

# Degradation of polypropylene using ultrasound-induced acoustic cavitation

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## Abstract

Cavitation results in generation of hot spots as well as turbulence associated with liquid circulation which can result in degradation of polymeric compounds. In the present work cavitation generated using ultrasound has been utilized for degradation of polypropylene and effect of different operating parameters on the extent of degradation has been investigated. Different concentrations (0.5%, 1% and 1.5%, w/v) and different volumes (50, 75 and 125 ml) were subjected to ultrasonic irradiation using a horn-type reactor. Two different solvents (*p*-xylene and decalin) have also been used to investigate the dependency of the intensity of cavitation on the type of the solvent. It was found that extent of degradation increases with a decrease in reaction volume and concentration. Use of *p*-xylene as a solvent resulted in higher extent of degradation. It was also observed that a constant solution viscosity is reached beyond which ultrasonic irradiation could not further degrade polypropylene. The limiting viscosity was also observed to depend on the volume and concentration of polypropylene.

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## 1. Introduction

Ultrasonic irradiation has been recently looked upon as a new technique for degradation of polymer compounds, mainly due to the fact that the reduction in the molecular weight is simply by splitting the most susceptible chemical bond without causing any changes in the chemical nature of the polymer [1,2]. Ultrasonic irradiation results in formation, subsequent growth and violent collapse of bubbles or cavities in the medium, which has been described as acoustic cavitation [3,4]. Apart from generation of local hot spots (conditions of high temperature and pressure) and generation of highly reactive free radicals, cavitation also results in liquid turbulence associated with liquid shear [4]. The shear forces are usually of sufficient magnitude to cause the rupture of chemical bonds binding the polymer compounds. Another unique feature of ultrasonic degradation is the fact that, in contrast to all chemical and thermal decomposition reactions, the ultrasound depolymerization is a non-random process which produces fragmentation at the mid-point of the chain. It is now well established that prolonged exposure of solutions of macromolecules to high

energy ultrasonic sound waves produces a permanent reduction in viscosity. Even when the irradiated polymers are isolated and redissolved their viscosity remains low in comparison with that of non-irradiated solutions [5]. Earlier work on application of ultrasonic irradiation for degradation of polymeric compounds includes studies with HDPE melt [1], polyvinyl alcohol [2,6,7], xylan [8,9], polybutadine [10] and dextrans [11] as the parent polymer compound. The present work involves application of cavitation induced using ultrasound for degradation of polypropylene.

Polypropylene is an important commercial polymer with potential uses for producing package films, pipes, storage tanks, seat covers, monofilaments, ropes and also in washing machines. However, there have not been many studies reporting the application of ultrasound-induced cavitation for degradation of polypropylene. Chakraborty et al. [10] studied the ultrasonic degradation of isotactic PP in *o*-dichlorobenzene as solvent for different temperatures and reported that ultrasound was indeed able to degrade polypropylene and the degradation rate decreased with an increase in the temperature. The present work aims at a more detailed investigation of effect of different operating parameters including initial concentration of the polymer, power density into the system and type of solvent, on the extent of degradation of polypropylene. Earlier studies [6–15], though with different polymer species, have indeed indicated that these

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operating parameters play a crucial role in deciding the extent of degradation.

## 2. Experimental

### 2.1. Materials

The material used was polypropylene (REPOL), obtained from Reliance, India. PP has the melt flow index of 3 g/10 min (203 °C/2.16 kg). The solvents (reagent grade) used were *p*-xylene and decalin, supplied by Loba Chemie, India.

### 2.2. Equipment and procedure

Solutions of polypropylene in *p*-xylene and decahydronaphthalene with different concentrations (0.5%, 1.0% and 1.5%, w/v) were prepared with precision of  $\pm 1 \times 10^{-2}$  g/l, respectively. The ultrasonic generator (Dakshin, 22.5 kHz, Horn tip diameter of 2 cm) with total supplied power input of 240 W was used. The actual power dissipated in the system was estimated using calorimetric measurements [16] and was observed to be equal to 15.5 W giving an energy efficiency of approximately 7%. The specific power density, defined as ultrasonic power dissipation per unit volume, varied in the range 125–210 W/l. Calorimetric measurements for each run also indicates that the ultrasonic power dissipated in the solution is the same for each of the initial viscosities (change in polymer concentration) investigated in the present work. The degradation of solutions was carried out in the same glass beaker for all of the concentrations and volumes. The beaker was wrapped with aluminum foil to the sonic horn to minimize solvent evaporation. The experiments were conducted by covering the beaker to ensure that no air entered into the system during degradation. All the experiments were repeated and the experimental errors between each set were found to be less than  $\pm 2\%$ .

