



Ultrasonic Degradation of Polyvinyl Pyrrolidone (PVP): Effect of Power of Ultrasound, Temperature and Concentration

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Authors' contributions

This work was carried out in collaboration between both authors. Author MTT designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author RA managed the analyses of the study. Author RA managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

The ultrasonic degradation of polyvinyl pyrrolidone (PVP) was carried out in a range of different concentration of polymer solution to investigate on the changes of molecular weights. Also the ultrasonic degradation at different temperatures and power of ultrasound (30-150 W) was investigated. Most of the effects involved in controlling molecular weight can be attributed to the large shear gradients and shock waves generated around collapsing cavitation bubbles. The calculated rate constants indicated that the degradation rate of the PVP solutions decreased as the temperature increased. The average molecular weight of ultrasonicated PVP was determined by measurements of relative viscosity of samples. The degradation rate of this polymer was followed by a kinetic model based on viscosity measurements. Rate constants of ultrasonic degradation were calculated, and the results showed their dependence on polymer concentration.

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1. INTRODUCTION

The ultrasonic polymer degradation has several unique characteristics that make it interesting both from practical and theoretical viewpoints [1]. High-intensity ultrasonic treatment can be applied to degrade polymers and to facilitate emulsifying and cleaning processes in homogenous liquid phase [2]. The degradation of several polymers such as polystyrene [3], polyvinyl acetate [4], polypropylene [5], poly(methylmethacrylate) [6], dextran [7], hydroxy propyl cellulose [8], carboxymethyl cellulose [9], polyacrylamide [10] and poly(ϵ -caprolactone) [11] has been investigated. This work has been summarized in a review paper by Price [12]. Ultrasonic irradiation induces the production of cavitation bubbles in the liquid through which it is transmitted. These microbubbles grow during the subsequent compression–rarefaction cycles until they reach a critical size. Further compression leads to the collapse of the bubbles, with the concomitant release of heat and production of chemically active species during the last phase of the bubble collapse [13]. Indeed, energy concentrated in the bubbles is sufficient to break strong chemical bonds [14]. 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 [15]. Application of high-intensity ultrasound to dispersions of macromolecules can lead to depolymerization because of the intense mechanical and chemical effects associated with cavitation [16]. Cavitation thermolysis may produce hydroxyl radicals and hydrogen atoms that can be followed by formation of hydrogen peroxide [17]. Some cavities exist only for one cycle of the sound field and collapse violently (transient cavities), while other are long-lived and oscillate around some equilibrium size (stable cavities) [18]. 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 polymers [19].

A variety of different theoretical models have been proposed to attempt to explain the way in which the factors such as frequency, intensity, solvent, temperature, nature of dissolved gas, external pressure and the molecular mass distribution influence the rate and final molecular

mass of degraded species [20]. Three models are proposed to account for this chemical change based on cavitation induced by ultrasound [21]. In the first model, the degradation is interpreted in terms of the high temperature and pressure generated during bubble collapse. The Jellinek model attributes chain scission to the increased frictional force generated on cavitation collapse. In the final model, Doulah [22] suggests that the shock-wave energy released on bubble collapse gives rise to a series of eddies which interact with the macromolecules in solution. The factors influencing ultrasonic degradation rate and final molecular weight of degraded species have also been studied and explained carefully based on these models [23]. The following conclusions were obtained:

- (1) In general, ultrasound with greater intensity or lower frequency leads to both faster degradation and a lower limiting molecular weight.
- (2) Different from majority of chemical processes, the ultrasonic degradation of polymer solutions is inhibited by an increase of temperature. Moreover, the effect of temperature is greater than the variation due to the ultrasonic intensity and frequency.
- (3) In a certain range, the ultrasonic degradation rate increases with the reduction of solution concentration.
- (4) A solvent with higher volatility promotes cavitation and consequently can accelerate the ultrasonic degradation of polymer solutions.

In this study nine different concentration of poly (vinyl-pyrrolidone) (PVP) are examined. PVP is a biocompatible material and has wide applications as biomaterials. The objective was 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 to average molecular weight (M_v) and number average molecular weight (M_n). Finally, these quantities are correlated with the molar concentration with a meaningful expression.

