Ultrasonic degradation of butadiene, styrene and their copolymers

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Ultrasonic degradation of commercially important polymers, styrene–butadiene (SBR) rubber, acrylonitrile–butadiene (NBR) rubber, styrene–acrylonitrile (SAN), polybutadiene rubber and polystyrene were investigated. The molecular weight distributions were measured using gel permeation chromatography (GPC). A model based on continuous distribution kinetics approach was used to study the time evolution of molecular weight distribution for these polymers during degradation. The effect of solvent properties and ultrasound intensity on the degradation of SBR rubber was investigated using different pure solvents and mixed solvents of varying volatility and different ultrasonic intensities.

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1. Introduction

Styrene–butadiene (SBR), acrylonitrile–butadiene (NBR) polymers find major applications in the automobile sector for tires and as conveyor belts, hose pipes, etc. Styrene–acrylonitrile (SAN) has major applications in computer products, packaging, electrical and electronic applications. The high consumption of these polymers require proper disposal and hence, many techniques have been applied to degrade these polymers.

Polymer degradation can be achieved by various methods such as application of thermal, photochemical and ultrasound energy. The scission of the polymer backbone occurs mainly at chain end and/or randomly by thermal degradation. However, the scission occurs preferentially at the midpoint for ultrasonic degradation [1]. The degradation mechanism using ultrasound is attributed to the hydrodynamic forces that are created due to the increased frictional forces between ultrasonically accelerated faster moving solvent molecules and the less mobile polymer molecules or from the high pressure associated with the collapse of bubbles [2]. The ultrasonic effects are attributed to cavitation, growth and rapid collapse of microscopic bubbles as the alternate rarefaction and compression phases of the longitudinal sound wave pass through the liquid [1]. The growth and collapse of bubbles, which occur on a microsecond timescale, cause movement of solvent molecules around the bubbles and sets up large shear fields. The polymer molecules near the shear field move faster than the polymer mol-

ecules far away from cavitation. The polymer gets cleaved in the backbone due to the relative motion of polymer chains and mechanical stress generated [3,4]. The cleavage happens at the midpoint as the force distribution induced in the polymer chain due to the relative motion is the maximum at the centre of the uncoiled chain [5].

The effect of solvent, polymer concentration, ultrasound intensity, temperature, dissolved gases, viscosity, initial molecular weight on the degradation of few polymer solutions has been studied previously [1,3,6–9]. The effect of temperature increment during the ultrasonic degradation process was shown to have a decreased rate of degradation, which indicated that the degradation during ultrasonic process is due to the hydro-mechanical process [1]. The ultrasonic degradation of polymers such as polyvinyl alcohol [6], polyethyleneoxide [7], polyvinyl acetate [8,9], polystyrene [1], polybutadiene [10], polypropylene [10,11], poly(vinylpyrrolidone) [12,13], poly(acrylates) [14] and dextran [15] has been investigated.

In ultrasonic degradation, the molecular weight decreases exponentially and reaches a limiting molecular weight [1] and many theoretical models have been proposed [16–18] to evaluate the kinetics of the degradation. Continuous distribution kinetics has also been used to model the degradation process and the rate coefficient is obtained by fitting the experimental values with the model [19]. This model provides a better method to determine the rate coefficients since the rates are determined from the time evolution of the molecular weight distribution (MWD). Continuous distribution population balances provide the governing integro-differential equations, which can be solved to obtain the time evolution of the number-average molecular weight by applying

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moments [19]. Madras et al. have studied the ultrasonic degradation of polystyrene and poly(vinyl acetate) and showed that continuous distribution kinetics predicts the time evolution of MWDs satisfactorily [19]. Akyüz et al. have compared all the theoretical models in the literature with their online experimental data and have shown that the OHM (Ovenall/Harrington/Madras) model correlates the experimental results well [18].

Though the ultrasonic degradation of polystyrene [1], polybutadiene [10,20], polyacrylonitrile [21], and styrene–butadiene [22] has been studied, the ultrasonic degradation of the copolymers of styrene, butadiene and acrylonitrile has not been systematically studied. The objective of this work is to study the effect of ultrasonic degradation of SBR, NBR and SAN copolymer and compare the degradation rates of these copolymers to that of the homopolymers. The effect of various solvents and the ultrasonic intensity on the degradation of SBR polymers has also been examined. The rate coefficients were determined using the continuous distribution model and the variation of the degradation rate coefficients with the vapor pressure of the solvent, kinematic viscosity, Flory–Huggins interaction parameter and the ultrasound intensity were also studied.

2. Experimental section

2.1. Materials and methods

Styrene monomer, polybutadiene (PB, initial number-average molecular weight, M_{n0}: 120,000), poly(styrene–butadiene) (SBR, 45 wt% styrene, M_{n0}: 110,000), poly(styrene–acrylonitrile) (SAN, 70 wt% styrene, M_{n0}: 70,000), poly(acrylonitrile–butadiene) (NBR, acrylonitrile: 37–39 wt%, M_{n0}: 90,000) were obtained from Sigma–Aldrich. Styrene monomer was washed with 10% NaOH solution to remove the inhibitors. The solvents benzene, toluene, p-xylene, chlorobenzene, o-dichlorobenzene and the initiators azo-bis-isobutyronitrile (AIBN) were purchased from S.D Fine Chemicals (India). Tetrahydrofuran was purchased from Merck, India. The solvents were distilled and filtered through 0.2 μm nylon filter paper before use.

