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Aquasonolysis of superabsorbent hydrogels crosslinked by methylenbisacrylamide

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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^[1,2]. Continuous exposure to high-energy ultrasonic waves depolymerizes macromolecules in solutions and produces a permanent reduction in viscosity^[3-7]. 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^[8,9]. This shear forces are sufficient to break chemical bonds in polymers. 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^[7,10]. Viscometry is a practical approach for monitoring the degradation of polymers in a solution^[5,7,11-14]. The elucidated merits of the present ultrasonic process are:

- The process does not require any chemicals and additives;
 - The process can be simple and rapid, which means that the process is cost effective; and
 - The process will not induce large changes in the chemical structure and the properties of hydrogel.
- Also, the ultrasonic process has been confirmed to be

applicable for many kinds of hydrogels and gels.

RESULTS AND DISCUSSION

The ultrasonic degradation is a fluid mechanical process, thus viscosity of the solvent plays an important role in determining the degradation rate. Figure 1 shows the typical changes in viscosity η_r and swelling of the hydrogel solution which have been observed by sonicating (intensity 85% and pulse 8).

It is clear that η_r greatly decreases at the beginning, then increases with the irradiation time, and finally decreases toward a limited and constant value. 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 Figure 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.

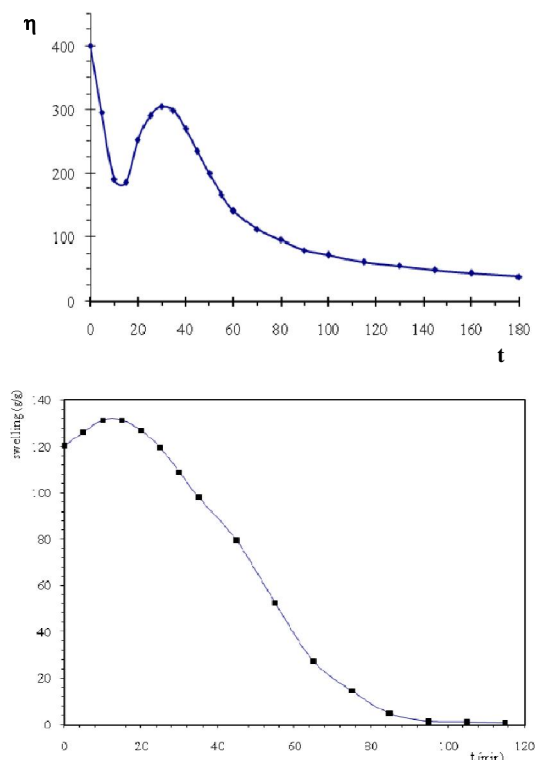


Figure 1 : Typical changes in viscosity and swelling by sonicating of the hydrogel solution (intensity 85% and pulse 8).

$$\text{Water Absorbance} = \frac{(W_s - W_D)}{W_D}$$

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 (figure 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 nucleophile 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.

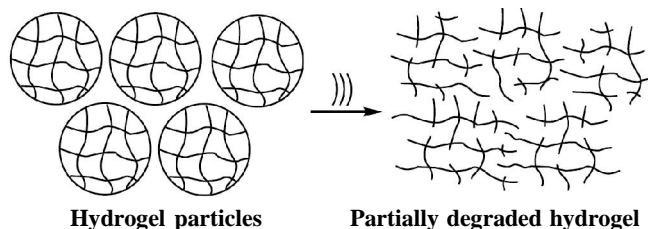


Figure 2 : A diagrammatic description of gelatinization and partially degradation of hydrogel by ultrasound

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.

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. 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. Also some of samples centrifuged at 7000 rpm for 1-20 min and oily semi-solid were precipitated. After radiation, total sample was gelatinized and the separation of liquid portion was impossible even by centrifuge. pH and refractive index were about 6.6 and 1.334 respectively.

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 (Figure 3). 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 increment of oxygen content in degraded hydrogel. This indicates that the oxygen in the air participates in the termination of macroradicals produced by ultrasonic irradiation.

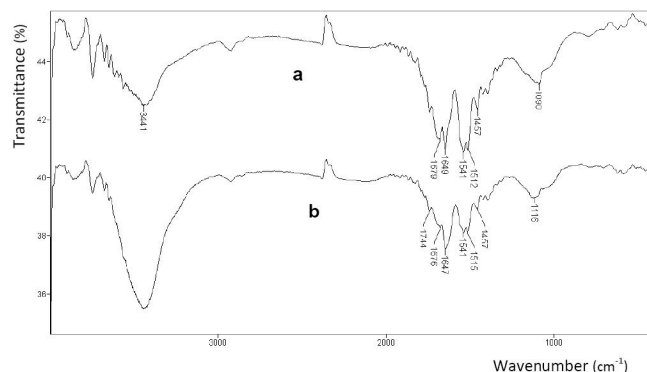


Figure 3 : FT-IR spectra of (a) undegraded and (b) degraded hydrogel after 180 min of ultrasound irradiation.