2. MATERIALS AND METHODS

2.1 Materials

Polyvinyl pyrrolidone (PVP) with weight-average molecular weight ($M_w=1300000$ kDa) was

purchased from Across Co. Ltd. Molecular weight was ($M_v=756000$ kDa), which was determined by viscometer. All other chemicals were of laboratory reagent grade and were purchased from Merck. All solutions were prepared using distilled and deionized water.

2.2 Methods

2.2.1 PVP solution preparation

PVP solutions containing 5, 10, 15, 20, 25, 30, 35, 40 and 45 g/L PVP were prepared. The solutions were stirred overnight to ensure complete solubilisation of the PVP molecules, and then filtered to remove any impurities and 100 ml samples were immediately sonicated.

2.2.2 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 150 W nominal value, in aqueous media was used for sonication experiments. A titanium-made H3 sonotrode ($\phi=3$ 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 PVP 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 $25\pm 1^\circ\text{C}$ 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.

2.3 Viscosity Measurements

The intrinsic viscosities of the original PVP and its degraded solutions at 25°C were measured using the capillary viscometer (Setavic Kinematic viscometer). Efflux times were measured for PVP 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 PVP solution.

$$\eta_r = \frac{t}{t_0} \quad (1)$$

$$\eta_{sp} = \eta_r - 1 \quad (2)$$

The intrinsic viscosity $[\eta]$ values can be related to the specific viscosity, η_{sp} , and relative viscosity, η_r , by the Huggins and Kramer equations [24]. The conditions used in this work ($\alpha=0.55$ and $k=6.67\times 10^{-5}$ L/g) were adopted on the basis of previous findings in the literature [25].

2.4 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 [26]:

$$R = \frac{dM}{dt} = kM^n \quad (3)$$

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. was found that the order of ultrasonic degradation reaction for poly (vinyl alcohol) obtained from this kinetic model is -1 [27].

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. (3) is:

$$M^{1-n} - M_0^{1-n} = (1-n)kt \quad (4)$$

Where M_0 is the initial total molar concentration of polymer. The total molar concentration is related to the number average molecular weight through [28]:

$$M = \frac{C}{M_n} \quad (5)$$

Moreover, viscosity average molecular weight, M_v , is related to the number average molecular weight, M_n , through [29].

$$M_v = \left[(1+\alpha) \Gamma(1+\alpha) \right]^{\frac{1}{\alpha}} M_n \quad (6)$$

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

$$M_v = \left(\frac{[\eta]}{K} \right)^{1/\alpha} \quad (7)$$

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:

$$\frac{\eta_{sp}}{C} = [\eta] + K'[\eta]^2 C \quad (8)$$

$$\frac{Ln\eta_r}{C} = [\eta] + (K' - 0.5)[\eta]^2 C \quad (9)$$

From Eq. (8) and (9), intrinsic viscosity is:

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - Ln\eta_r)}}{C} \quad (10)$$

Substitution of Eq. (10) in (7) and Eq. (7) in (6) yields

$$M_n = \left[\frac{\sqrt{2(\eta_{sp} - Ln\eta_r)}}{(1+\alpha)\Gamma(1+\alpha)KC} \right]^{1/\alpha} \quad (11)$$

Finally, the substitution Eq. (11) in (5) yields:

$$M = \left[\frac{(1+\alpha)\Gamma(1+\alpha)KC^{1+\alpha}}{\sqrt{2}} \right]^{1/\alpha} \Delta\eta \quad (12)$$

In addition, substitution Eq. (12) in (4) yields:

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = (1-n) \left[\frac{\sqrt{2}}{(1+\alpha)\Gamma(1+\alpha)KC^{1+\alpha}} \right]^{(1-n)/\alpha} k t \quad (13)$$

Or

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = k' t \quad (14)$$

3. RESULTS AND DISCUSSION

3.1 Determination of Reaction Order of Degradation of PVP

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 [30,31] 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. In general, polymer mechanochemistry induced by an acoustic field is a non-random process; for example, the scission of polymer chains in solution occurs at a preferential position near the midpoint [32]. Moore et al. approved this idea by an isotope labeling experiment on ultrasonic degradation of linear 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 [33].

