A Kinetic Study of Ultrasonic Degradation of Carboxymethyl Cellulose

Mohammad Taghi Taghizadeh, Helen Rad, Reza Abdollahi

Department of Physical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

ABSTRACT: In this study, the effect of power of ultrasound, temperature, and concentration of carboxymethyl cellulose (CMC) solution on the rate of ultrasonic degradation were investigated, and a kinetic model based on viscometry data was used to calculate the rate constants in different conditions. To investigation of effect of ultrasonic power on the degradation of CMC, the power of ultrasound was increased and observed that the viscosity of the CMC solution was decreased with an increase in the power of ultrasound, but the extent of the degradation in a constant power was found to decrease with an increase in concentration or temperature. The ultrasonic degradation of CMC solutions was carried out at different temperatures to investigate the effect of the temperature on the rate of degradation. The calculated rate constants indicated that the degradation rate of the CMC solutions decreased as the temperature increased. The degraded CMCs were characterized by gel permeation chromatography, and average molecular weights of ultrasonicated CMCs were compared in different reaction conditions. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1896–1904, 2012

Key words: carboxymethyl cellulose; degradation; viscosity; gel permeation chromatography

INTRODUCTION

Cellulose is a polysaccharide with a diverse range of applications that is built up as a linear homopolymer from 1, 4-β-glycosidically linked glucose. Figure 1 shows the structural formula of the native cellulose.[1] Carboxymethyl cellulose (CMC) is a cellulose derivative with carboxymethyl groups bound to the hydroxyl groups of the glucose unit.[2–4] Chemically modified CMC with improved properties is gaining increasing in many fields not only because it is low in cost but also mainly the polysaccharide portions of the products are biocompatible and biodegradable.[5]

CMC is an industrially important cellulose derivative. Examples of industrial applications are found in the food industry as a thickener[6] and a binder.[7] In recent years, CMC evoked considerable interest as a texturing additive for foodstuffs[8,9] and preparation of hydrogels from graft copolymerization of the hydrophilic monomers onto CMC.[10–12] In addition, CMC was used in the oil industry as a lubricant for drilling, and in the cosmetic industry as a stabilizer and a binder. Because of its nontoxicity, biodegradability, and biocompatibility, CMC solution has also been widely used as a carrier for a bone graft.[13] It has been reported that CMC can improve the clinical properties of calcium sulfate when used as a binder for particulate bone grafts.[14]

The ultrasonic polymer degradation has several unique characteristics that make it interesting both from practical and theoretical viewpoints.[15] High-intensity ultrasonic treatment can be applied to degrade polymers and to facilitate emulsifying and cleaning processes in homogenous liquid phase.[16] The ultrasonic energy is dissipated in solution, resulting in cavitations. Cavitation produces vibrational wave energy, shear stresses at the cavitation interphase, and local high pressure and temperature. These are the major factors causing the degradation of polymers.[17–20] Application of high-intensity ultrasound to dispersions of carbohydrates can lead to depolymerization because of the intense mechanical and chemical effects associated with cavitation.[21–24] Cavitational thermolysis may produce hydroxyl radicals and hydrogen atoms that can be followed by formation of hydrogen peroxide.[25–27] Some cavities exist only for one cycle of the sound field and collapse violently (transient cavities), whereas other are long lived and oscillate around some equilibrium size (stable cavities).[28] These transient reactive species can subsequently react with carbohydrates. In addition, hydrolysis and cleavage due to the strong mechanical forces has been reported for a variety of polysaccharides.[29] Recently, Byun and coworkers[30] were investigated on radiation degradation of CMC in homogenous phase.
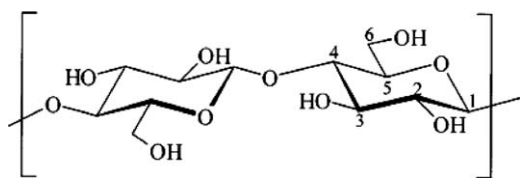
Figure 1 Structure of water-soluble cellulose derivatives (carboxymethyl cellulose; R = CH₂COONa).

Recently, Gogate and coworkers[31] were investigated on some conditions and parameters, in the presence of additives, which affected the ultrasonic degradation of CMC and poly(vinyl alcohol) (PVA). Also, Antti et al.[32] previously worked on ultrasonic degradation of CMC and studied the effect of different molecular mass and concentrations by dynamic viscosity measurements.

The objective of this study was to present new experimental data for the ultrasonic degradation of CMC with different concentrations and to introduce a simple kinetic model for the evaluation of degradation rate of polymers via viscometry. This was performed by the correlation of viscosity measurements at different sonication times. The variation of the rate coefficients with concentration is attributed to the change in the viscosity. Finally, these quantities are correlated with the molar concentration of polymer, resulting in a kinetically meaningful expression. Additionally, gel permeation chromatography (GPC) analysis was performed to compare the effect of different conditions on reducing of molecular weight of CMC.

