

Effect of Intensity - Temperature on Ultrasonic Dextran Degradation

Ali Akyüz¹, Durmuş Temiz², Kazım Kumaş³

¹Asst. Prof. Dr., Dept. of Biomedical Device Technology, Burdur Mehmet Akif Ersoy University, Burdur, Turkey

²Lecturer, Dept. of Electricity and Energy, Burdur Mehmet Akif Ersoy University, Burdur, Turkey

³Lecturer, Dept. of Electricity and Energy, Burdur Mehmet Akif Ersoy University, Burdur, Turkey

Abstract - The ultrasonic dextran degradation in solution was investigated at different ultrasound intensities and temperatures. The specific viscosity of dextran solutions were determined by capillary viscometer. Theoretical Ginzburg and Madras models were used to figure out the degradation constants and limit viscosities. The degradation experiments shows that the degradation constants and limit specific viscosity are found to be reasonably sensitive to ultrasound intensity. Also, when the temperature increased, the degradation constants lowered because of the vapour pressure effect.

Key Words: Ultrasound, Degradation, Dextran, Ultrasound Intensity, Temperature

1. INTRODUCTION

Dextran is a common expression for a group of glucans produced by polymerization of α -D-glucopyranosyl moiety of sucrose in catalysis of dextransucrase. The typical characteristic is a majority of bacteria generate dextrans with molecular weight sequences together with structures different from somewhat to extremely branched [1]. Dextran has already been extensively considered delivering antigen because of important biological usage in body, availability and low-priced. However, second rate of medical dextran (unknown or high molecular weight) could lead to bad situations. For medical purposes, low molecular weight dextran is used. Low molecular weight dextran solutions have generally low viscosity and it is separated from some other natural polymers [2]. Dextran is mainly taken off in kidneys because of this needs to be prevented in users with reduced kidney function. Dextran usage also has several dangers of sensitive effect. Desired molecular weight is challenging to be directly handled because of the variety as well as complication of dextran branches and long chains [3]. Different molecular weight dextrans is provided by enzymatic, chemical and physical techniques. In enzymatic techniques, dextransucrase-dextransucrose are used to create with wanted molecular weight. On the other hand, the end products may possess many impurities. In chemical techniques, the production of dextran is primarily carried out by acid hydrolysis and then by the use of organic solvents. Extrusion, jet cooking and sonication are among the physical techniques used to obtain dextran at different molecular weight. All techniques have advantages and disadvantages [4,5].

The ultrasound has a frequency range from 20 kHz to 10 MHz that the human ear cannot hear. Ultrasound has two different fields of use: high frequency / low intensity and low frequency / high intensity according to frequency and intensity values. Low intensity ultrasound does not cause any change in materials and is used as an analytical technique in researches. High-intensity ultrasound can cause physical and chemical changes in a material. This type of use is called sonochemistry in the literature. Sonochemistry is used in a wide range of both academic and industrial sense, such as physics and various fields of chemistry, material science, food engineering. When a low-frequency high-intensity ultrasound passes through a liquid medium and a sufficiently strong negative pressure is applied during the expansion phase, the critical distance between the liquid molecules is exceeded and bubbles form in the liquid and collapse severely at one point. This event is called the cavitation phenomenon. [1-5]

The first effect of ultrasound application (sonication) on polymer solutions is polymer chain scission (polymer degradation). In the classical term, the degradation is the alteration of the chemical structure. In polymer technology it means a decrease in molecular weight or a decrease in the viscosity of the polymer solution. How the polymer chains in the solution break down during the sonication process is a debate among investigators in this issue. However, in recent years it has been concluded that chain breaking occurs due to ultrasonic cavitation and hydrodynamic forces [6-8].

Unlike chemical, thermal, enzymatic and photo polymer degradation methods, the scission of polymer chains by ultrasound is a non-random mechanism. The polymer chains in the solution (if there is a relatively weaker bond in the chain) are broken off from adjacent bonds to middle of the chain. In the initial stages of the sonication, long polymer chains are broken and chain breakage is rapid, then it slows down and approaches a limit value (limit molecular weight). The existence of this limit value indicates that chain breakage does not occur after this value. Ultrasonic chain scission does not result in monomer and oligomer formation, i.e. the polymer obtained at any moment of breaking is similar to the starting polymer, but the chain is shorter and the side chain reactions do not occur, provide various advantages according to their usage areas.

