.

In order to study the effects of ultrasonic irradiation time on the degradation of hydrogel, viscosities at the various cycles and powers were also measured. Some data are shown in Fig. 2. It is clear that η_r greatly decreases at the beginning, then increases with the irradiation time, and finally decrease toward a limited and constant value, which is sometimes the characteristic of mechanochemical degradation of the polymers in aqueous solutions.



observation; first, the sonochemical cleavage of polymer chains in solution leads to the formation of macroradicals, and a new polymer can be formed by recombination of different macroradicals and this raises the viscosity. Second, the increase in viscosity after the initial decrease could be something concern to the hydrogen bonding structures and viscoelastic effects rather than permanent molecular changes. Third, as shown in scheme 1, it seems that partial degradation of the hydrogel increases the contact surface of the hydrogel particles and the chain of polymer can be interpenetrated to each other more intensely.

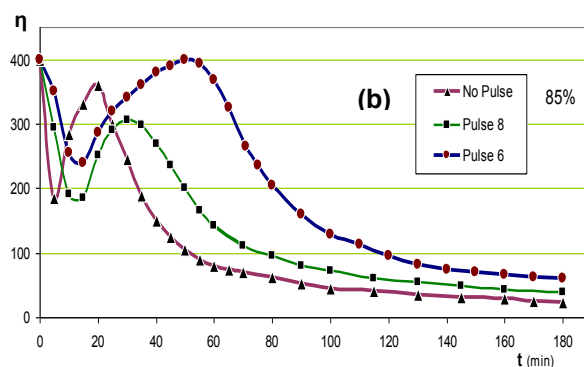
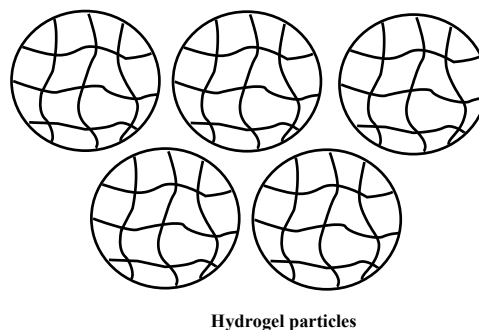
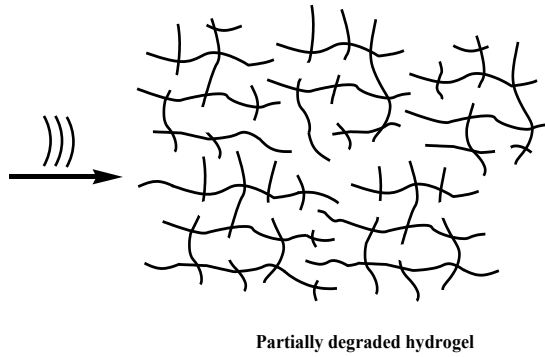


Fig. 2: Viscosity variations with irradiation time in different powers in pulse 8 (a) and in different pulses in power 85%(b).

We found that there was no appreciable degradation under pulse 5 and under power 70%. Pulse makes irradiation time be different from degradation reaction time and allows the reaction mixture to cool down. At the end of the ultrasonic treatment, the viscosity is near to that of water (about 10mPa.s after 5h of irradiation under our conditions). The best compromise between the duration of sonication and the reduction of the molar mass is found after 3h. The viscosity increases with increasing the irradiation time between about 10 to 30min. We propose the following reasons for this



Hydrogel particles



Scheme 1. Schematic representation of partially degradation of hydrogel by ultrasonic irradiation

It can be deduced that there is a limiting molecular weight that below which chain scission does not occur. The relative viscosity limit of the hydrogel solution was about 38. Below the limit, the polymer chain was so short that it followed ultrasonic vibration flexibly and cleavage at the center of the molecule did not take place anymore. From Fig.1, it was found that the viscosity decreased more and faster at first. This indicates that the chain scission of higher molecular weight polymer is prior to that of lower molecular weight. The viscosity corresponding to the peak value is 305. Observation of the time dependence of the ultrasonic degradation of the hydrogel revealed that the hydrogel network was most effectively depolymerized in the course of the initial 60 min, apparently when the chain of the hydrogel network is still large enough for effective degradation by ultrasound under the above-mentioned experimental conditions.

3.2. REPRODUCIBILITY OF ULTRASONIC DEGRADATION

The reproducibility of the ultrasonic degradation and the stability of the viscosity changes were studied using several hydrogel solutions. Fig. 3 shows reproducibility for the ultrasonic degradation of the hydrogel solution (no pulse and power 75%, with a various shape respect to the older). The viscosity of the studied hydrogel changed equally in both cases. It was also seen that the viscosity decreased considerably and rapidly during the first hour of ultrasonic treatment and the degradation was stabilized in 120 min. Thus the changes in dynamic viscosity were calculated at 180 min in this study.