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 [34]. 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 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 [35]. Although, a number of different rate models have been proposed for the degradation of polymers [36], but in this study a simple model was employed via viscometry, Using Eq. (12). A negative order for the dependence of the reaction rate on total molar concentration of PVP 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 Fig. 1. The data of these three concentrations overlapping by the data resulted from concentration of 30 g/L. Therefore, the results of these temperatures were not reported.

Previous studies were proved that with an increase in concentration, the rate constant, k , was decreased obviously [37,38]. 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 cavitation 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 [39]. The slopes of plots give the initial rate of degradation using Eq. 14, the plot of $\log V$ versus $\log[M]$ are linear and it is shown in Fig. 2.

The slope of curve is -0.5, which suggest the order of reactions with respect to total molar concentration of polymer. From substitution of the value of "n" in Eq.14, we obtain the following:

$$\Delta\eta^{1.5} - \Delta\eta_0^{1.5} = k't \tag{15}$$

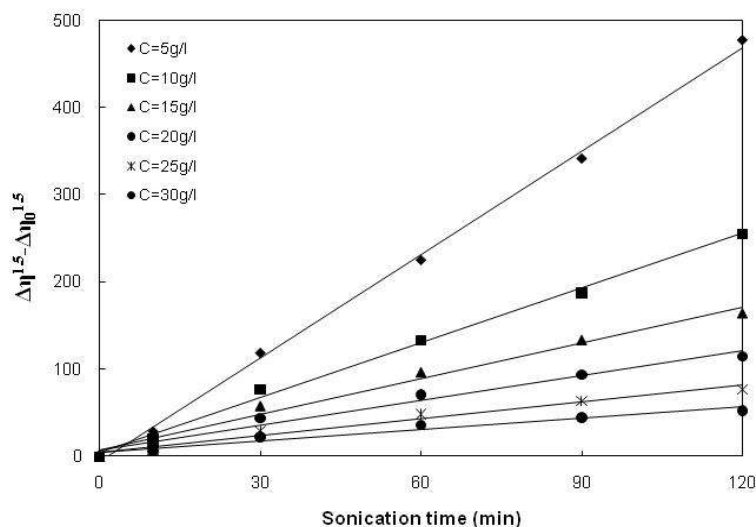


Fig. 1. The plot of $\Delta\eta^{1.5} - \Delta\eta_0^{1.5}$ versus the sonication time for different concentration of PVP solution at 25°C

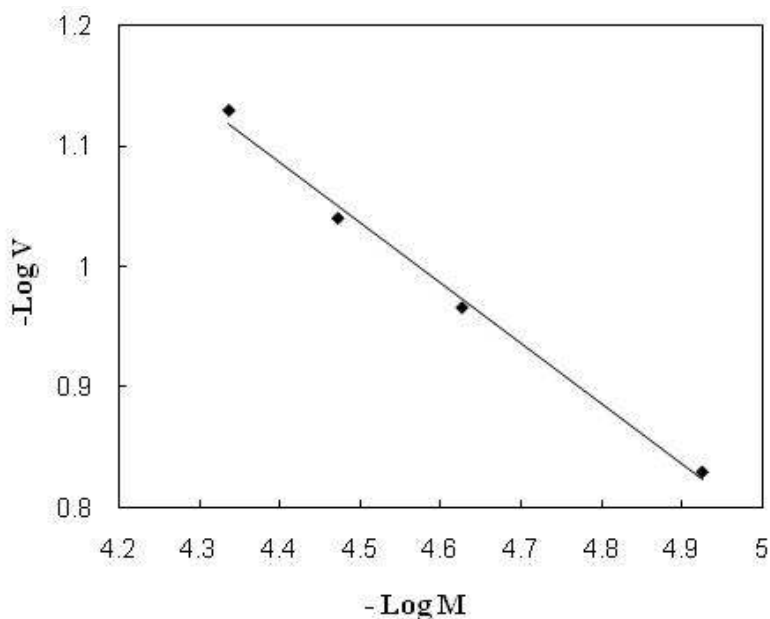


Fig. 2. The plot of $\log V$ versus $\log M$ for degraded PVP at 25°C

3.2 Effect of Concentration on the Rate of PVP Degradation

The data of limited viscosities (relative and intrinsic) listed in Table 1 show that the viscosity increases with increasing of concentration of polymer, at the end of 240 min.