Basedow and Ebert studied the effect of ultrasonic degradation of dextran in various solvents and noticed that solvent properties had a significant effect on degradation efficiency. They observed that expanded dextran chains have

been broken more easily and also the enthalpy of vaporization of the solvent was a significant parameter for the degradation process [13]. Lorimer et al. investigated the sonication of dextran solutions for 30, 50, 70 °C and 20, 35, 60 W of ultrasound power. Sonication has been obtained to decrease definitely the molecular weight of dextran. For the reduction in molecular weight determined by GPC for 480 minutes' sonication time, were the highest for 60 W ultrasound power and 30 °C [14]. Zoua et al. studied the effect of initial molecular weight (range from 9300 to 1700000 Da) and solution concentration (0.001, 0.01, 0.02 g/mL) on ultrasonic dextran degradation. Their results show that molecular weight and polydispersity index reduced with ultrasound treatment time. Also, they reported that the dextran degradation continued more quickly for higher initial molecular weight in addition to lower solution concentrations. In the above studies, 1st degree kinetic analysis was performed and Malhotra model was used. Malhotra's kinetic equation does not include limit molecular weight information [15]. Pua et al. analysed the ultrasonic degradation mechanism of dextran by High Performance Gel Permeation Chromatography. They used Malhotra and Madras midpoint scission model for kinetic analysis of dextran degradation [16].

In this study, the fixed molecular weight of dextran in aqueous solution was sonicated at fixed concentration of 0.001 g / mL C for four different ultrasound intensities and four different temperatures. So the effect of intensity and temperature on dextran degradation was investigated. The majority of degradation researches in the literature have been carried out the removal of samples from the sonication medium and determining their molecular weights. It was considered that the volume change could be important parameter instead of sampling from the sonication medium and individual sonication was applied to the dextran solutions. The kinetic analysis of degradation has been characterized by the change in specific viscosity of the samples. The specific viscosity data have been analyzed on the basis of the theoretical Giz and Madras model.

2. MATERIALS and METHODS

Commercial dextran (Mw = 500000 g/mol, Alfa Aesar) and distilled water were used in this study. A 50 mL round-bottom flask was selected as the sonication cell. Dextran concentration was arranged 0.001 g/mL for all degradation experiments. Sonication was carried out using Sonopuls Ultrasonic Homogenizer GM-3100 Bandelin Sonopuls at a nominal frequency of 20 kHz. Ultrasound probe was immersed to 2 cm into the solution. On supplier information, for micro-tip MS 73 probe pressure amplitude arranged at 100% leads to an amplitude of 245 μm for the highest power output. Four amplitudes 20 % (49 μm) , 50% (122.5 μm), 80% (196 μm), 100% (245 μm) were selected in this study. For these amplitudes, the ultrasound intensities (I) were determined calorimetrically based on approach (equation 1) presented by Price [3]. In equation m = 50 g is the sample mass, c= 4.18 J/g °C is the heat capacity of the solution,

(dT/dt) is the time-dependent change of sample temperature, and r = 0.003 m is the radius of MS 73 probe. The intensity values obtained from equation (1) are 19.20, 25.94, 31.57, 34.60 W/cm², respectively. For intensity effect experiments the temperature was fixed at 25 °C.

$$I = mc\pi^{-1}r^{-2}(dT/dt) \quad (1)$$

To investigate the temperature effect, the intensity was fixed at 31.57 W/cm². The temperature values were chosen as 10,15,20,25 °C respectively. Samples were subjected to sonication at 5-15-30-45-60-75-90-105-120-135-150 minutes to avoid volume change instead of withdraw sample from reaction medium. It is thought that the volume change can affect the sonication environment and the results.

For specific viscosity measurements, a capillary with a length of 20 cm and a radius of 0.025 cm connected to a Validyne Engineering DP15-28 pressure transducer was used. The voltage output of the converter is proportional to the pressure change. The detailed technique of specific viscosity measurement has been described in reference 11.