### 2.3. Measurement and characterization

Periodically samples of sonicated solutions were removed for viscosity measurement (at  $88 \pm 1$  °C) by Ubbelohde viscometer (Technico, Number 1). Relative and specific viscosities ( $\eta_r$  and  $\eta_{sp}$ , respectively) were calculated using following formulae:

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

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

where  $t$  and  $t_0$  are the efflux time for polymer solution and solvent, respectively. Reproducibility of the efflux time was within 0.3 s. Experiments were repeated twice to check the reproducibility of the obtained data for the variation of concentration against time for all the sets. It has been observed that experimental errors were within  $\pm 2\%$ . The  $\eta$  values for the PP solution at different concentrations were calculated by the one-point intrinsic viscosity equation [17].

$$\eta = \frac{[2(\eta_{sp} - \ln \eta_r)]^{0.5}}{c} \quad (3)$$

The variation of either molecular weight or the intrinsic viscosity in the presence of ultrasonic irradiation reflects the ultrasonic degradation of polymer. In this work, it was found that all degraded samples were dissolved completely in *p*-xylene as well as decalin, indicating that no cross-linking took place under ultrasonic irradiation. The extent of ultrasonic degradation of polymer solutions has been quantified by using a parameter,  $\varphi = (([\eta] - [\eta_\infty])/[\eta]) \times 100$ , where  $[\eta]$  and  $[\eta_\infty]$  is initial intrinsic viscosity and limiting intrinsic viscosity, respectively.

## 3. Results and discussion

### 3.1. Effect of reaction volume

Operating reaction volume plays a crucial role in deciding the extent of degradation, particularly where ultrasonic irradiation is achieved using horn-type reactor. Effect of reaction volume on the extent of degradation has been investigated at constant power dissipation of the ultrasonic reactor and constant concentration of the polymer species. Fig. 1 shows the effect of the reaction volume on the extent of degradation depicted in terms of the change in  $[\eta]$  at 0.5% polymer concentration with *p*-xylene as the solvent. It can be easily seen from the figure that the extent of degradation decreases with increase in the reaction volume at same supplied ultrasonic power dissipation. To give a quantitative idea, in 75 min of irradiation time, the extent of degradation for 75 ml of 0.5% concentration solution is almost two times higher as compared to degradation for 125 ml volume. The effect of volume was also investigated at two different concentrations (1.0 and 1.5%) and the similar trends for variation of extent of degradation with the reaction volume have been observed. The obtained results can be attributed to the fact that, increase in the reaction volume decreases the power density of the system (power dissipation per unit volume) resulting in a corresponding decrease in the cavitation activity. With a decrease in the operating power density, the number of cavitation events occurring in the system decreases lowering the effective cavitation intensity. Also in the case of cavitation horn, the active cavitation volume is restricted very near to the transducer surface, resulting in non-uniform distribution of the cavitation activity. With an increase in the operating volume, there exists

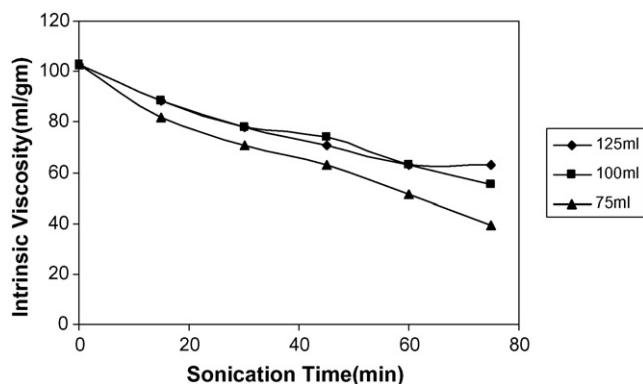


Fig. 1. Effect of reaction volume on the progress of ultrasonic degradation at 0.5% polypropylene solution and *p*-xylene as solvent.

enhanced number of dead zones where the cavitation activity is minimal resulting into detrimental effects. Sivakumar and Pandit [18] have reported similar trend for the effect of power density on the extent of degradation of Rhodamine B whereas Harkal et al. [7] have reported similar results for the degradation of polyvinyl alcohol.