EXPERIMENTAL

Materials

CMC in form of sodium salt (ultra high viscosity) was purchased from Fluka (Sigma-Aldrich, Germany). Molecular weight was 460,000 kDa, which was determined by viscometer. All other chemicals were of laboratory reagent grade and were purchased from Merck (Germany GmbH). All solutions were prepared using distilled and deionized water.

Methods

CMC solution preparation

CMC solutions containing 0.5, 1.0, 1.5, 2.0, and 2.5 g/L CMC in 0.1 mol/L NaCl were prepared; because of Mark–Houwink constants were reported in the NaCl solution. However, in the presence of salt, CMC formed molecular associates and was not solved thoroughly.[33] Therefore, the solution was stirred overnight to ensure complete solubilization of the CMC molecules. The solution was then filtered to remove any impurities, and 100 mL samples were immediately sonicated.

Experimental setup and procedure

Reactions were carried out in a cylindrical 100 mL Pyrex glass vessel. An ultrasound generator (Dr. Hielscher Ultrasonic Processor UP200 H) operating at a fix frequency of 24 kHz, and a variable power output up to 100 W nominal value, in aqueous media was used for sonication experiments. A titanium-made H3 sonotrode (φ = 3 mm) immersed in liquid from the open to the atmosphere top of the vessel was used to deliver the ultrasound energy in the reaction mixture. The vessel was fed with a 100 mL CMC solution and the reaction temperature in the case of sonolysis processes for the study of effect of concentration and power of ultrasound was kept constant at 25 ± 1°C through the use of cooling water circulating through the double-walled compartment, thus acting as cooling jacket. The reaction vessel was covered with a dark cloth to avoid unwanted photochemical reactions induced by natural light.

GPC characterization

GPC (HLC6A, Shimadzu) was used to compare molecular weight of the original CMC and degraded samples at the end of 75 min and at different concentrations, power of ultrasound, and temperature.

Viscosity measurements

The intrinsic viscosities of the original CMC and its degraded solutions at 25°C were measured using the capillary viscometer (Setavic Kinematic viscometer). The internal capillary diameter was 0.05 mm. Efflux times were measured for CMC solutions (t_s) and the solvent (t_0). measurement of efflux times were repeated two times, and average efflux time was then converted to the ratio of t_s/t_0, which is proportional to relative viscosity, η_r, of CMC solution.

$$\eta_r = \frac{t}{t_0}, \eta_{sp} = \eta_r - 1, \qquad (1)$$

The intrinsic viscosity [η] values can be related to the specific viscosity, η_{sp}, and relative viscosity, η_r, by the Huggins and Kramer equations.[34] The conditions used in this work (α = 0.91 and k = 12.3 × 10^{-6} L/g) were adopted on the basis of previous findings in the literature.[35]

Kinetic model

The rate of degradation is defined as the number of scission that occurs in 1 L in unit time, and we must keep in mind that a scission in a chain yields two pieces. Thus, the rate equation of the degradation is as follows[36]:

$$R = \frac{dM}{dt} = kM^n, \qquad (2)$$

where M is the total molar concentration of the polymer, k is the rate constant, and n is the order of reaction with respect to the total molar concentration of the polymer. From the experimental data, it is clear that the degradation rate decreases with increasing solution concentration, so "n" is negative. Harkal et al.[37] was found that the order of ultrasonic degradation reaction for PVA obtained from this kinetic model is -1.

It is noted that solution concentration (g/L) is constant, and the total molar concentration (mol/L) increases during the degradation of polymer. The solution of differential eq. (2) is

$$M^{1-n} - M_0^{1-n} = (1-n)kt, \qquad (3)$$

where M_0 is the initial total molar concentration of polymer. The total molar concentration is related to the number average molecular weight through[38]:

$$M = \frac{C}{M_n}. \qquad (4)$$

Moreover, viscosity average molecular weight, M_v, is related to the number average molecular weight, M_n, through[39]:

$$M_v = [(1+\alpha)\Gamma(1+\alpha)]^{-\frac{1}{\alpha}} M_n, \qquad (5)$$

where, $\Gamma(1+\alpha) = \int_0^\infty e^{-t} t^\alpha dt$, M_v is related to the intrinsic viscosity, $[\eta]$, through Mark–Houwink equation:

$$M_v = \left(\frac{[\eta]}{K}\right)^{1/\alpha}, \qquad (6)$$

where α and k are the Mark–Houwink constants.