3. RESULTS and DISCUSSION

Various mechanisms and mathematical models have been developed to explain how ultrasound breaks down the polymer chains in solution. At the beginning of the sonication, the polymer chain breaks fast, then decelerates to a limit value in general, common in these models. The polymer that reaches the limit molecular weight value will no longer be affected by the ultrasound effect. Another important parameter that defines polymer degradation is degradation constant. This constant gives information about the effect of chain scission. According to Giz model, ultrasonic polymer degradation has heterogeneous nature. First, the long chains begin to break quickly and then the degradation is slowed down to a limit value. The degradation process has a variety of time constants. This variation is described in the stretched exponential form (equation 2). In the continuous distribution kinetics model of Madras, the integral form of the change of the viscosity is given as (3). Here $\eta_{sp,t}$ is the specific viscosity at sonication time t, the initial specific viscosity is denoted as $\eta_{sp,0}$ and the limit specific viscosity as $\eta_{sp,lim}$. The scission constant for the Giz model is denoted by k_1 , stretch factor is β and k_2 is Madras degradation constant.

$$\eta_{sp,t} = \eta_{sp,lim} + (\eta_{sp,0} - \eta_{sp,lim})e^{-(k_1 t)^\beta} \quad (2)$$

$$\ln[(\eta_{sp,lim})^{-1} - (\eta_{sp,t})^{-1}] = \ln[(\eta_{sp,lim})^{-1} - (\eta_{sp,0})^{-1}] - k_2 t \quad (3)$$

Specific viscosity changes in ultrasonic dextran degradation experiments are given in Figure 1-2. Initial specific viscosity was determined to be 0.061 for 0.001 g / mL. In Figure 1, viscosities appear to decrease rapidly in the initial phases the sonication in four different ultrasound intensity at 25 °C and then approach the limit values. In Figure 2, the change in viscosities are similar to that in Figure 1. However, the viscosity values are very close to each other.

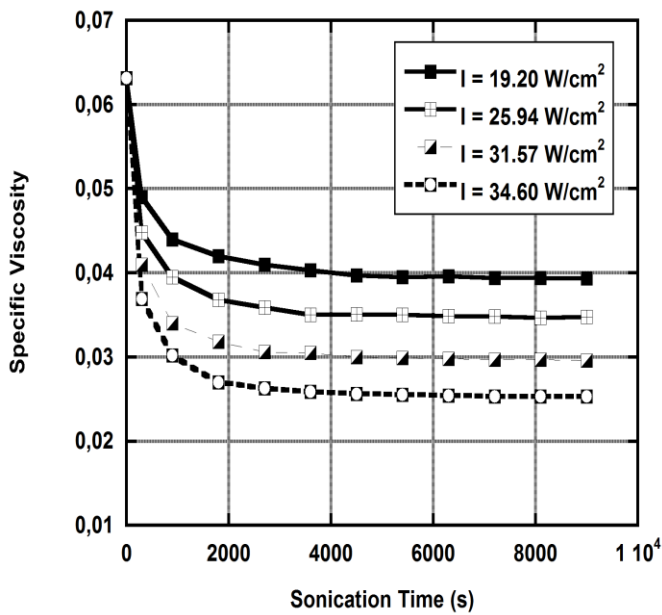


Fig -1: Specific viscosity evolution data for different ultrasound intensity at 25 °C

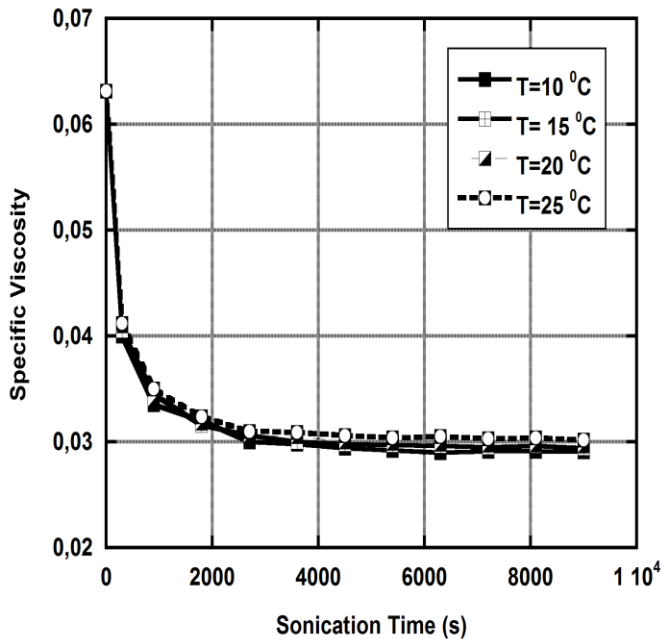


Fig -2: Specific viscosity evolution data for different temperature at 31.57 W/cm²