Ultrasonic irradiation also produced a permanent reduction in viscosity. The viscosity was measured one and three months after ultrasonic treatment in sealed containers. The viscosity values were within 1% and 2% of the previous values measured immediately after the cessation of irradiation.

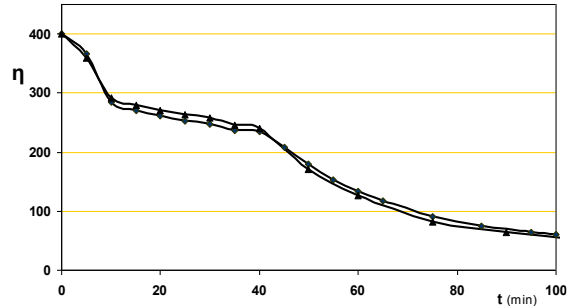


Fig. 3: Reproducibility of ultrasonic degradation of hydrogel solution (no pulse and power 75%).

3.3. ULTRASONIC DEGRADATION KINETICS (REACTION ORDER AND RATE CONSTANT)

Ultrasonic irradiations of aqueous solutions of the hydrogel lead to the first-order kinetics (just in final reduction section, after climax) as shown in Fig. 4. The rate constants were deducted from the slopes of curves issued from equation 2.

$$\ln\left(\frac{n_t - n_{\infty}}{n_0 - n_{\infty}}\right) = -kt \quad (2)$$

where k is the rate constant, η_0 the initial hydrogel viscosity (400 mPaS), η_t its value at later times and η_{∞} the final hydrogel viscosity. Rate constants of sonodegradation listed in Table 1, ranged from 0.762 h⁻¹ (power 75% and pulse 6) to 1.806 h⁻¹ (power 95% and no pulse). The average experimental error is about 3% according to the standard deviations of the slopes.

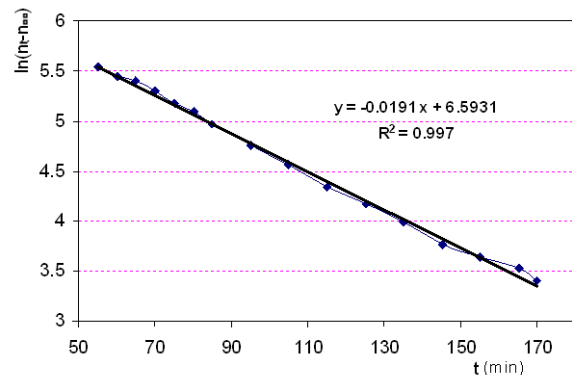


Fig.4: The plot of $\ln(\eta_t - \eta_{\infty})$ versus sonication for time hydrogel degradation (power 75% and pulse 8).

Table 1. The relationship between the calculated rate constant k (h^{-1}) with power and pulse

	Power 75%	Power 85%	Power 95%
No pulse	1.234	1.476	1.806
Pulse 8	1.046	1.134	1.230
Pulse 6	0.762	1.068	1.108

3.4. EFFECT OF POWER (INTENSITY) ON THE RATE OF DEGRADATION

The effect of ultrasound intensity on the ultrasonic degradation of the hydrogel was investigated. The data listed in Fig. 2a also shows that the increase of the ultrasonic intensity reduces intrinsic viscosity of the hydrogel more rapidly, indicating that the extent of degradation of hydrogel increases with the rise of ultrasonic intensity. The rate of changes in viscosity becomes faster with increasing the power of ultrasonic radiation.

Table 1 and Fig. 5 show that the degradation rate coefficient of the hydrogel increases with increasing in ultrasound intensity, as reported for other polymers [18,19]. The relationship between the degradation rate coefficient and intensity is linear as observed in Fig. 5 and in the other studies[20,21]. This is because an increase in intensity leads to formation of large number of cavitation bubbles. Above the cavitation threshold, the bubble reaches the maximum radius, and the radius is proportional to the square root of intensity[22,23]. The larger cavitation bubbles collapse and produce high shear forces, so the gel degrades faster at higher intensities[24].

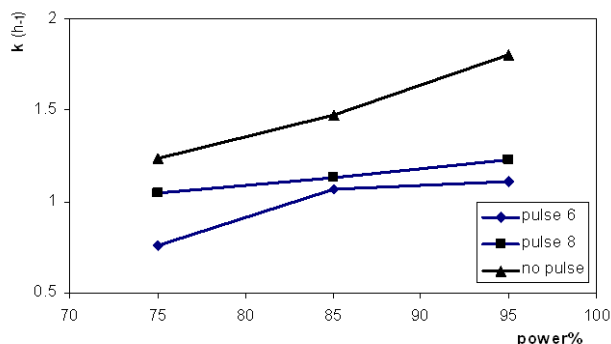


Fig. 5: Variation of degradation rate coefficient of hydrogel with ultrasonic intensity.