Finally, $[\eta]$ can be related to the specific viscosity, η_{sp}, and relative viscosity, η_r, by Huggins and Kramer equations:

$$\frac{\eta_{sp}}{C} = [\eta] + K'[\eta]^2 C, \qquad (7)$$

$$\frac{Ln\eta_r}{C} = [\eta] + (K' - 0.5)[\eta]^2 C. \qquad (8)$$

From eqs. (7) to (8), intrinsic viscosity is

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - Ln\eta_r)}}{C}. \qquad (9)$$

Substitution of eq. (9) in (6) and eq. (6) in (5) yields

$$M_n = \left[\frac{\sqrt{2(\eta_{sp} - Ln\eta_r)}}{(1+\alpha)\Gamma(1+\alpha)KC}\right]^{1/\alpha}. \qquad (10)$$

Finally, the substitution eq. (10) in (5) yields:

$$M = \left[\frac{(1+\alpha)\Gamma(1+\alpha)KC^{1+\alpha}}{\sqrt{2}}\right]^{1/\alpha} \Delta\eta. \qquad (11)$$

In addition, substitution eq. (11) in (3) yields:

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = (1-n)$$
$$\times \left[\frac{\sqrt{2}}{(1+\alpha)\Gamma(1+\alpha)KC^{1+\alpha}}\right]^{(1-n)/\alpha} kt. \qquad (12)$$

or

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = k't. \qquad (13)$$

RESULTS AND DISCUSSION

Determination of reaction order of degradation of CMC

At the level of interatomic distances within the macromolecules, there is still some debate regarding the place where the bond breakage occurs. By analogy with the chemical degradation, it is expected to take place at the weakest links in the polymer backbone, but some works, suggested that it mainly occurs at the midpoint of the polymer chains and the existence of a final limiting molecular weight is predicted; below which ultrasounds have no more effect.[40,41] In general, polymer mechanochemistry induced by an acoustic field is a nonrandom process; for example, the scission of polymer chains in solution occurs at a preferential position near the midpoint.[42–44] Moore et al. approved this idea by an isotope labeling experiment on ultrasonic degradation of linear polyethylene glycol (PEG). They demonstrated that when a single weak azo link was positioned at the center of a linear PEG chain, mechanically induced cleavage was localized almost exclusively to the single weak site.[45]

Several studies propose a random chain breakage but still consider that some bonds are more resistant, in relation to the decrease in the scission rate constant as lower values of degree of polymerization are reached.[46] Due to the polydisperse nature of most polymers, an accurate analysis of the degradation kinetics is almost impossible without information about the location of chain scission and the dependence of rate coefficients on the molecular
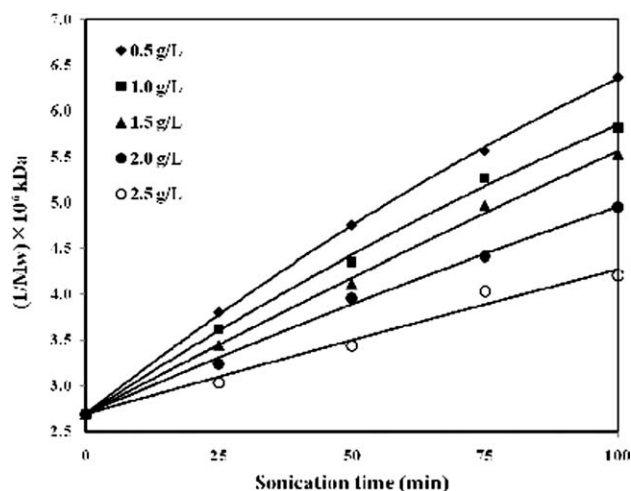
Figure 2 The plot of $\Delta\eta^{1.6} - \Delta\eta_0^{1.6}$ versus the sonication time for different concentration of CMC solution at 25°C.

weight of the polymer. Two simplified models, based on different assumptions of the location of chain scission, have been proposed to quantitatively describe the degradation process of polymers.[47]

Although, a number of different rate models have been proposed for the degradation of polymers,[48,49] but in this study, a simple model was employed via viscometry. Using eq. (11), a negative order for the dependence of the reaction rate on total molar concentration of CMC solution within the degradation process was suggested. In the initial sonication times, for different concentration of polymer we calculate total molar concentration of polymer. The results are depicted in Figure 2. Previous studies were proved that with an increase in concentration, the rate constant, k, was decreased obviously.[50,51] These observations are explained in terms of viscosity changes for different polymer concentrations. At higher concentrations, the solution viscosity increases. An increase in viscosity raises the cavita-
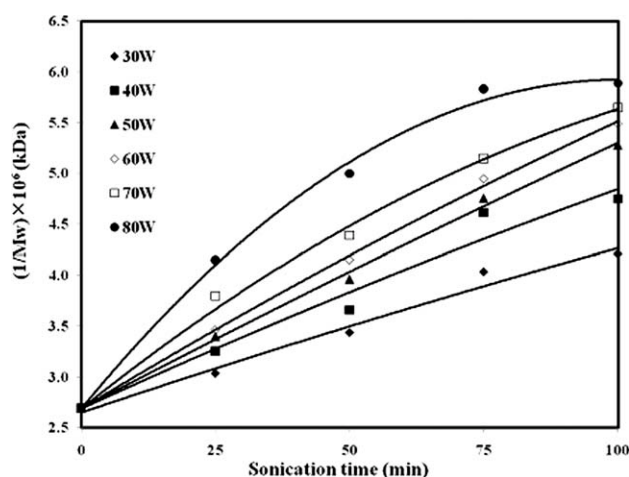
TABLE I
η_r, [η], and M_v of CMC Samples Degraded by Ultrasonic Irradiation in Various Concentrations and 25°C at the End of 70 min