Figures 3 and 4 show that the specific viscosity values are compared with the Giz and Madras model using the nonlinear curve fitting method, respectively, $R^2 = 0.998$ (Giz) - 0.997 (Madras) for 19.20 W/cm², $R^2 = 0.998$ (Giz) - 0.998 (Madras) for 25.94 W/cm², $R^2 = 0.998$ (Giz) - 0.998 (Madras) for 31.57 W/cm² and $R^2 = 0.998$ (Giz) - 0.998 (Madras) for 34.60 W/cm². As can be seen from the R^2 values, it is consistent with the experimental data of the Giz and Madras models [8, 11, 17, 18].

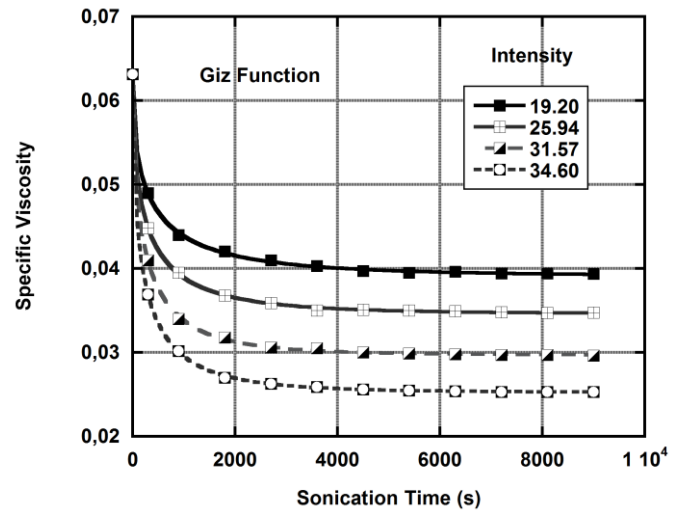


Fig -3: The prediction of the Giz model for different ultrasound intensity

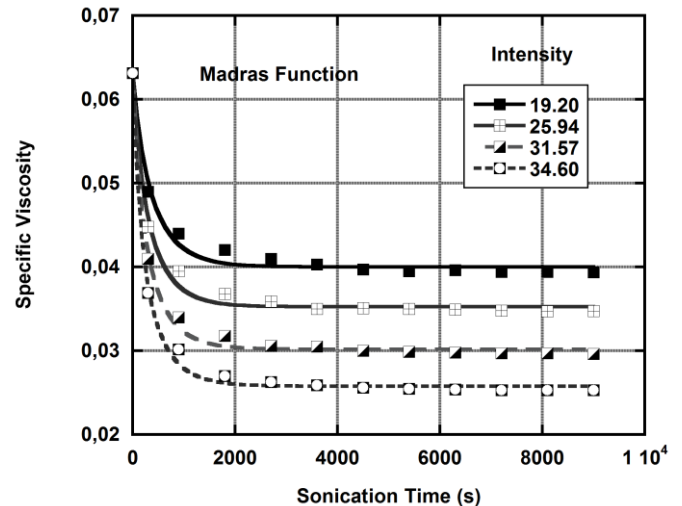


Fig -4: The prediction of the Madras model for different ultrasound intensity

According to the Giz model, the limit viscosities were determined as 0.0391, 0.0346, 0.0296, 0.0252 respectively. In addition, the Giz degradation constants were found to be 0.00266, 0.00348, 0.00400, 0.00457 s⁻¹. For Figure 4, the limit viscosities were determined as 0.0400, 0.0352, 0.0310, 0.0257 respectively. The Madras degradation constants were obtained to be 0.00195, 0.00209, 0.00205, 0.00212 s⁻¹. Figures 5 and 6 give the specific viscosity values are compared with the Giz and Madras model for fixed intensity at different temperatures. $R^2 = 0.998$ (Giz) - 0.998 (Madras) for 10 °C, $R^2 = 0.998$ (Giz) - 0.998 (Madras) for 15 °C, $R^2 = 0.998$ (Giz) - 0.997 (Madras) for 20 °C and $R^2 = 0.998$ (Giz) - 0.998 (Madras) for 25 °C. As can be seen from the R^2 values, it is consistent with the experimental data of the Giz and Madras models.

