Ultrasonic Degradation of Poly(acrylic acid co acrylamide) Hydrogels in Aqueous Solutions

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Abstract

Continuous exposure to high-energy ultrasonic waves depolymerizes macromolecules in solutions and produces a permanent reduction in viscosity. Different factors affect the efficiency of this process. 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 pulse) on the rate of degradation was investigated. A method of viscometry was used to study the degradation behavior of the hydrogel and a first order kinetic equation was employed 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 and UV spectrometry measurements confirmed that the degradation proceeds by mechanical forces and also involves radical scission mechanism. Finally a mechanism was proposed according to the experimental data. The elucidated merits of the present ultrasonic process are: a) The process does not require any chemicals and additives; b) The process can be simple and rapid, which means that the process is cost effective; and c) The process will not induce large changes in the chemical structure, and in particular, the properties of hydrogel. Also, the ultrasonic process has been confirmed to be applicable for many kinds of hydrogels and gels.

Keywords: Sonication, Degradation, Hydrogel, Viscosity, Kinetics.
1. Introduction

Depending on the application, polymers and gels may need to be degraded. For certain applications, polymers with lower molecular mass have 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 such as thermal, photo and catalytic degradation. The methods like UV, gamma radiation, microwave are also important. Polymers can be degraded thermally by pyrolysis, but the process consumes much energy. Therefore, alternative techniques that can reduce energy of degradation process are important. Ultrasound, photo and chemical methods require less energy for polymer degradation. Further, interaction between them and the polymeric systems can help finding the degradation pathways or mechanisms.

Polymers undergo degradation when they are subjected to high intensity ultrasound. Many Scientists have investigated the ultrasound degradation of polymers. The effects of various parameters like ultrasound pulse and intensity, frequency, temperature, vapor pressure, volume, solvent, dissolved gases, molecular weight, and polymer concentration on the ultrasonic degradation of polymers have been investigated.

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 forces. This shear forces are sufficient to break chemical bonds in polymers. In the degradation of polymers in solution, the heat generated has minor importance as hot spots are highly localized and quenched in a very short time. The degradation rate coefficient decreased with increasing temperature, and this was attributed to lower viscosity at higher temperatures. It was showed that the cavitation collapse in viscous liquids is stronger than collapse in less viscous liquid. According to cavitation mechanism in the polymer solutions, the degradation of a polymer is hardly carried out when the viscosity of solution is about 2.0 mPa s due to the disappearance of cavitation. Viscometry is a practical approach for monitoring the degradation of polymers in a solution.

One of the 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. The existence of certain and limiting molecular weight, below which ultrasonic degradation does not take place, has the additional effect in which the initial molecular weight distribution is broad and then becomes narrow during degradation. For any polymer degradation process to become acceptable to industry, it is important to be able to specify the sonication conditions to produce a particular relative molecular mass distribution.

Acrylic acid (AA) and acrylamide (AAm) are two water-soluble important monomers in industry that the research work on their polymers and gels and some another hydrogels in solution mainly focused on following categories:
- Synthesis and gelation, without ultrasound\textsuperscript{3,36-43} and in the presence of ultrasound\textsuperscript{43-46}.
- Degradation, without ultrasound\textsuperscript{4,47,48} and in the presence of ultrasound\textsuperscript{5,7,8,12,17,27}.
- Swelling and degradation, without ultrasound\textsuperscript{49-51} and in the presence of ultrasound\textsuperscript{6}.

In the synthesis, the initiator, monomer and cross-linker concentration has been investigated and the degradation process has been studied in the presence of different oxidizing agents, at different temperatures, and in various binary solvent mixtures.

The hydrogels based on acrylic acid and acrylamide are important commercial polymeric gels. Although their sonochemical polymerization has been reported,\textsuperscript{43-45} but ultrasonic degradation not been investigated. The purpose of this study is to present new experimental data for the ultrasonic degradation of these hydrogels in water. The effectiveness of the ultrasonic process has been evaluated by measuring the changes in viscosity. It is shown that the rate of ultrasonic degradation of the hydrogels follows a first order dependency of the viscosity with irradiation time. The effects of other parameters such as concentration, external pressure, temperature, volume and solvent will be carried out in the next work.

2. Results and Discussion

2.1. 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. It was not observed any appreciable degradation under pulse 5 and power 70%. Fig. 1 shows the typical changes in viscosity $\eta$ which have been observed by sonicating (intensity 85% and pulse 8) of the hydrogel solution after gelatinization.