3.5. EFFECT OF THE PULSE ON THE REACTION RATE

The data listed in Table 1 and Figure 6 show that the extent of degradation of the hydrogel increases with the rise of ultrasonic pulse. With increasing the ultrasonic pulse, the rate of changes in viscosity becomes faster. Similar behavior was observed for the increasing in ultrasonic power as mentioned in section 3.4.

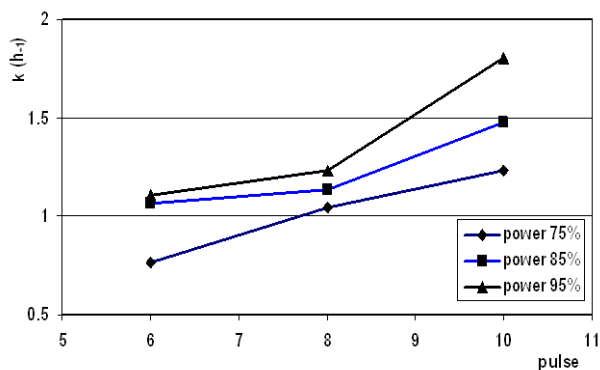


Fig. 6: Variation of rate coefficient with ultrasonic pulse.

3.6. FTIR SPECTROSCOPY MEASUREMENTS

It is assumed that hydrogel undergoes changes mainly by the breakage of crosslinker (MBA) bonds. To confirm this assumption, FTIR spectra were taken before and after irradiation. Fig. 7a shows the characteristic absorption band of the hydrogel before irradiation. In the spectrum of the hydrogel the peaks at 3441 cm^{-1} , 1679 cm^{-1} and 1090 cm^{-1} are attributed to hydroxyl, carbonyl of amide and C–N–C stretching mode, respectively. Peaks at 1649 and 1744 cm^{-1} were taken as the reference peaks due to the fact that carbonyl groups do not change after degradation. The scission of C–N bonds in crosslinker leads to the formation of hydroxyl group, which is manifested as an increase in the ratio of hydroxyl group peak (3441 cm^{-1}) to the references peak. Results also confirm the increase of oxygen content in degraded hydrogel. This indicates that the oxygen in the air participates in the termination of macroradicals produced by ultrasonic irradiation.

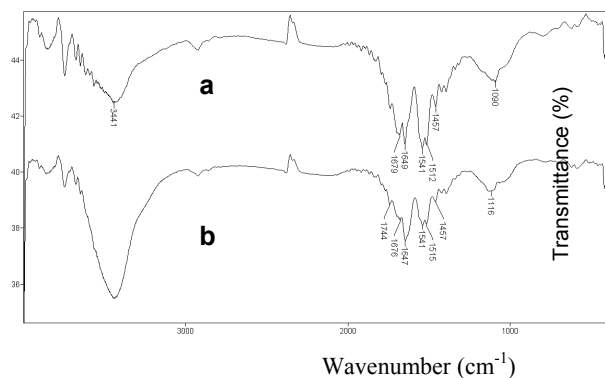


Fig. 7: FT-IR spectra of undegraded (a) and degraded (b) hydrogel after 180 min of ultrasound irradiation (pulse 8 and power 85%).

3.7. SWELLING PROPERTIES

The swelling capacity was investigated as a function of ultrasonic exposure time. Swelling of a sample (intensity 85% and pulse 8) was measured at mentioned time intervals and the results are shown in Fig. 9. According to this figure, the absorbency is increased by passing the time from 0 up to 15 min and, then, it decreases considerably with a further increase in the time of ultrasonic exposure. The maximum absorbency (130g/g) is obtained after 15 min. The initial increase in swelling capacity can be attributed to the degradation of some crosslinkers which lead to a hydrogel network with low density of cross linking. As a result swelling capacity increases. The swelling decrease after the maximum can be attributed to the ultrasonic degradation of the hydrogel network. At first, methylene bisacrylamide can be attacked by a nucleophile such as protic solvent water under ultrasonic conditions. Then, reduction of the polymer molar mass is done with further irradiation. Finally, swelling decreases toward a limited and constant value. Almost all of the degraded samples passed from the tea bag.

