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Operating parameters in ultrasonic decomposition of superabsorbents

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ABSTRACT

Prolonged 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. The experimental results in our previous work indicated that the rate of ultrasonic degradation of acrylic acid co acrylamide hydrogel increased with increasing ultrasonic power and pulse. In this work, at constant power and pulse, the effects of different operating parameters such as time of irradiation, temperature, solution concentration, volume, solvent, immersion depth of horn on the rate of degradation has been investigated in aqueous solution using laboratory scale operation. A method of viscometry was used to study the degradation behavior of the hydrogel. The experimental results show that the viscosity of polymer solution decreased with an increase in the ultrasonic irradiation time and approached a limiting value. The present work has enabled us to understand the role of the different operating parameters in deciding the extent of viscosity reduction in hydrogel systems.

KEYWORDS

Operating parameters;
Sonication;
Decomposition;
Hydrogel;
Viscosity.

INTRODUCTION

Controlling degradation behavior has been one of critical issues in general biomaterials research, and has been widely investigated to date[1-5]. In general, biomaterials need to be cleared from the body once they complete their roles in the body, and degradable materials could be ideal for this purpose. In addition, drug molecules may be covalently bound to nondegradable polymer networks with a degradable linkage. As such, the rate of release for these gels is dependent on the cleavage kinetics of the drug-network linkage. Shortening of the macromolecular chains can be achieved by various methods such as thermal, photo and catalytic degradation[6-8]. The methods like UV[9-13], gamma radiation[13,14], microwave[14,15] are also important. Ultrasound, photo and chemical methods require less energy for polymer degradation. Further, interaction between them and the polymeric systems can help find the degradation pathways or mechanisms[8-10,16-18]. Many Scientists have investigated the ultrasound degradation of polymers[7,10,12-14,16-36]. The effects of various parameters like ultrasound pulse and intensity[12,17-20,31], frequency[20,21], temperature[17,23-25,31,32], vapor pressure[32], volume[19,24,25], solvent [17,23,32], dissolved gases[21,31], molecular weight [26,27], polymer concentration[12,19,20,24-29] on the ultrasonic degradation of polymers have been investigated.

Desai et al.[37] studied the ultrasonic degradation of low density polyethylene at different concentrations (1%, 1.2%, and 1.4%, w/v) and different volumes (50, 75 and 100 ml) at two different operating temperatures (60 and 80°C). It was found that extent of degradation increases with a decrease in reaction volume and concentration at same supplied ultrasonic power. Kanwal et al.[38] also observed that as the concentration of polymer solution is increased from 1% to 15%, the rate of degradation decreased. Since at high concentrations, entanglements influence the energy transfer processes between solvent and polymer and appears to reduce the probability of degradation. Taghizadeh et al.[39] studied the degradation of aqueous polyvinyl alcohol at 25ºC and it has been observed that the degradation rate of PVA solution decreases with increasing of solution concentration. Harkal et al.[40] studied the ultrasonic degradation of aqueous polyvinyl alcohol at different concentrations and different volumes. The decrease in rate constant is attributed to the fact that at higher concentration and at higher volume, the intensity of cavitation phenomenon is depressed and therefore the extent of polymer chain breaking decreases.

Sonochemistry is the study of the effect of acoustic waves on chemical, biological, and physical systems. The sonochemistry effects are based on a physical process known as acoustic cavitation that is the formation, growth, and the implosion of bubbles in a liquid[41,42]. The resulted shear forces are sufficient to break chemical bonds in polymers[43,44]. 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[44]. 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[18,26]. viscometry is a practical approach for monitoring the degradation of polymers in a solution[12-14,19,20,24-29].