Table 1. Limiting relative viscosity, η_r and limiting viscosity-average molecular weight, M_v of PVP samples degraded by ultrasonic irradiation in various concentrations and 25°C at the end of 240 min

C (g/L)	Limiting η_r	Limiting M_v (kDa)
5	1.119	40679
10	1.157	66514
15	1.189	90855
20	1.221	119042
25	1.260	156552
30	1.298	197143
35	1.334	238453
40	1.371	283806
45	1.399	319741

Sonication was carried out for nine different PVP concentrations at 25°C. The relationship between η_r and sonication time are presented in Fig. 3.

Based on these findings, it is clear 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. Under the same conditions, the decrease in η_r of the sample with a high polymer concentration is lower than of the sample with a low polymer concentration. The relationship between the limiting value of η_r and solution concentration is presented in Fig. 4.

These results indicate that the extent of degradation is more pronounced in more 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 [40].

3.3 Effect of Power of Ultrasound on the Rate of PVP Degradation

Fig. 5 shows the effect of increasing changing ultrasound power on relative viscosity (η_r) of PVP solution as a function of the sonication time at 15 g/L initial PVP concentration under air. As seen, η_r decreases with increasing the nominal applied power from 30 to 150 W.

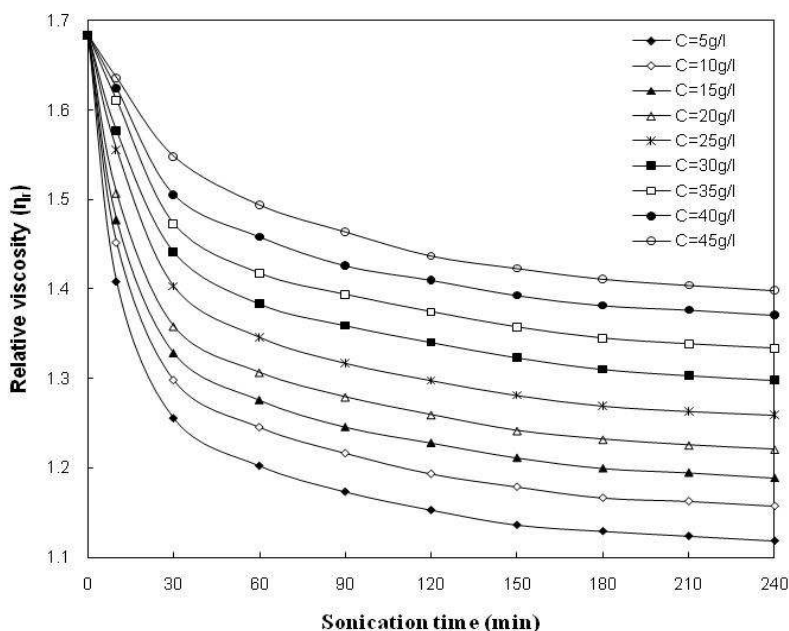


Fig. 3. The relationship between η_r and sonication time for different PVP concentrations at 25°C and fixed power of ultrasonic irradiation (150 W)

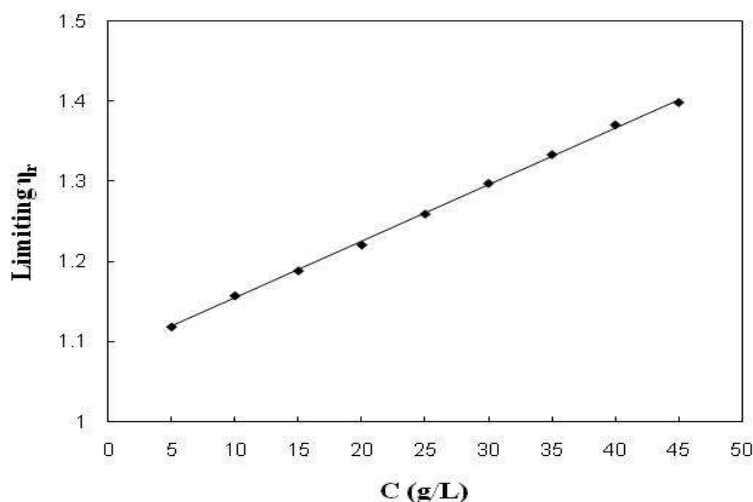


Fig. 4. The relationship between the limiting value of η_r and solutions concentration