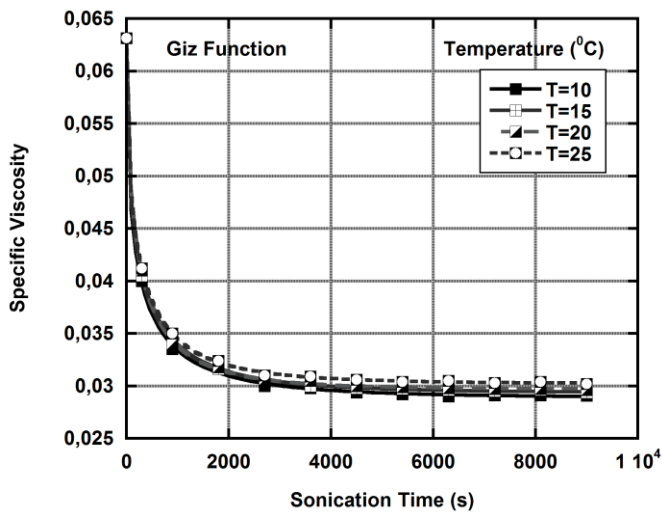


Fig -5: The prediction of the Giz model for different temperatures

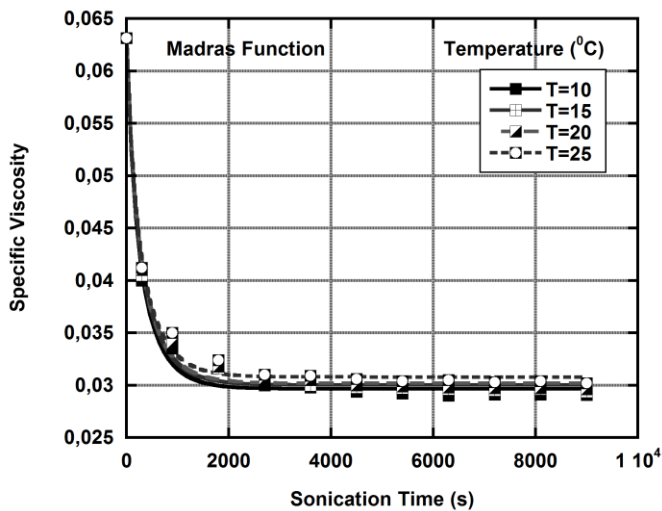


Fig -6: The prediction of the Madras model for different temperatures

The limit viscosities were determined as 0.0290, 0.0294, 0.0296, 0.0302 respectively. The Giz degradation constants were determined as 0.00420, 0.00412, 0.00400, 0.00395 s⁻¹. For Figure 6, the limit viscosities were determined as 0.0296, 0.0300, 0.0301, 0.0307 respectively. The Madras degradation constants were obtained to be 0.00217, 0.00211, 0.00205, 0.00205 s⁻¹.

Figure 7 shows the variation of degradation constants for different ultrasound intensity obtained from Giz and Madras model. For Giz model, the highest degradation constant at 34.60 W/cm² and the lowest degradation constant at 19.20 W/cm² were obtained. For Madras model, the highest degradation constant at 34.60 W/cm² and the lowest degradation constant at 19.20 W/cm² were obtained. As it is definitely predicted, a higher intensity of ultrasound gives rapid degradation including a lower limiting viscosity. A representation of this situation is shown in Figure 8. The limit viscosity is a linear function of the ultrasound intensity with the expression $\eta_{lim} = 0.0565 - 0.00087xI$, $R^2 = 0.975$ for

Giz model and $\eta_{lim} = 0.0569 - 0.0009xI$, $R^2 = 0.980$ for Madras model.