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[3,36-43] and in the presence of ultrasound[53-56]
- Degradation, without ultrasound[4,47,48] and in the presence of ultrasound[10,12,13,17,22,32]
- Swelling and degradation, without ultrasound[58-60] and in the presence of ultrasound[11]

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[53-55], but ultrasonic degradation and parameters optimization have not been investigated. In our previous work, we investigated the effects of sonication parameters and showed that the rate of degradation increases with increasing ultrasonic power and pulse[61]. The present work has focused on the optimization of different operating parameters using laboratory scale operation with ultrasonic horn reactor. The extent of degradation has been quantified in terms of the change in the intrinsic viscosity of the polymer solution, which is a simple method for monitoring the rate of degradation of polymer systems. Studies are currently underway to improve the first experimental conditions. The purpose of this study is to present new experimental data over an extensive temperature range, the effect of concentration, volume, solvent and some other parameters on degradation of these hydrogels in water. Effect of depth of the horn has also been investigated as the physical effect is considered to be predominant in the case of polymer degradation. The ultrasonic process has been confirmed to be applicable for many kinds of hydrogels and gels.

EXPERIMENTS

Materials and hydrogel formation

The monomer, acrylic acid (AA, Merck) was used after vacuum distillation. Acrylamide (AAm), ammonium persulfate (APs) and methylene bisacrylamide (MBAAm) were of laboratory reagent grade and were purchased from Fluka. All solutions were prepared using distilled and deionized water. Polymer gels are generally produced by (I) copolymerization of a monomer and a cross linker in the presence of a solvent or (II) introduction of cross-links into a homogenous polymer solution. The hydrogel was prepared according to early our works in optimum conditions[47,48,61]. After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat and light.

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. The equilibrated swollen gel was allowed to drain by removing the tea bag from water and hanging until no drop drained (2min). The bag was then weighed to determine the weight of the swollen gel. The equilibrium swelling was calculated using the following equation[9,61]

$$\textbf{Water Absorbance} = \frac{(W_S - W_D)}{W_D} \qquad (1)$$

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). A few degraded samples were filtered and their swellings were measured.

Hydrogel degradation and viscosity measurements

The reaction was carried out in a 20-ml stainless steel cylinder and distilled water was used as solvent. 12ml hydrogel sample (containing 0.1g gel) was taken each time and the cylinder was held in a constant temperature (25°C) circulator water bath (±0.1°C). Ultrasound was coupled directly to the reaction system by a horn type homogenizer (Sonopuls HD 2070, Bandelin, Germany) with HF-power of 70 W and frequency 20 KHz. The diameter of the horn tip was 2 mm. The probe was immersed 20mm below the liquid surface (center of the solution). The cylinder was put in a sound proof box with clear acrylic glass door.

Periodically, samples of sonicated solutions were removed for viscosity measurements using a rotational viscometer (DV-II + Pro RV, Brookfield, USA). The viscometer had a Small Sample Adapter with a cylindrical spindle type (#62) and was rotated at 100 rpm. The result was a direct reading of the viscosity value in cP or mPas between 0 to 2300. Experiments have been repeated at least twice to check the reproducibility of the obtained data for the variation of viscosity against time for all the sets.

RESULTS AND DISCUSSION

Variation of viscosity and the swelling of hydrogel with sonication time

The ultrasonic degradation is a fluid mechanical process, thus viscosity of the solvent plays an important role in determining the degradation rate. The effect of sonication time on the intrinsic viscosity of the hydrogel solution has been investigated at 12 ml reaction volume, depth of horn as 2 cm, and operating temperature at 25°C. Figure 1 shows the effect of sonication time on the viscosity and swelling of hydrogel sample. It can be seen from the figure that with the use of sonication, viscosity decreased significantly for the hydrogel. The study also revealed that the degradation of bonds continued only to a certain limiting viscosity. The limiting intrinsic viscosity of solution is 2mPas, near to that of water whereas initial viscosities were between 1850 to 1900mPas. Below the limiting viscosity, the polymer chain was so short that it followed ultrasonic vibrations flexibly and cleavage at the center of the molecule did not take place anymore[26-28]. The best compromise between the duration of sonication and the reduction of the molar mass is found after 15min.

The increase in viscosity after the initial decrease was adequately explained in our previous paper[61]. We proposed three reasons such as; (1) the formation of macroradicals, and recombination of them, (2) the hydrogen bonding structures and viscoelastic effects and (3) the increase in the contact surface of the hydrogel particles and the chain of polymer.