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Degradation process was monitored by UV spectrometry and the results are shown in Figure 4. Absorption band at about 204 and 208 nm has appeared which is attributed to the $n \rightarrow \pi^*$ 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.

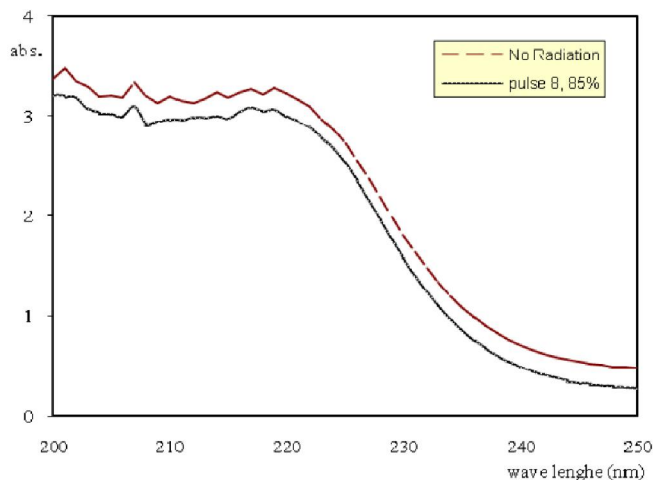


Figure 4 : UV-Vis absorption spectra of the initial and irradiated hydrogel (at pulse 8 and power 85%).

The samples were analyzed by gel permeation chromatography (GPC). No crosslinking was observed because the GPC did not show any molecular weight above the initial molecular weight (Figure 5).

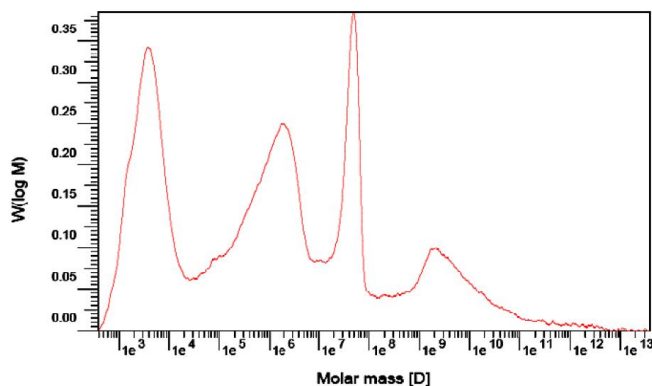


Figure 5 : GPC representation of the degraded hydrogel by ultrasonic irradiation in distilled water solution after 3h.

Degradation reaction and mechanism

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 (Figure 5). The shear forces generated by the rapid motion of the solvent are responsible for the breakage of the chemical bonds within the polymer^[15]. 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^[10,16,17]. 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 (Figure 6).

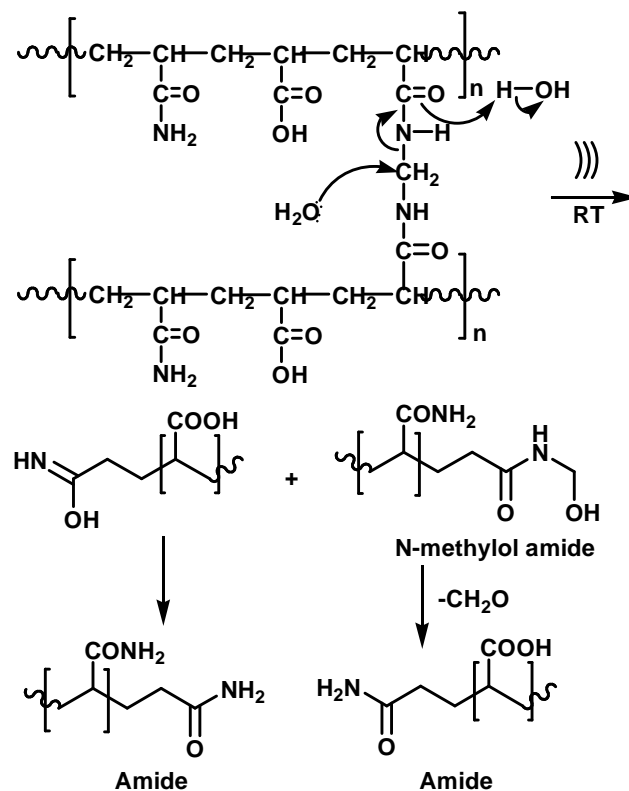


Figure 6 : Schematic representation of chemical structure and ultrasonic degradation of of the hydrogel containing N,N-methylene bisacrylamide

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 acryl amid. 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. 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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