C (g/L)	Limiting η_r	[η] (L/g)	Limiting M_v (kDa)
0.5	1.073	0.143	29,382
1.0	1.098	0.191	40,289
1.5	1.118	0.228	48,902
2.0	1.144	0.276	60,440
2.5	1.164	0.312	69,112

tion threshold. This increased threshold makes it more difficult for cavitation bubbles to form. More importantly, the velocity gradients around collapsing bubbles become smaller, and the elongation of the polymer backbone is reduced.[52]

The slopes of plots give the initial rate of degradation using eq. (19), the plot of ln R versus ln[M] are linear and it is shown in Figure 3. The slope of curve is −0.6, which suggest the order of reactions with respect to total molar concentration of polymer.[53]

From substitution of the value of "n" in eq. (13), we obtain the following:

$$\Delta\eta^{1.6} - \Delta\eta_0^{1.6} = k't. \tag{14}$$

Effect of concentration on the rate of CMC degradation

The data of limited viscosities (relative and intrinsic) listed in Table I show that the viscosity increases with increasing of concentration of polymer, at the end of 70 min. Sonication was carried out for five different CMC concentrations at 25°C. The relationship between η_r and sonication time is presented in Figure 4. On the basis of these findings, it is clear
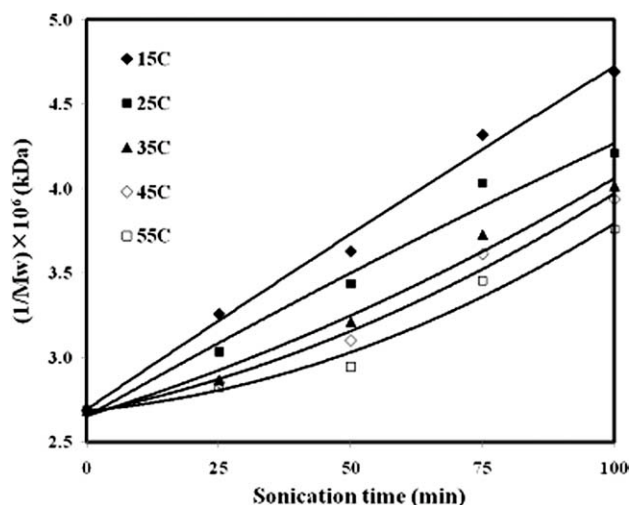

Figure 3 The plot of ln R versus ln M for degraded CMC at 25°C.

Figure 4 The relationship between η_r and sonication time for different concentrations at 25°C and fixed power of ultrasonic irradiation (30 W).
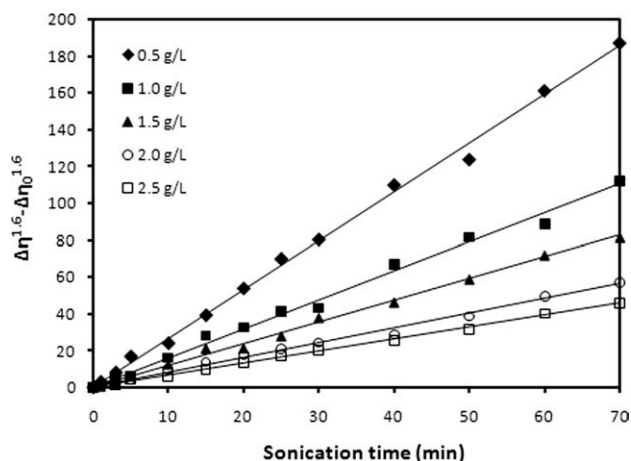
Figure 5 The relationship between the limiting value of η_r and solutions concentration.

that η_0 decreases with sonication time and tends to have a constant value. It can be deduced that there is a limiting molecular weight that below which chain scission does not occur. The relationship between the limiting value of η_r and solution concentration is presented in Figure 5. These results indicated that the extent of degradation is more pronounced in dilute solutions. This might be due to the fact that the probability of chemical bond scission caused by efficient shearing in the polymer chain is greater in dilute solution. These findings are consistent with the results of other investigators.[54]