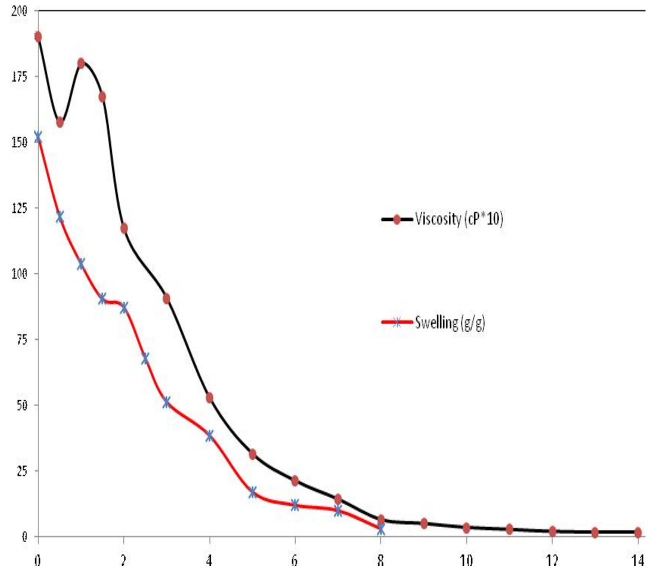


Figure 1 : Typical changes in viscosity and swelling of the hydrogel solution as a function of ultrasonic exposure time in 25ºC.

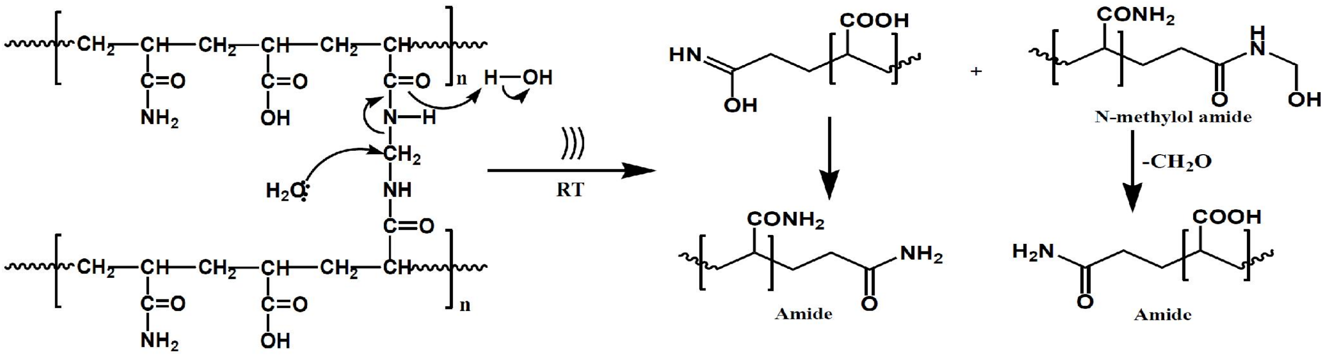
The swelling decrease can be attributed to the ultrasonic degradation of the hydrogel network. At first, methylene bisacrylamide can be attacked by a neuclophile such as water under ultrasonic conditions Scheme 1. Then, reduction of the polymer molar mass is done with further irradiation. Finally, swelling decreases toward a limited and constant value. Almost all of the degraded samples passed through the tea bag and swelling becomes zero.

Ultrasonic degradation reproducibility

Experiments were repeated at least twice to check the reproducibility of the obtained data for the variation of the viscosity against time for all the sets and it has been observed that experimental errors were within the standard accuracy (i.e. within ±4%). 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.