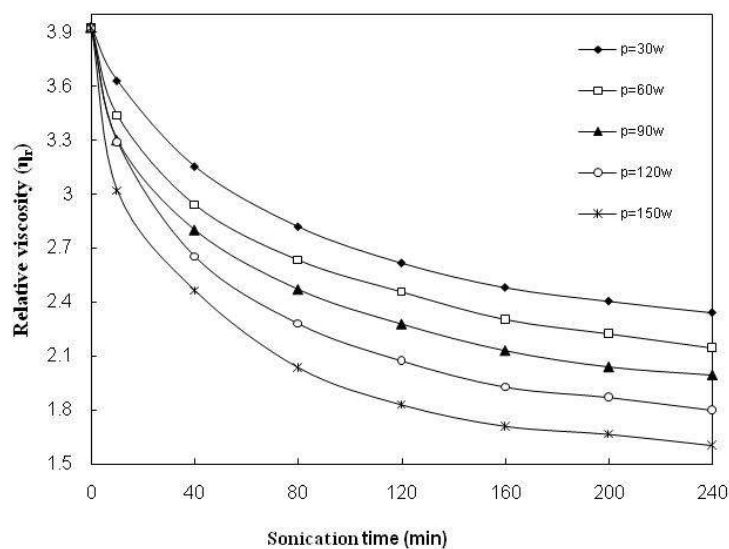
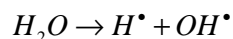


Fig. 5. The relationship between η_r and sonication time in for different power of ultrasound at 25°C and 15 g/L

In aqueous solutions, the main pyrolytic reaction is the dissociation of water. This thermal dissociation leads to the production of highly reactive radicals (OH^\bullet , H^\bullet) inside the bubbles [41].

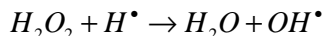
In aqueous phase sonolysis, there are three potential sites for sonochemical activity, namely: (i) The gaseous region of the cavitation bubble where volatile and hydrophobic species are easily degraded through pyrolytic reactions as well as reactions involving the participation of hydroxyl radicals with the latter being formed

through water sonolysis. The heat from the cavity implosion decomposes water into extremely reactive hydrogen atoms (H^\bullet) and hydroxyl radicals (OH^\bullet) [42].



(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:



Given that PVP is a non-volatile and soluble 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 cavity of the bubble, and the solvodynamic shear elongates the polymer backbone, leading to scission [43]. Ulanski et al. 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 [44]. The plots of $\Delta\eta^{1.5}-\Delta\eta_0^{1.5}$ versus sonication time for different powers of ultrasound are presented in Fig. 6.

The apparent degradation rate constant, k' , defined in Eq. 14, can be estimated from the slopes of the plots of this Figure. It can be seen

that at the same concentration (15 g/L), the extent of degradation increases with an increase in applied ultrasound power. In quantitative terms, in 240 min of irradiation time the extent of degradation at 150 W is seven times higher as compared to degradation at 30 W.

3.4 Effect of Temperature on the Rate of PVP 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 lower temperature [45]. Fig. 7 shows relative viscosity-sonication time curves during the ultrasonic degradation of PVP at an initial concentration of 15 g/L and various temperatures,

And plots of the $\Delta\eta^{1.5}-\Delta\eta_0^{1.5}$ versus sonication time are presented in Fig. 8.

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 [46].

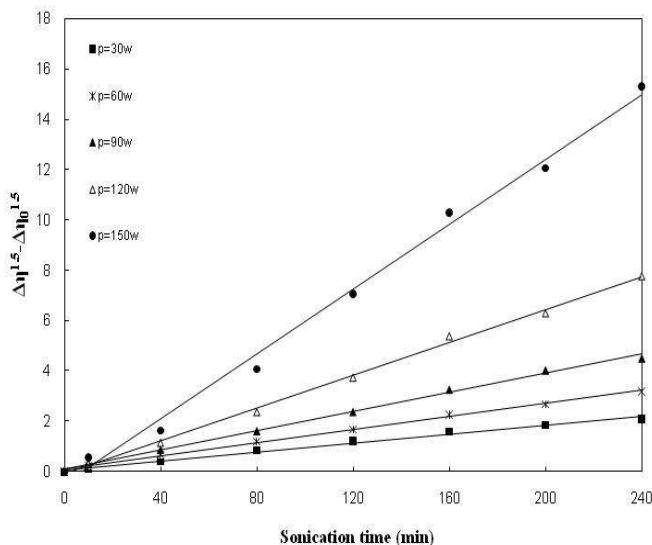


Fig. 6. The plot of $\Delta\eta^{1.5}-\Delta\eta_0^{1.5}$ versus the sonication time for different power of ultrasound at 25°C and 15 g/L