Effect of power of ultrasound on the rate of CMC degradation

Figure 6 shows the effect of increasing changing ultrasound power on relative viscosity (η_r)of CMC
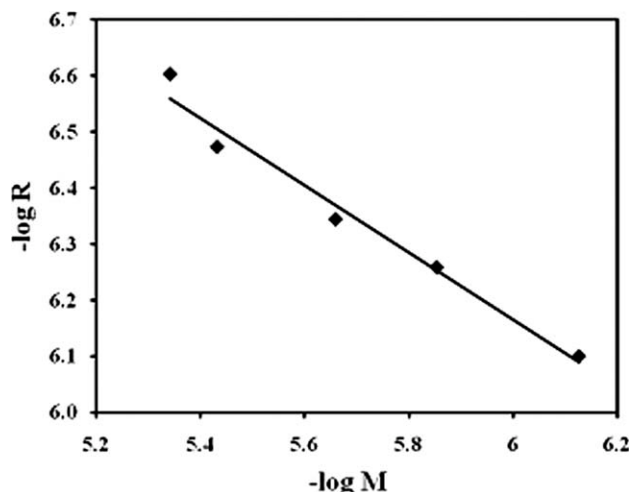
solution as a function of the sonication time at 2.5 g/L initial CMC concentration under air. As seen, η_r decreases with increasing the nominal applied power from 30 to 80 W. When sonolysis occurred in aqueous phase, there are three potential sites for sonochemical activity, namely: (i) the gaseous region of the cavitation bubble where volatile and hydrophobic species are easily degraded through pyrolytic reactions as well as reactions involving the participation of hydroxyl radicals with the latter being formed through water sonolysis:

$$H_2O \rightarrow H^\bullet + OH^\bullet \tag{15}$$

(ii) the bubble–liquid interface where hydroxyl radicals are localized and, therefore, radical reactions predominate although pyrolytic reactions may also, to a lesser extent, occur, and (iii) the liquid bulk where secondary sonochemical activity may take place mainly due to free radicals that have escaped from the interface and migrated to the liquid bulk. It should be pointed out that hydroxyl radicals could recombine yielding hydrogen peroxide, which may in turn react with hydrogen to regenerate hydroxyl radicals:

$$OH^\bullet + OH^\bullet \rightarrow H_2O_2 \tag{16}$$

$$H_2O_2 + H^\bullet \rightarrow H_2O + OH^\bullet \tag{17}$$

Given that CMC is a nonvolatile and soluble natural polymer, hydroxyl radical-mediated reactions occurring primarily in the liquid bulks as well as at the bubble interface are likely to be the dominant degradation pathway. A polymer molecule near the vicinity of a collapsing bubble is pulled toward the

Figure 6 The relationship between η_r and sonication time in for different power of ultrasound at 25°C and 2.5 g/L.
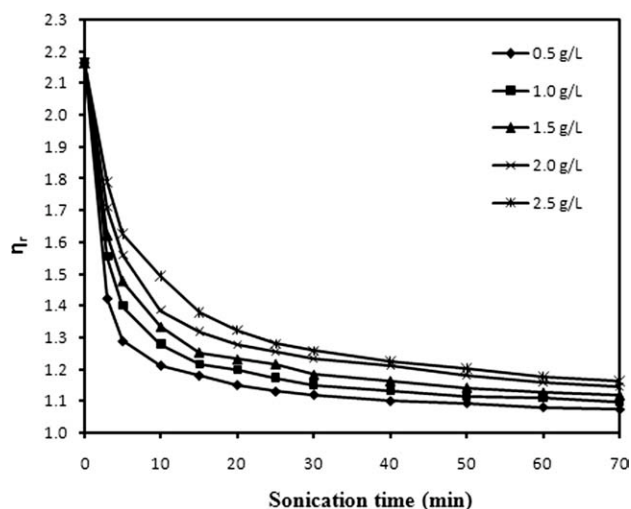

Figure 7 The plot of $\Delta\eta^{1.6} - \Delta\eta_0^{1.6}$ versus the sonication time for different power of ultrasound at 25°C and 2.5 g/L.

cavity of the bubble, and the solvodynamic shear elongates the polymer backbone, leading to scission.[54] Ulanski et al.[28] have been study the effect of power of ultrasound on degradation of carbohydrates and found that the mechanism of ultrasonic was complex and could be mainly ascribe to radical random scissions, accompanied too some extend with mechanical breakage caused by hydrodynamic and shear forces. The plots of $\Delta\eta^{1.6} - \Delta\eta_0^{1.6}$ versus sonication time for different powers of ultrasound are presented in Figure 7. The apparent degradation rate constant, k, defined in eq. (13), can be estimated from the slopes of the plots in Figure 7. On the basis of these results, degradation rate constants, k, were calculated that are shown in Table II. It can be seen that at the same concentration (2.5 g/L), the extent of degradation increases with an increase in applied ultrasound power. In quantitative terms, in 70 min of irradiation time the extent of degradation at 80 W is three times higher when compared with degradation at 30 W.