Effect of temperature on the rate of degradation

The effect of temperature on the degradation of hydrogel was studied; the variation of η with sonication time at different temperatures is illustrated in Figure 2. The results indicate that the cavitation effects at lower temperature were more effective than the mechanical effects at higher temperature in the viscosity depression of hydrogel solutions. Also, the rate coefficient is higher at low temperature and decreases at higher temperature. At higher temperature, clearly the vapor pressure will be higher and so the vapor will enter the cavitation bubble, which leads to the cushioning effect[31,26]. The cushioning effect reduces the shock wave intensity and thus the rate of degradation. The increased viscosity of the solvent at lower temperatures increases rapid transmission of shock waves and favors the defragmentation of polymer chain at low strain rates[31].



Scheme 1 : Schematic representation of chemical structure of the crosslinked hydrogel and its ultrasonic degradation.

The rate coefficients, k for degradation reaction decreased from 0.311 to 0.283 as the temperature increased from 20 to 35ºC. As the rate coefficients decrease with an increase in temperature, an Arrhenius plot would yield negative activation energies and would not have any physical meaning. The decrease of degradation rate with an increase of temperature is similar to that observed for mechanical breakage of polymers. As the temperature of the solution increases, a large quantity of the solvent vapour enters the cavitation bubbles during their expansion and exerts a cushioning effect during the collapse leading to diminishing of the intensity of the shock wave, reducing the jet velocity leading to reduced degradation at higher temperatures.

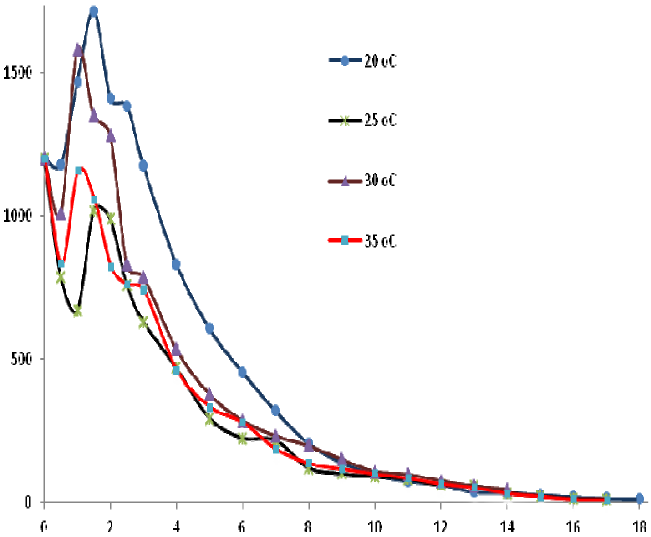


Figure 2 : Effect of temperature on sonochemical degradation of hydrogel.

Effect of concentration of hydrogel

Effect of concentration was investigated at a constant reaction volume of 12 ml for different concentrations of C, 3C/4, C/2, and C/4, respectively and the obtained results have been given in Figure 3. Under the same conditions, the decrease in η of the sample with a high concentration is more than of the sample with a low concentration. These results indicate that the extent of degradation is more pronounced in more concentrated solutions. Kinetic analysis revealed that the rate constant for degradation was the maximum (0.635 min^{-1}) for the most concentration and it decreased to 0.21 min^{-1} when the concentration was decreased to C/4. It should be noted here that independent bubble dynamics studies have clearly indicated that an increase in the viscosity results in an increase in the collapse pressure generated due to cavitation. So an increase in viscosity with concentration results in the molecules to become more mobile in solution and the velocity gradients around the collapsing bubbles to therefore become larger, resulting in more extents of viscosity reduction. Indeed there are more molecules to be degraded when the concentration is higher and that is why the degradation is faster.

Effect of volume on the rate of degradation

The observed dependence of the efficiency of ultrasonic depolymerization on the volume of the sonicated sample can be explained by the fact that the most efficient depolymerization occurs in the proximity of the inserted probe, since the energy of the ultrasonic waves decreases with increasing distance from the probe. Therefore the best yields of ultrasonication were obtained for the equipment used in the small volumes of solution. Indeed with an increase in the operating volume, the non-uniformity of the cavitational activity increases (more dead zones where the cavitational activity is minimal) resulting into detrimental effects.