As the extent of polymer degradation is strongly dependent on the reaction volume in the present case, it can be said here that using ultrasonic horn-type reactor for large-scale operations is certainly not a good idea as dissipating large powers through single transducer might not be feasible. Even if maximum power dissipation is allowed using a single transducer, restriction of the cavitationally active volume just near the transducer surface will mean that the single transducer-based reactor will still give lower extent of degradation. The best approach for large-scale operations is to use multiple transducers with possibility of multiple frequency irradiation (increases the cavitation intensity due to more violent collapse of the generated cavities). The earlier work of Gogate et al. [19] and Kumar et al. [20] is recommended for more details about these types of reactors.

### 3.2. Effect of initial concentration of polymer

Initial concentration of the reactants (polymer in the present case) also significantly affects the extent of ultrasonic degradation [21–24]. The variation in the extent of viscosity reduction with the initial concentration of the polymer has been shown in Fig. 2 at 75 ml of operating capacity and *p*-xylene as solvent. It can be clearly seen from the figure that the extent of viscosity reduction is maximum at lowest concentration of the polymer species at same supplied ultrasonic power, perhaps due to lower content of the polymer in the system. Quantitatively speaking, the extent of net viscosity reduction estimated as percentage degradation of the polymer at 0.5% concentration is more than 2.5 times higher as compared to 1.5% concentration (3 times lower polymer content). The observed decrease in the extent of viscosity reduction can be attributed to a strong dependence of viscosity of the polymeric solution on the concentration which severely suppresses the degree of cavitation. It should be noted here that the intensity of cavitation remarkably falls down with an increase in the viscosity of the medium.

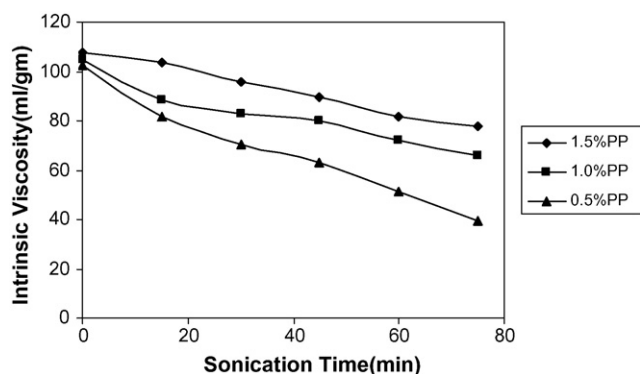


Fig. 2. Effect of polymer concentration on the progress of ultrasonic degradation at 75 ml of operating capacity and *p*-xylene as solvent.

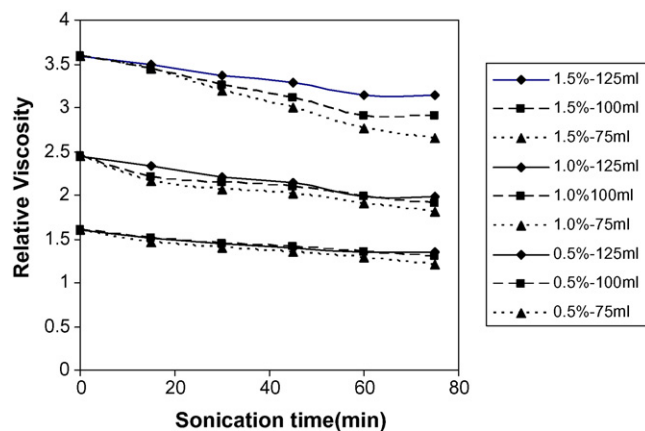


Fig. 3. Effect of concentration and volume on limiting viscosity of polypropylene for the case of *p*-xylene as solvent.

### 3.3. Effect of reaction volume and concentration on limiting viscosity

Fig. 3 shows the effect of reaction volume on the limiting viscosity of polypropylene solution when it is subjected to ultrasonic irradiation at 80 °C. Fig. 3 shows that, for each concentration investigated in the present work, the limiting viscosities at 100 and 75 ml reaction volume are nearly equal. The actual value of the limiting viscosity is however dependent on the concentration and increases with an increase in the concentration. It can also be seen from figure that for 125 ml solution the limiting viscosity is higher than that of 100 and 75 ml reaction volume. This can be attributed to lower intensity of cavitation at higher volumes of operation and higher solution concentrations. The obtained results are consistent with the results reported for the ultrasonic degradation of poly(vinyl alcohol) [7].