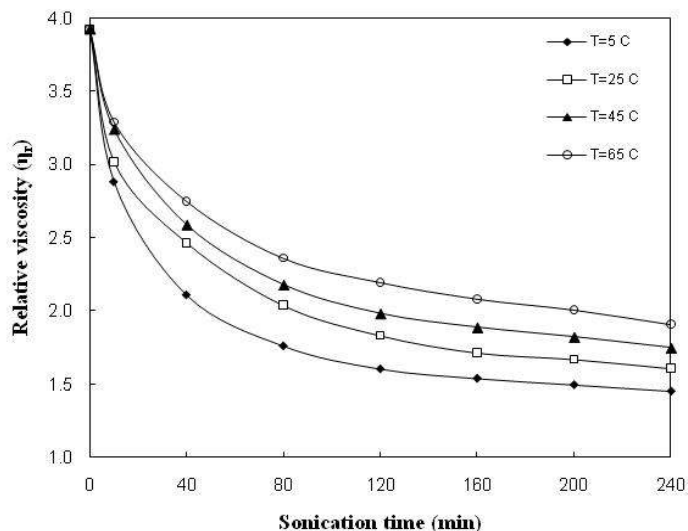


Fig. 7. The relationship between η_r and sonication time in for different temperatures at 150 W and 15 g/L

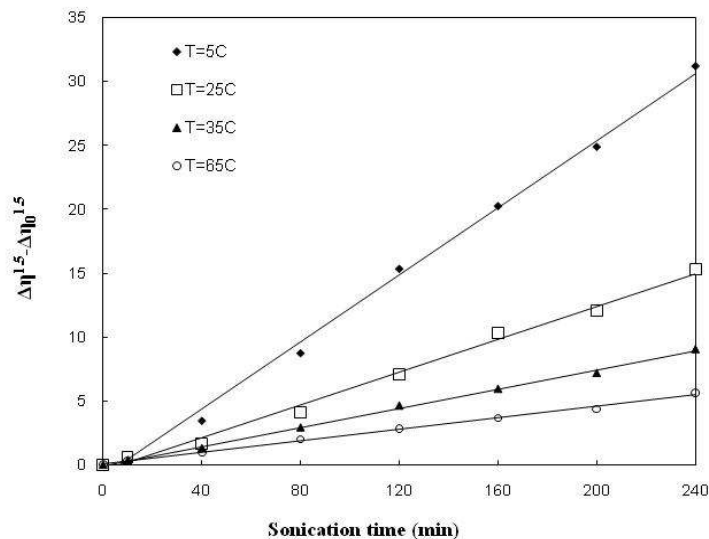


Fig. 8. The plot of $\Delta\eta^{1.5} - \Delta\eta_0^{1.5}$ versus the sonication time for different temperatures at 150 W and 15 g/L

4. CONCLUSIONS

It was found that the ultrasonic degradation of PVP solution increased with increasing temperature and with decreasing concentration. The results of ultrasonic degradation behavior of polyvinyl pyrrolidone (PVP) solution were studied under various conditions, such as power of sonication, reaction temperature and solution concentration, by kinematics viscometry. It was found that the ultrasonic degradation of PVP solution increased with increasing temperature and with decreasing concentration. It was found

that, the ultrasonic degradation is an efficient procedure for reduction of molecular weight of PVP. The degradation rate reduced with increasing solution concentration and temperature. The effect of concentration of polymer and different reaction temperature, the results of ultrasonic degradation of PVP in solution indicated that the degradation rate reduced with increasing solution concentration and temperature. The most extensive degradation took place when using an ultrasonic input power of 150 W. The possible explanation for the degradation is the shear forces created by

ultrasonic waves. As the power of the wave increases, the shear forces will be complemented by the increased cavitation effects.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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