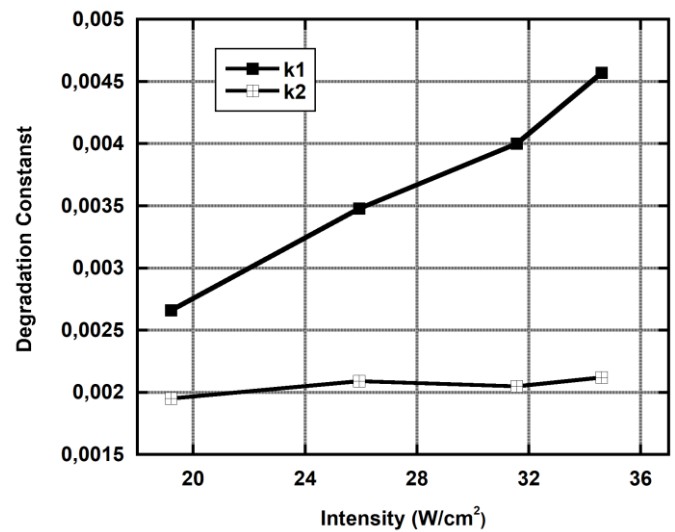


Fig -7: The degradation constants for Giz and Madras model versus ultrasound intensity

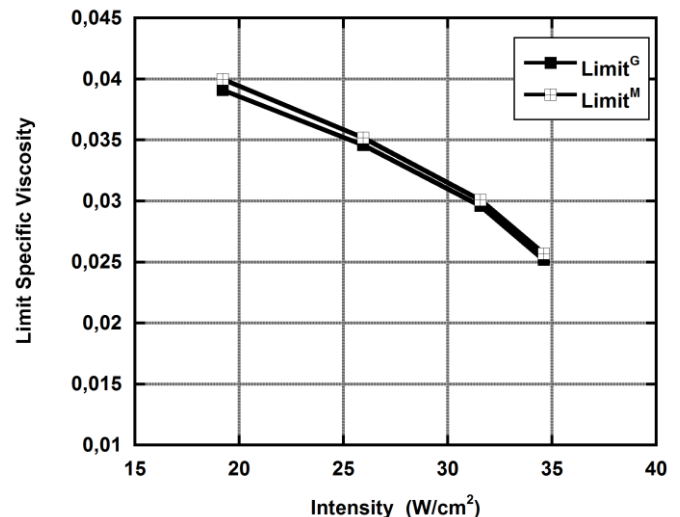


Fig -8: The limit specific viscosities for Giz and Madras model versus ultrasound intensity

Figure 9 gives the variation of degradation constants at different temperatures determined from Giz and Madras model. For Giz and Madras model, the highest degradation constant at 10 °C and the lowest degradation constant at 25 °C were obtained. As the temperature increases, the efficiency of breaking the polymer to the polymer chains is reduced. In Figure 10, the limit values obtained from the Giz and Madras models are given according to the temperature. The specific viscosity is a linear function of the temperature with the expression $\eta_{lim} = 0.0282 - 0.00007xT$, $R^2 = 0.962$ for Giz model and $\eta_{lim} = 0.0289 - 0.00006xT$, $R^2 = 0.932$ for Madras model.