Effect of temperature on the rate of CMC degradation

Majority of chemical reactions are accelerated by an increase of temperature. However, opposite effect is often seen for the chemical reaction induced by ultrasound. Indeed, the negative "temperature coefficient" has been cited as proof that a solution process is mechanical in origin. Ultrasonic degradation of polymer solution often gives faster rate at lowe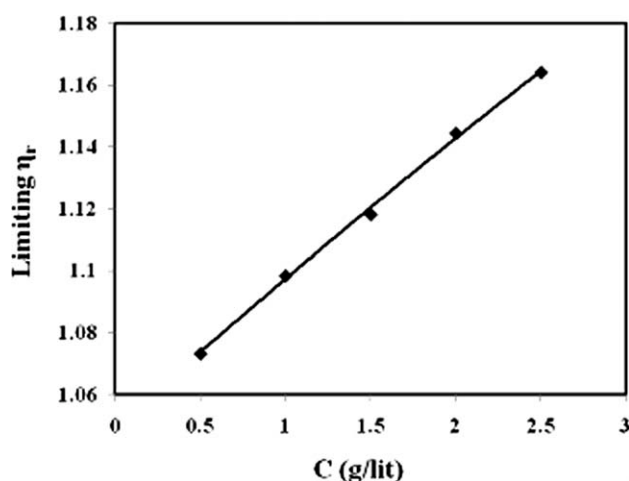r temperature.[55] Figure 8 shows relative viscosity–sonication time curves during the ultrasonic degradation of CMC at an initial concentration of 2.5 g/L and various temperatures, and plots of the $\Delta\eta^{1.6} - \Delta\eta_0^{1.6}$ versus sonication time are presented in Figure 9, whereas values of degradation rate constants are summarized in Table III. Our results indicated that the extent of degradation is more pronounced at low temperatures. This might be because, with increasing temperature, v_p of the solvent increases, and so the vapor enters the cavitation bubbles during their growth. This causes a reduction in collapsing shock because of a cushioning effect; therefore, the extent of degradation is reduced.[56]

Gel permeation chromatography analysis

Figure 10 shows the relation of $(1/M_w)$ versus sonication time for different concentration of CMC solutions. This curve shows that a linear relationship did exist between the inverse of molecular weight and degradation time at low concentration and with an increase in concentration; this data flow lost its linearity. Therefore, in lower concentrations, reduce in molecular weight has a linear arrangement behavior to the end of the degradation process. These data were obtained for initial CMC and CMCs in 15 min intervals for 0.5, 1.0, 1.5, 2.0, and 2.5 g/L concentrations. The curves of molecular weight of degraded CMC in different reaction conditions and at 75 min showed a shift toward lower molecular weights because of the degradation could be observed for

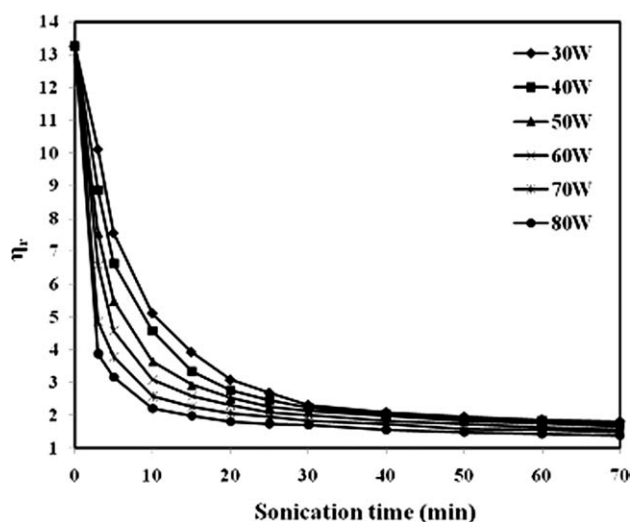**Figure 8** The relationship between η_r and sonication time in for different temperatures at 30 W and 2.5 g/L.

Figure 9 The plot of $\Delta\eta^{1.6} - \Delta\eta_0^{1.6}$ versus the sonication time for different temperatures at 30 W and 2.5 g/L.