![Figure 1. Typical changes in viscosity by sonicating (intensity 85% and pulse 8) of the hydrogel solution after gelatinization.](image-url)
It is clear that $\eta_r$ greatly decreases at the beginning, then increases with the irradiation time, and finally decreases toward a limited and constant value, which is sometimes the characteristic of mechanochemical degradation of the polymers in aqueous solutions. The increase in viscosity after the initial decrease was not adequately explained in literature. We propose the following reasons for this 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 rises the viscosity.

Second, it could be something concern to the hydrogen bonding structures and viscoelastic effects rather than permanent molecular changes.

Third, as shown in Fig. 2, it seems that partial degradation of the hydrogel increases the contact surface of the hydrogel particles and the chain of polymer can interpenetrated to each other more intensely.

It can be deduced that there is a limiting molecular weight that below which chain scission does not occur. The viscosity limit of the hydrogel solution was about 38 in 25°C. Below the limit, the polymer chain was so short that cleavage at the center of the molecule did not take place anymore. At the end of the ultrasonic treatment, the viscosity is near to that of water (about 10 mPa s). The best compromise between the duration of sonication and the reduction of the molar mass is found after 3h.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{A diagrammatic description of gelatinization and partially degradation of hydrogel by ultrasound}
\end{figure}

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.3.
2.2. Ultrasonic degradation reproducibility

The reproducibility of the ultrasonic degradation and the stability of the viscosity changes were studied using several hydrogel solutions. The viscosity of the studied hydrogel changed equally in all cases. Ultrasonic irradiation also produced a permanent reduction in viscosity. The viscosity was measured 1 and 3 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.

2.3. Ultrasonic degradation kinetics (reaction order and rate constants)

Ultrasonic irradiations to hydrogel aqueous solutions lead to the first-order reaction (for reduction port, after climax) as shown in Fig. 4. The rate constants were deducted from the slopes of curves issued from equation 2.\textsuperscript{13,16}
\[ \ln \left( \frac{\eta_t - \eta_\infty}{\eta_0 - \eta_\infty} \right) = -kt \quad \text{or} \quad \eta_t = \eta_\infty + (\eta_0 - \eta_\infty)e^{-kt} \]  

(2)

Where \( k \) is the rate constant, \( \eta_0 \) the initial hydrogel viscosity (400 mPa s), \( \eta_t \) its value at later times and \( \eta_\infty \) 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 was about 3\% according to the standard deviations of the slopes.

![Graph](image)

**Figure 4.** The plot of \( \ln(\eta_t - \eta_\infty) \) versus sonication time for hydrogel degradation (power 75\% and pulse 8).

<table>
<thead>
<tr>
<th></th>
<th>Power  75%</th>
<th>Power  85%</th>
<th>Power  95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>No pulse</td>
<td>1.234</td>
<td>1.476</td>
<td>1.806</td>
</tr>
<tr>
<td>Pulse 8</td>
<td>1.046</td>
<td>1.134</td>
<td>1.230</td>
</tr>
<tr>
<td>Pulse 6</td>
<td>0.762</td>
<td>1.068</td>
<td>1.108</td>
</tr>
</tbody>
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**Table 1.** The relationships between the calculated rate constant \( k \) (h\(^{-1}\)) with power and pulse of ultrasound.

**2.4. Effect of power on the rate of degradation**

The effect of ultrasound intensity on the ultrasonic degradation of the hydrogel was investigated. The data listed in Fig. 3a shows that the increment of the ultrasonic intensity reduces intrinsic viscosity of the hydrogel more rapidly, indicating that the extent of degradation of hydrogel increases with the
increased 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. The relationship between the degradation rate coefficient and intensity is linear as observed in Fig. 4 and in the other studies. This is because an increase in intensity leads to formation of further number of the cavitation bubbles. Above the cavitation threshold, the bubble reaches the maximum radius, and the radius is proportional to the square root of intensity. The larger cavitation bubbles collapse and produce high shear forces, so the gel degrades faster at higher intensities.

![Graph of degradation rate coefficient of hydrogel with ultrasonic intensity.](image)

**Figure 5.** Variation of degradation rate coefficient of hydrogel with ultrasonic intensity.

### 2.5. Effect of the pulse on the rate of degradation

The data listed in Table 1 and Fig. 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). Pulse 5 means in any 1 second, 0.5 sec irradiate and 0.5 sec keep silent, no pulse is related to full irradiation and so on. Pulse makes irradiation time be different from degradation reaction time. On the other hand, when the pulse is different, the irradiation time is different, even if the reaction time is the same. Pulse allows the reaction mixture to cool down.
2.6. Spectroscopy measurements

It is assumed that hydrogel changes mainly contain the breakage of the crosslinker (MBAAm) bonds. To confirm this assumption, FTIR spectra were taken before and after irradiation (Fig. 7). In the spectrum of the hydrogel (before irradiation) the peaks at 3441, 1679 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 increscent of oxygen content in degraded hydrogel. This indicates that the oxygen in the air participates in the termination of macroradicals produced by ultrasonic irradiation.