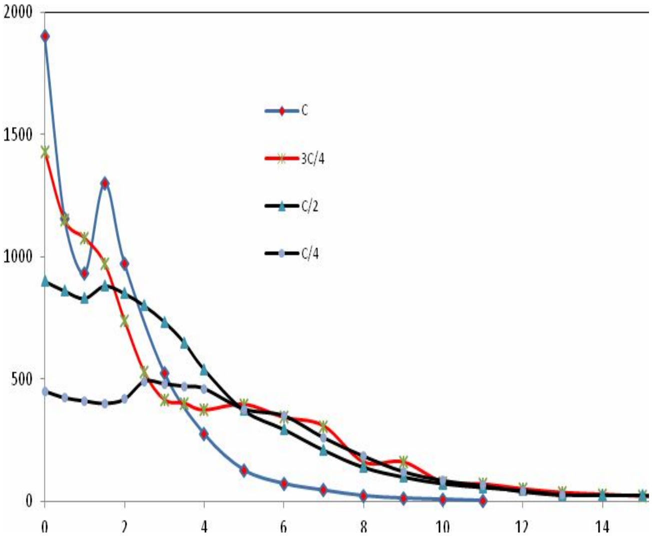


Figure 3 : Effect of concentration of hydrogel on the extent of viscosity reduction.

Figure 4 shows the effect of reaction volume on the limiting viscosity of hydrogel solution when it is subjected to ultrasonic degradation. It shows that the limiting viscosities for hydrogel

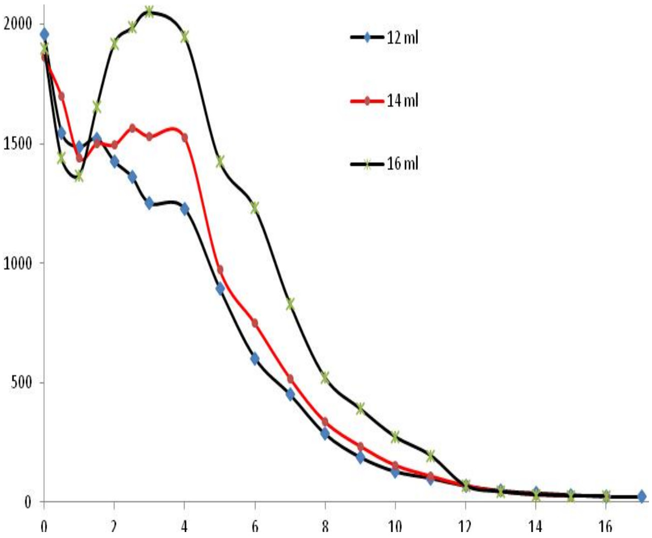


Figure 4 : Effect of volume on viscosity changes and related degradation rate constant (k).

solution at 12, 14 and 16 ml reaction volume is nearly equal, but for 16 ml sample has a delay.

Effect of solvent on the rate of degradation

The effect of solvent on the ultrasonic degradation was studied by investigating the degradation of hydrogel at 30°C using different ethanol/water ratio as solvent and Figure 5 depicts the results. The variation in rate coefficient for different solvents is mainly attributed to their cavitation capacity which governs the intensity of shock waves radiated from the collapsing cavity. The degradation rate in a particular solvent mainly depends upon the properties of solvent like vapor pressure and kinematic viscosity[62] which primarily affect the cavitation capacity [63] of the solvent. It was observed that the rate is maximum for pure water (ETOH 0%).

The same phenomena can be used to explain the decrease of the degradation rate coefficients with an increase in the vapour pressure of the solvent. While kinematic viscosity of the solvent was assumed to play a role in the ultrasonic degradation[29], a more detailed study indicated that this could be a crucial parameter.