The Effect of Temperature on the Degradation Rate Constants at 2.5 g/L Concentration of CMC and Fixed Power of Ultrasonic Irradiation (30 W)

Temperature (°C)	15	25	35	45	55
$k \times 10^9$ (mol$^{1.6}$ L$^{-1.6}$ min^{-1})	3.648	2.784	2.340	2.013	1.765

Figure 11 Changes in weight-average molecular weight (M_w) of degraded samples with different power of ultrasound.

the five samples in comparison by initial CMC molecular weight. These results follow by the results of viscometery method that had gave a reducing order of molecular weights during the degradation process. In the case of study of power and temperature effects, on reducing of molecular weight, the same flow could be seen. These results indicated that in the case of optimum conditions (0.5 g/L, 30 W, and 25°C) the linearity of curves is observable and with the change in reaction conditions, correlation of (1/M_w) versus time lost this property (Figs. 11 and 12).

Table IV presented the M_w, M_n, and polydispersity (PD) of CMC oligomers obtained at different concentration of CMCs, degraded at 30 W and 25°C. If simultaneously the number of bonds that can be broken within a given time (100 min) remains constant but the number of available molecules increases (increase in concentration), it would consequently lead to a decrease in CMC degradation as well because fewer bonds can be broken per available molecule.[57] Table V Summarizes the M_w, M_n, and PD of CMC oligomers prepared by ultrasonic degradation of CMCs at 2.5 g/L concentration and 25°C. Degradation of CMCs at powers 30–80 W gave oligomers with M_w ranging from about 23.76 × 10^4 to 16.99 × 10^4 kDa. Also, Table VI summarizes

obtained data for CMCs degraded at different temperatures at 30 W and 2.5 g/L concentration. As seen from these results, with an increase in temperature, M_w of oligomers was decreased, simultaneously. This result is in accordance with findings in study of temperature effect on ultrasonic degradation of CMC (Effect of temperature on the rate of CMC degradation section).

CONCLUSIONS

It has been demonstrated on CMC that treatment with a variety of output ultrasound powers in aqueous solution is an efficient procedure for reduction of molecular weight of CMC. Under sonolysis conditions, degradation is caused by OH radicals and mechanochemical effects. The effect of concentration of polysaccharide and different reaction temperature,
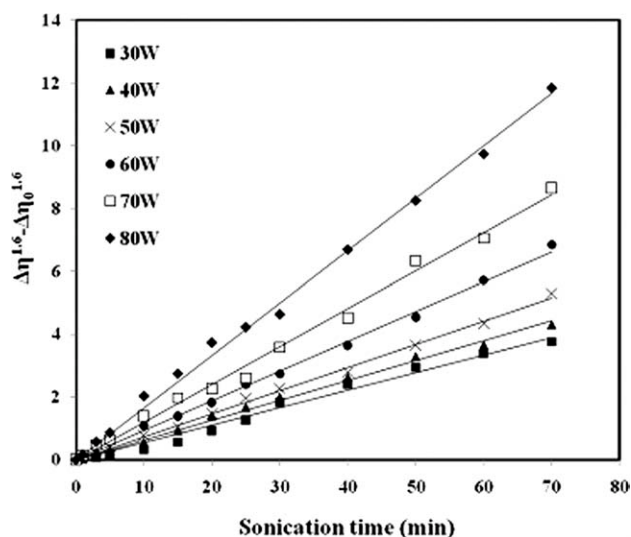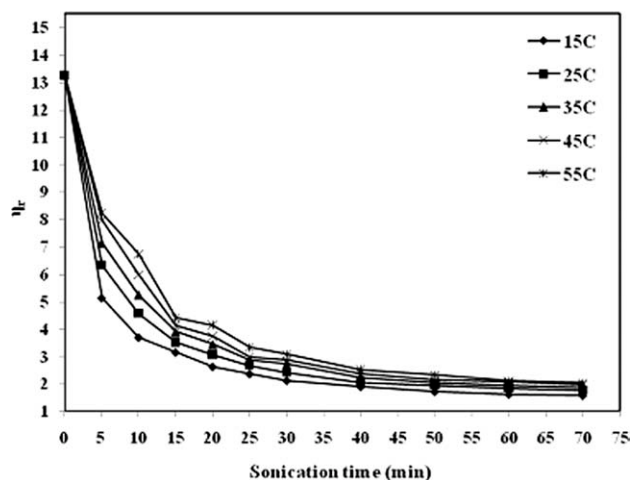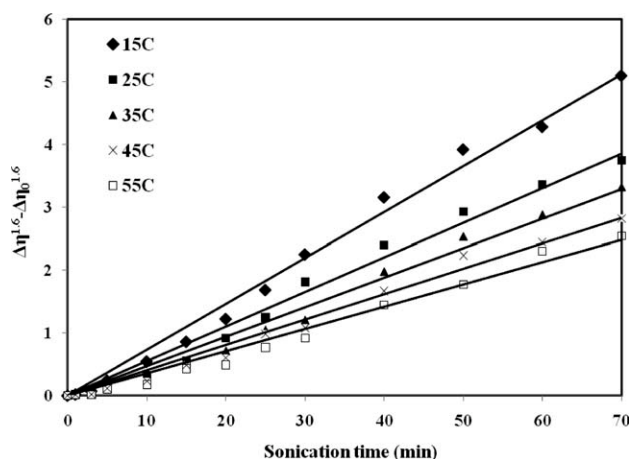

Figure 10 Changes in weight-average molecular weight (M_w) of degraded samples with different concentrations.