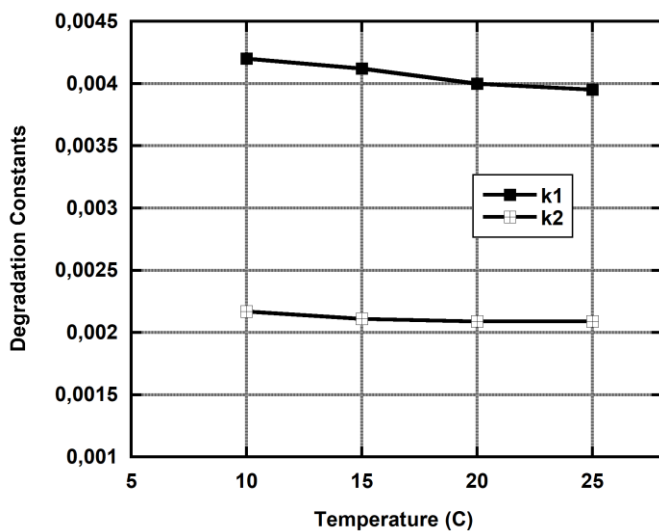


Fig -9: The degradation constants for Giz and Madras model versus temperature

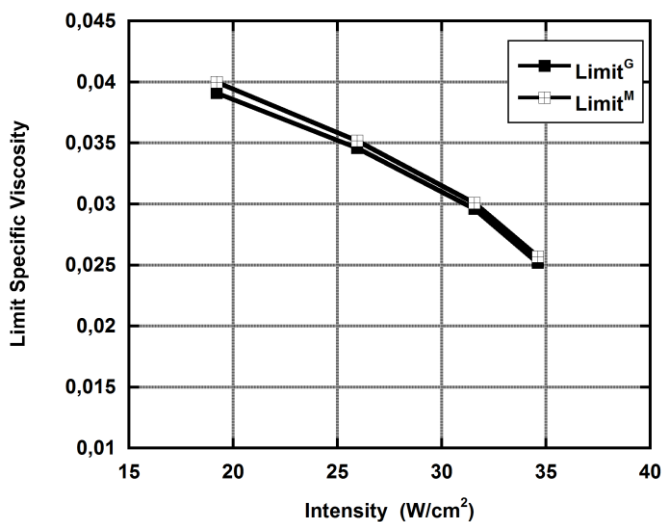


Fig -10: The limit specific viscosities for Giz and Madras model versus temperature

3. CONCLUSION

The effect of ultrasound intensity and temperature on the chain degradation of dextran is presented in this study. It can be concluded that the extent of degradation and the specific viscosity reduction are affected by changing of intensity-temperature. The ultrasound converts electrical energy into mechanical energy. This energy is next to transferred into polymer solution. If ultrasound intensity is increased, the cavitation bubbles in polymer solution grow in size and also the number density of bubbles increase. In this way the hydrodynamic forces on polymer chains increase so that the chain scission becomes more faster. The degradation has been found to be higher for 34.60 W/cm² intensity as compared to 19.20 W/cm² intensity about two times. The experiments also show that the limit specific viscosity is found to be reasonably sensitive to ultrasound intensity. In

cases where the temperature of the sonication medium increases, the vapor pressure of the solution will increase. In this case, the formation of cavitation bubbles will be facilitated in the sonication environment and the bubble will be produced concurrently. However, the violent bubbles collapse will decrease. The effect of ultrasound energy on the solution medium will be suppressed. Because of selected temperatures for experiments are close to each other; although it was difficult to determine the temperature effect experimentally, the use of the Giz and Madras models revealed the difference in temperature effect.

REFERENCES

1. K. Goulasa, D. A. Fisher, G. K. Grimble, A. S. Grandison and R. A. Rastall, "Synthesis of Isomaltooligosaccharides and Oligodextrans by the Combined Use of Dextranucrase and Dextranase," *Enzyme and Microbial Technology*, vol. 35, Sep. 2004, pp.327-338,
2. doi: 10.1016/j.enzymictec.2004.05.008.
3. Svensén and P. Rodhe, *Pharmacology and Physiology for Anesthesia, Intravascular Volume Replacement Therapy*, Chapter 33. Philadelphia, PA: Elsevier Inc., 2013.
4. S. Karandikar, A. Mirani, V. Waybhave, V. B. Patravale, S. Patankar, *Nanostructures for Oral Medicine, - Nanovaccines for Oral Delivery-Formulation Strategies and Challenges*, Chapter 10. Philadelphia, PA: Elsevier Inc., Elsevier Inc., 2017.
5. G. L. Cotea and J. L. Willet, "Thermomechanical Depolymerization of Dextran," *Carbohydrate Polymers*, vol. 39, Jun.1999, pp.119-126, doi: 10.1016/S0144-8617(98)00165-9.
6. Q. Zo, Y. Pu, S. Li, Q. Wang, X. Wang, S. Chen, M. Young, " Ultrasonic Degradation of Dextran in Aqueous Solution," *Advanced Materials Research*, vol. 396, Nov. 2012, pp.1624-1627, doi: 10.4028/www.scientific.net/AMR.396-398.1624.
7. M. Schaefer, B. Icli, C. Weder, M. Lattuada, A. F. M. Kilbinger and Y. C. Simon, "The Role of Mass and Length in the Sonochemistry of Polymers," *Macromolecules*, vol. 49, Feb. 2016, pp.1630-1636, doi: 10.1021/acs.macromol.5b02362.
8. E. V. Chubarova, E. M. Yu and V. V. Shamanin, "Chain Degradation under Low-Intensity Sonication of Polymer Solutions in the Presence of Filler: Mechanism of Ultrasonic Degradation of Flexible Chain Macromolecules," *Journal of Macromolecular Science, Part B*, vol. 52, Oct. 2013, pp. 873-896, doi: 10.1080/00222348.2012.738576.