### 3.4. Effect of type of solvent

Solvent plays a crucial role in deciding the cavitation intensity in the system. Viscosity, surface tension and vapor pressure of the solvent are the important parameters affecting cavitation phenomena. These properties of the solvent critically affect the extent of cavitation intensity (number of cavitation events as well as the extent of shear forces generated due to the collapse of the bubble). Thus it is expected that the extent of ultrasound-induced degradation of polymers depends on the type of the solvent. Vijayalakshmi and Madras [25] and Madras and Chattopadhyay [15] have clearly demonstrated the dependency of ultrasound-induced polymer degradation process on the type of solvent used in the work.

In the present work, *p*-xylene and decalin have been used as solvents. The two solvents differ mainly in terms of viscosity and surface tension. The variation in the extent of degradation (defined as percentage change in viscosity per unit initial viscosity) in 75 min of treatment time for 75 ml of solution has been shown in Fig. 4. It can be seen that the variation in the effect of initial concentration almost follows a similar path in both solvents. Similar variation was also observed for the effect of reaction volume for the two solvents. The observed trends

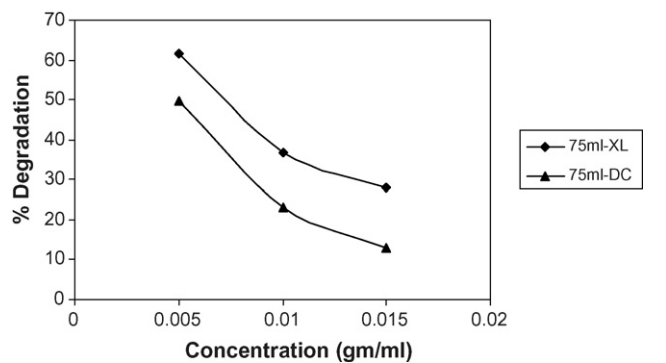


Fig. 4. Effect of solvent on extent of degradation of polypropylene of 75 ml volume.

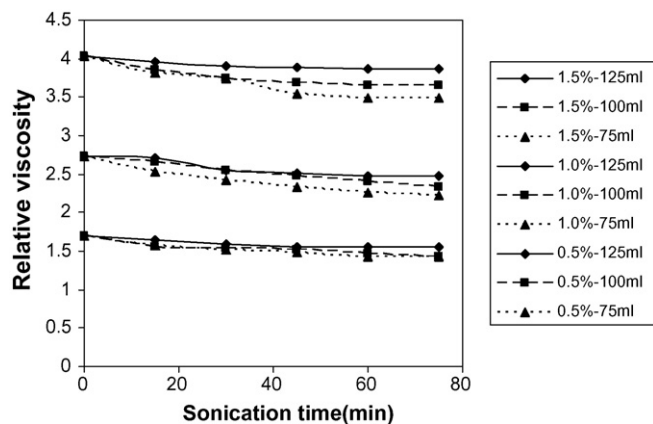


Fig. 5. Effect of concentration and volume on limiting viscosity of polypropylene for the case of decalin as solvent.

for the variation of the limiting viscosity were also similar for decalin as solvent as shown in Fig. 5.

When the extent of degradation is compared for two solvents, it can be said that degradation of polypropylene is much faster in *p*-xylene as solvent as compared to the decalin as solvent. Viscosity of the decalin is higher than the *p*-xylene, which has been confirmed by the efflux time for both the solvents through viscometer. The formation of voids or vapor-filled microbubbles (cavities) in a liquid requires that the negative pressure in the rarefaction region overcome the natural cohesive forces acting within the liquid. It follows therefore that cavitation should be more difficult to produce in viscous liquids where such forces are large. Another important property of the solvent which can play a role here is the surface tension. Surface tension of decalin is 28.72 dyne/cm at 25 °C while that of *p*-xylene is 25.50 dyne/cm at 25 °C. Solvents with higher surface tension offer higher resistance to the formation of the cavities in the system and hence the expected cavitation intensity in the case of *p*-xylene as solvent is higher resulting in higher extent of degradation.

#### 4. Conclusions

The effect of reaction volume, concentration and type of the solvent on the ultrasonic degradation of polypropylene has been investigated. The results indicate that the percentage degradation

reduced with increasing reaction volume and increasing concentration which affects the cavitation intensity in the system. Also use of *p*-xylene as solvent resulted in higher extent of degradation as compared to the use of decalin as solvent. The limiting viscosity was also dependent on the solution concentration and the operating volume. The present work has clearly illustrated the suitability of ultrasound-induced cavitation phenomena as a technique for degradation of polypropylene.

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