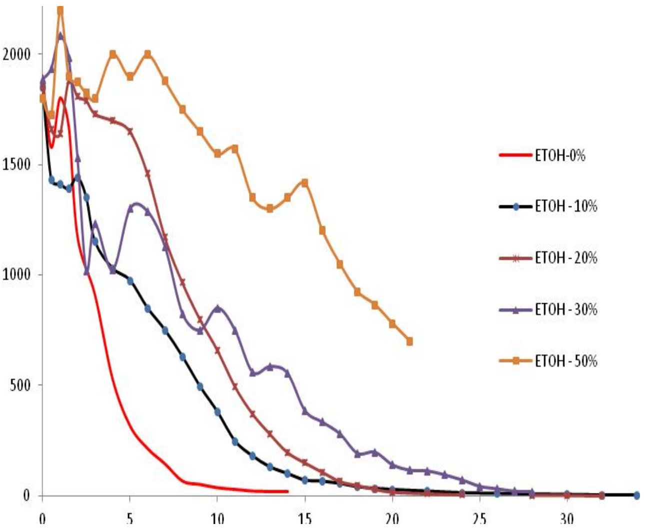


Figure 5 : Effect of solvent on the extent of viscosity reduction of hydrogel solution.

Effect of depth of horn on the rate of degradation

The extent of mixing in the reactor is dependent on the immersion depth of the horn tip. The observed results can be attributed to the fact that, flow pattern of liquid in terms of direct circulation currents generated due to the acoustic streaming and reflections from the bottom of the reactor, depends on the distance of horn tip immersed in the solution. Figure 6 shows the effect of depth of horn on the viscosity reduction for samples of hydrogel at constant volume of 12 ml. It has been observed that, during the initial stages of operation, the extent of viscosity reduction is higher for the operation with depth as 3 and 4cm. However, the final extent of reduction in intrinsic viscosity is marginally higher at a depth of 3cm. The least effect is related to 1cm depth. Flow visualization studies using dispersion of red ink solution indicated that the ink was most effectively dispersed at a medium depth suggesting that better mixing resulted at this immersion depth. Since the polymer degradation is controlled by the physical effects of ultrasonic irradiation i.e. liquid circulation currents along with the local shear rates, any changes in flow pattern of liquid due to horn immersion depth will affect the degradation rate. It appears that an optimum immersion depth needs to be selected so as to get maximum cavitational effects in the reactor, which will result maximum extent of degradation in the reactor.

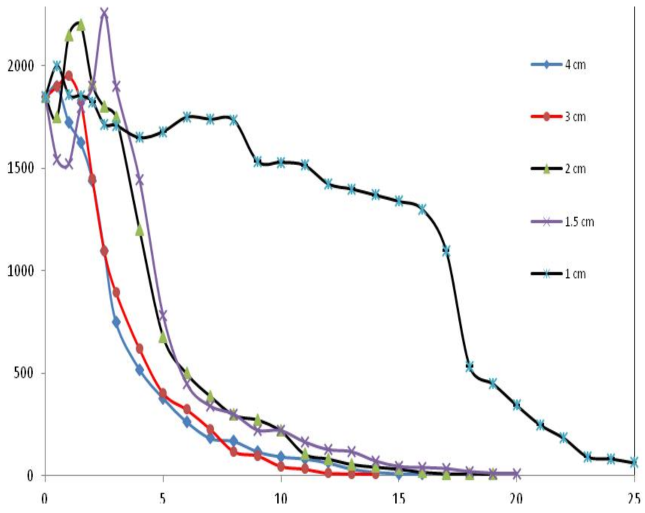


Figure 6 : Effect of depth of horn on the extent of viscosity reduction of hydrogel solution.

CONCLUSIONS

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 deliveries and tissue engineering applications. The present research shows that the power ultrasound can effectively reduce the viscosity of the hydrogel solutions below 10 mPa s after 20 min at 25ºC. 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. A commercially important hydrogel, based on acrylic acid and acryl amid was investigated and the ultrasonic process can be developed to other kinds of hydrogels. The effect of solvent and temperature on the ultrasonic degradation of hydrogel was studied and it is mainly attributed to vapor pressure of the solvent and the variations of the rate coefficients with temperature, vapor pressure and kinematic viscosity was analyzed. The effect of vapor pressure on the ultrasonic degradation is very high compared to viscosity, which is clear from the exponential variation of degradation rate coefficient, k, with vapor pressure.

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