9. Akyüz, H. Catalgil-Giz and A. Giz, "Effect of Solvent Characteristics on the Ultrasonic Degradation of Poly(vinylpyrrolidone) Studied by On-line Monitoring," *Macromolecular Chemistry and Physics*, Aug. 2009, vol. 210, pp. 1331-1338, doi: 10.1002/macp.200900098.
10. S. Akbulatov, S. and R. Boulatov, "Experimental Polymer Mechanochemistry and Its Interpretational Frameworks," *ChemPhysChem*, Mar. 2017, vol. 18, pp. 1422-1450, doi: 10.1002/cphc.201601354.
11. Pawar, P. J. Joshi, A. D. Kadam, N. B. Pande, P. H. Kamble, S. P. Hinge and P. R. Gogate, "Ultrasound-Based Treatment Approaches for Intrinsic Viscosity Reduction of Polyvinylpyrrolidone (PVP)," *Ultrasonics Sonochemistry*, May 2014, vol. 2, pp. 1108-1116, doi: 10.1016/j.ultsonch.2013.12.013.
12. Akyüz, O. Kamer and A. Giz, "Online Viscometric Monitoring of Ultrasonic Sodium Poly(styrene sulfonate) scission," *Journal of Macromolecular Science, Pure and Applied Chemistry*, Apr. 2013, vol. 50, pp. 535-540, doi: 10.1080/10601325.2013.781459.
13. S. Koda, K. Taguchi and K. Futamura, "Effect of Frequency and a Radical Scavenger on Ultrasonic Degradation Watersoluble Polymers," *Ultrasonics Sonochemistry*, June 2011, vol. 18, pp. 276-281, doi: 10.1016/j.ultsonch.2010.06.007.
14. M. Basedow, K. H. Ebert and E. Foßhag, "Ultrasonic Degradation of Polymers in Mixed Solvents," *Macromolecular Chemistry and Physics*, Oct. 1978, vol. 179, pp. 2565-2568, doi: 10.1002/macp.1978.021791023.
15. J.P. Lorimer, T.J. Mason, T.C. Cuthbert and E.A. Brookfield, "Effect of Ultrasound on the Degradation of Aqueous Native Dextran," *Ultrasonics Sonochemistry*, Sep. 1995 vol. 2, pp. 55-57, doi: 10.1016/1350-4177(94)00013.
16. Q. Zoua, Y. Pua, Z. Hanb, N. Fuc, S. Li, M. Liua, L. Huang, A. Lua, J. Mo, S. Chen, "Ultrasonic Degradation of Aqueous Dextran: Effect of Initial Molecular Weight and Concentration," *Carbohydrate Polymers*, Sep. 2012, vol. 90 pp. 447-451, doi: 10.1016/j.carbpol.2012.05.064.
17. Y. Pua, Q. Zoua, D. Houa, Y. Zhang, S. Chen, "Molecular Weight Kinetics and Chain Scission Models for Dextran Polymers during Ultrasonic Degradation," *Carbohydrate Polymers*, Jan. 2017, vol.156, pp. 71-76, doi: 10.1016/j.carbpol.2016.09.017.
18. S. P. Vijayalakkshmi and G. Madras, "Effect of Temperature on the Ultrasonic Degradation of Polyacrylamide and Polyethyleneoxide," *Polymer Degradation and Stability*, May 2004, vol. 84, pp. 341-344, doi: 10.1016/j.polyimdegadstab.2004.02.007.
19. S. P. Vijayalakkshmi and G. Madras "Effect of Initial Molecular Weight and Solvents on the Ultrasonic Degradation of Polyethyleneoxide," *Polymer Degradation and Stability*, Oct. 2005, vol. 90, pp. 116-122, doi: 10.1016/j.polyimdegadstab.2005.02.018.