Degradation process was monitored by UV spectrometry and the results are shown in Figure 8. Absorption band at about 204 and 208 nm has appeared which is attributed to the n→π\(^*\) transitions of carbonyl groups in CONH\(_2\) and COOH functional groups in the polymer structure. There is no new absorption band in the UV spectrum of the degraded hydrogel which means that there is no change in the unsaturated system.

![Figure 8](image)

**Figure 8.** Uv-Vis absorption spectra of the initial and irradiated hydrogel (at pulse 8 and power 85%).

### 2.7. 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 Figure 10. 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 (130 g/g) is obtained in 15 min, where viscosity was minimum (figure 1). Similar variations was observed in degradation behavior of dextran hydrogels composed of positively and negatively charged microspheres.48
Figure 9. GPC representation of the degraded hydrogel by ultrasonic irradiation in distilled water solution after 3h.

Figure 10. Swelling of the hydrogel as a function of ultrasonic exposure time (intensity 85% and pulse 8).

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 (Fig. 2). 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
neucleophile such as 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 through the tea bag and swelling becomes zero.

Also some of samples centrifuged at 7000 rpm for 1-20 min and oily semisolid were precipitated. After radiation, whole sample was gelatinized and the separation of liquid portion was impossible even by centrifuge. Acidity (pp20, sartorius) and refractive index (T1, Atago) were about 6.6 and 1.334 respectively.

2.8. Degradation reaction and mechanism

To find the hydrogel degradation mechanism, chemical structure of the gel and crosslinker (MBAAm) is considered. It was reported that methylenebisacrylamide was hydrolytically unstable. 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 (Fig. 11).

![Figure 11. Schematic representation of chemical structure of the hydrogel](image_url)

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. 9). 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. Accordingly, ultrasonic degradation of hydrogel can be represented by the following mechanism (Fig. 12).

![Figure 12. Schematic representation of Ultrasonic degradation of the crosslinked hydrogel](image)

3. Experimental

3.1. 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.

3.2. Hydrogel preparation

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

3.3. Swelling measurements

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

\[ \text{Water Absorbance} = \frac{(W_S - W_D)}{W_D} \]  

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). All degraded samples were filtered and their swellings were measured.

3.4. Ultrasonic degradation

The reaction was carried out in a 250-ml beaker and distilled water was used as solvent. 120 ml hydrogel solution (1 g/140 ml H₂O) was taken each time and the beaker was held in a constant temperature (25 °C) circulator water bath (± 1 °C). 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 10 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 degrading samples were picked out at regular intervals (5 or 10 min) to measure their viscosities and then returned to continue irradiation (without sampling). A magnetic stirring for achieving homogeneous irradiation of ultrasound was applied.

3.5. 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 and was rotated at 100 rpm. The result was a direct reading of the viscosity value in cP or mPa s between 40 to 400. Samples were withdrawn
for viscosity analysis at every 5 min to 60 min and every 10 min to 180 min. The reproducibility of the ultrasonic degradation was also determined (section 3.2).

3.5. 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 400 cm\(^{-1}\). 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 2 cm\(^{-1}\) resolution.

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

The samples were analyzed by gel permeation chromatography. The system consists of a high pressure liquid chromatography (HPLC) pump (Waters 515, 7.8 mm×300 mm) for pumping the eluent. A differential refractive index detector (Waters RI 2410) was used for detecting and stored using a data acquisition system. Multiple analyses to determine the molecular weight of the same sample indicated the error was less than 1%. (Detector: RID A, Refractive index, signal delay volume: 0.00 ml, eluent = water, flow rate = 1 ml/min, acquisition interval = 0.21 s from GPC results).

4. Conclusion

Viscometry is a valid and practical approach for monitoring the degradation of polymers in solution. The possibility to tailor the network properties and degradation times of these hydrogels makes them attractive for various drug delivery and tissue engineering applications. 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 mPa s by the ultrasonic irradiation applied for 180 min at 25 °C. This work investigates a commercially important hydrogel, based on acrylic acid and acrylamid. The ultrasonic process can be developed to other kinds of hydrogels. The experimental results indicated 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 solutions. the 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 and UV spectrometry measurements confirm that the degradation proceeds by breakage of carbon-nitrogen 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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References and Notes