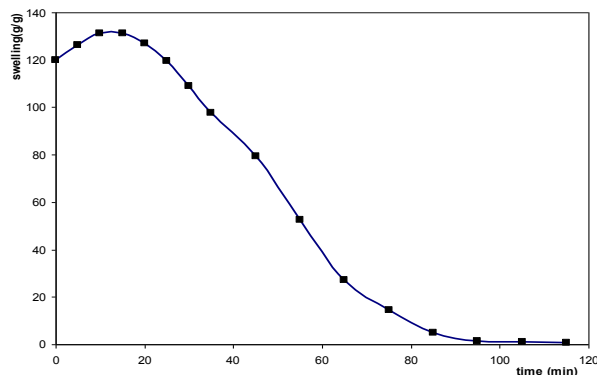


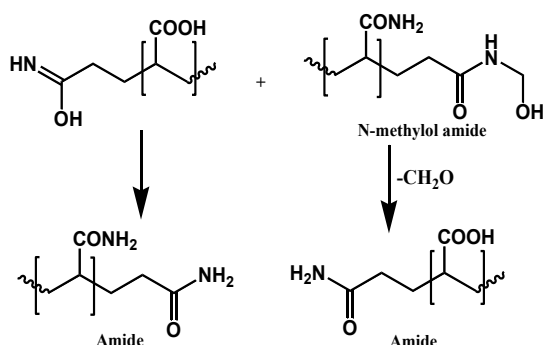
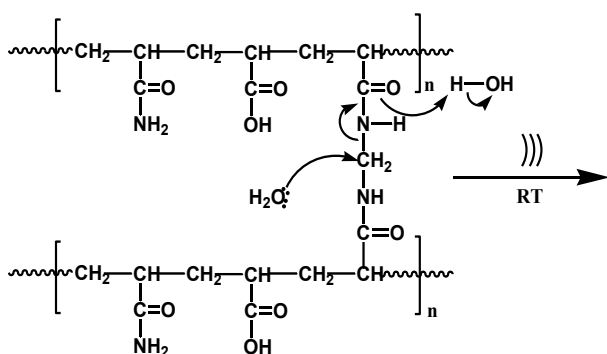
Fig.9: Swelling of the hydrogel as a function of ultrasonic exposure time (intensity 85% and pulse 8)

3.8. DEGRADATION REACTION AND MECHANISM

To find the hydrogel degradation mechanism, chemical structure of the gel and crosslinker (MBA) must be considered. It was reported that methylenbisacrylamide was hydrolytically unstable [25]. In this molecule, two electronegative atoms are bonded to a carbon atom. The methylene group has a relatively positive charge. So under normal conditions it can be attacked easily by a nucleophile such as water molecule. The reaction is catalyzed and progressed more easily by ultrasonic radiation (Scheme 2).

The chain scission of higher molecular weight polymer is easier than that of lower molecular weight due to longer relaxation time of higher molecular weight chains, indicating that molecular weight distribution broadens and high molecular weight grade decreases (Fig. 2). After some time of irradiation, the increase of short chains, the disappearance of quite long chains, and the ultrasonic activation of the wriggling motion of minor chain segments cause the disentanglement of hydrogel molecular chains. Methylenebisacrylamide in the midpoints and other point of the polymer chains are considered as the positions of initial and the next chain scission, respectively. This process shows approximately a wide molecular weight distribution under ultrasonic irradiation. When molecular weight of the polymer decreases to a limiting value, the stress induced by the deformation of chain is not enough to break down chemical bond, and mechanical degradation stops as shown by gel permeation chromatography (Fig. 10). The shear forces generated by the rapid motion of the solvent are

responsible for the breakage of the chemical bonds within the polymer. In the case of diluted aqueous solutions of the hydrogel, hydroxyl and hydrogen radicals are able to abstract hydrogen atoms from the gel structure. Thus, macroradicals are formed. Subsequent reactions of macroradicals can be: chain scission, hydrogen transfer, inter- and intramolecular recombination and finally disproportionation of macroradicals. The effect of chain scission can be followed by a reduction in the molecular weight of the polymer.



Scheme 2. Schematic representation of chemical structure of the hydrogel containing N,N-methylene bisacrylamide and Ultrasonic degradation of the crosslinked hydrogel

4. CONCLUSIONS

Viscometry is a valid and practical approach for monitoring the degradation of polymers in solution. The present research shows that the power ultrasound can effectively reduce the viscosity of the hydrogel solutions. The viscosity of the hydrogel solution after gelatinization can be reduced below 40 mPaS by the ultrasonic irradiation applied for 180 min at 25°C. This work investigates a commercially important hydrogel, based on acrylic acid and acryl amid.

The ultrasonic process can be used for other kinds of hydrogels. The experimental results indicate that the rate and extent of degradation of the hydrogels increase with increasing power and pulse of ultrasound and decrease with decreasing kinematic viscosity of the solvents (by degradation). Relative viscosity decreases with sonication time and inclines to a limiting value, below which no further degradation occurs and produces a convergence of the final solution viscosity value. The limiting value is independent of the initial molecular weight of the hydrogel. FTIR spectrometry measurements confirm that the degradation proceeds by breakage of carbon-carbon single bonds and it is governed by mechanical forces and involves radical scission mechanism. A mechanism was proposed based on experimental data.

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