Figure 12 Changes in weight-average molecular weight (M_w) of degraded samples with different temperatures.

TABLE IV
GPC Analysis for M_w, M_n, and Polydispersity of CMC Samples for Initial and Degraded CMC by Means of Different Applied Concentrations at 25°C and 30 W

Concentration (g/L)	Time (min)	$M_w \times 10^4$ (kDa)	$M_n \times 10^4$ (kDa)	Polydispersity
Initial sample	0	37.2	15.50	2.40
0.5	25	26.32	14.84	1.77
	50	21.03	14.43	1.46
	75	17.97	14.16	1.27
	100	15.70	13.75	1.14
1.0	25	27.68	15.09	1.83
	50	23.00	14.73	1.56
	75	18.99	14.62	1.30
	100	17.20	13.96	1.23
1.5	25	29.07	15.10	1.92
	50	24.32	14.90	1.63
	75	20.11	14.81	1.36
	100	18.09	14.45	1.25
2.0	25	30.90	15.29	2.02
	50	25.26	15.15	1.67
	75	22.68	15.00	1.51
	100	20.20	14.86	1.36
2.5	25	32.97	15.31	2.15
	50	29.11	15.25	1.91
	75	24.80	15.19	1.63
	100	23.76	15.04	1.58

TABLE VI
GPC Analysis for M_w, M_n, and Polydispersity of CMC Samples for Initial and Degraded CMC by Means of Different Applied Temperature at 2.5 g/L and 30 W

Temperature (°C)	Time (min)	$M_w \times 10^4$ (kDa)	$M_n \times 10^4$ (kDa)	Polydispersity
Initial sample	0	37.2	15.50	2.40
15	25	30.68	15.40	1.99
	50	27.54	15.12	1.82
	75	23.14	14.99	1.54
	100	21.30	14.81	1.44
25	25	32.97	15.31	2.15
	50	29.11	15.25	1.91
	75	24.80	15.19	1.63
	100	23.76	15.04	1.58
35	25	34.85	15.10	2.31
	50	31.13	14.71	2.12
	75	26.83	14.51	1.85
	100	24.90	14.43	1.73
45	25	35.02	15.03	2.33
	50	32.23	14.82	2.17
	75	27.68	14.47	1.91
	100	25.41	14.23	1.78
55	25	35.45	14.88	2.38
	50	33.97	14.63	2.32
	75	28.96	14.23	2.03
	100	26.62	14.00	1.90

the results of ultrasonic degradation of CMC in solution indicated that the degradation rate reduced with increasing solution concentration and tempera-

ture. This study confirms the general assumption that the shear forces generated by the rapid motion of the solvent following cavitational collapse are responsible for the breakage of the chemical bonds within the polymer. The effect of polymer concentration can be interpreted in terms of the increase in viscosity with concentration, causing the molecules to become less mobile in solution and the velocity gradients around the collapsing bubbles to, therefore, become smaller.

TABLE V
GPC Analysis for M_w, M_n, and Polydispersity of CMC Samples for Initial and Degraded CMC by Means of Different Applied Powers at 25°C and 2.5 g/L

Power (W)	Time (min)	$M_w \times 10^4$ (kDa)	$M_n \times 10^4$ (kDa)	Polydispersity
Initial sample	0	37.2	15.50	2.40
30	25	32.97	15.31	2.15
	50	29.11	15.25	1.91
	75	24.80	15.19	1.63
	100	23.76	15.04	1.58
40	25	30.76	15.30	2.01
	50	27.32	14.90	1.83
	75	21.66	14.73	1.47
	100	21.06	14.69	1.43
50	25	29.44	15.10	1.95
	50	25.25	14.71	1.72
	75	21.03	14.51	1.45
	100	18.94	14.43	1.31
60	25	28.90	15.03	1.92
	50	24.10	14.82	1.63
	75	20.23	14.47	1.40
	100	18.22	14.23	1.28
70	25	26.36	14.88	1.77
	50	22.79	14.63	1.56
	75	19.44	14.23	1.37
	100	17.71	14.00	1.26
80	25	24.11	14.52	1.66
	50	20.02	14.12	1.42
	75	17.15	13.97	1.23
	100	16.99	13.63	1.25

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