2.2. Polymerization

Polystyrene (PS) was synthesized by free radical polymerization technique using AIBN (2.5 wt%) as the initiator at 60 °C. The synthesized polymer was fractionated by dissolving in toluene and subsequent precipitation in methanol.

2.3. Ultrasonic degradation experiments

The reaction was carried out in a 100 ml beaker. Initially, polymer solutions of 2 g/l were prepared and 60 ml of the solution was taken each time with the beaker being held using clamp stand assembly in a constant temperature bath. This solution was subjected to ultrasonic degradation using a horn type ultrasonic processor (Vibronics, India) at a frequency maintained at 25 kHz. The temperature of the solution was maintained constant at 30 ± 2 °C. All the polymer solution samples (PS, PB, SBR, NBR, SAN) were degraded using o-dichlorobenzene as solvent at 175 J/min intensity and 30 °C. The ultrasonic degradation of SBR polymer solution was investigated in o-dichlorobenzene, chlorobenzene, p-xylene, toluene and benzene solvents at an intensity of 175 J/min and 30 °C to study the effect of solvent in the degradation rate. Similarly, the SBR solution was degraded in o-dichlorobenzene at different ultrasonic intensities by varying the input voltage to examine the effect of intensity on the degradation.

Samples of 200 μl were collected from the reaction vessel at definite time intervals for further analysis using gel permeation chromatography (GPC). The continuous distribution kinetics model to determine the degradation rate coefficient requires the limiting molecular weight of the polymer. Hence experiments were conducted for 10 h for all the polymers to determine the limiting molecular weight and no significant change in molecular weight was observed beyond 8 h. The number average molecular weight of the polymer after 10 h of degradation was used for the calculation. It was observed that the ratio of limiting molecular weight to the molecular weight after 4 h for different polymers tested varies approximately from 0.55 to 0.65. Many experiments were repeated three or four times while all the experiments were repeated at least twice and the error in the determination of degradation rate coefficient in all cases was less than ±3%.

2.4. Determination of MWDs by GPC

The molecular weight distributions of the samples were determined by GPC. GPC consisted of high pressure liquid chromatography pump (Waters 510), three 7.5 mm × 300 mm size exclusion columns packed with cross-linked poly(styrene–divinylbenzene) (Styragel HR 5E, HR 4, HR 1), a differential refractometer (Waters RI 2410) for detection and a data acquisition system. The columns were maintained at 50 °C with a column heater (Waters). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 ml/min. Samples were injected through a Rheodyne 7725 valve with a sample loop of 50 μl to obtain the chromatogram. The chromatogram was converted to MWD by the calibration curve prepared using monodisperse polystyrene standards.

2.5. Ultrasonic power measurement using calorimetry

Experiments were carried out to evaluate the actual ultrasound intensity absorbed by the liquid by calorimetry. The ultrasonic energy dissipated in the liquid can be determined by the following equation [23].

$$P = Mc_p(\mathrm{d}T/\mathrm{d}t) \tag{1}$$

Thus

$$T - T_0 = P/(Mc_p)t \tag{2}$$

where P is the power (J/min), M is the mass of the water (g), c_p is the specific heat of water (J g^{-1} K^{-1}), $\mathrm{d}T/\mathrm{d}t$ is the rate of temperature rise (K min^{-1}), T_0 is the initial temperature and T is the temperature as a function of time. Eq. (2) assumes that the liquid is pure and there is no heat loss from the system. The experiment was conducted with the same beaker used for polymer degradation experiments with the same amount of liquid. The experiments were conducted for 15 min and the increase of temperature of the liquid was monitored as a function of time. This was plotted and linearly regressed based on Eq. (2) to obtain the power supplied. The experiments were conducted with both chlorobenzene and water and all experiments were repeated thrice to check the consistency of the results. Because the value of c_p is different for chlorobenzene and water, the rise in temperature of the liquid was different but the value of the power obtained was the same in both the cases.

2.6. Theoretical model

Continuous distribution models provide an effective technique to study the dynamics of macromolecular reactions [24]. The polymer, $P(x)$, is considered to be a mixture of homologous molecules with MW, x, as continuous variable. The polymer, $P(x)$, undergoes chain scission at the midpoint to yield $P(x/2)$ with a rate coefficient

of $\kappa(x)$. Based on the molar concentration, the time dependent MWD of $P(x)$ is defined as $P(x, t)$. For chain scission, the distribution kinetics equation with loss and gain terms is [24]

$$\partial p(x, t)/\partial t = -\kappa(x)p(x, t) + 2 \int_x^\infty \kappa(x')p(x', t)\Omega(x, x')\mathrm{d}x' \qquad (3)$$

where $\Omega(x, x')$ is the stoichiometric kernel. The degradation rate coefficient depends on size and the rate coefficient can be assumed to be $\kappa(x) = k(x - x_l)$, where x_l is the limiting MW. This clearly indicates that no further degradation is possible after the polymer reaches its limiting molecular weight, which is consistent with the experimental observations. For chain scission yielding equal sized fragments, the stoichiometric kernel is $\Omega(x, x') = \delta(x - x'/2)$. Solving Eq. (3) by the moment technique [24] yields the time variation of the number-average molecular weight as

$$\ln\left\{\frac{\frac{1}{M_{no}} - \frac{1}{x_l}}{\frac{1}{M_n} - \frac{1}{x_l}}\right\} = \ln Y = kx_l t \qquad (4)$$

The above equation is derived based on the assumption of constant temperature, concentration and intensity throughout the reaction.

A rate model was proposed for the ultrasonic degradation of polymers [3,18] in terms of the solution concentration 'c' and monomer molecular weight 'm_o'

$$\ln\left\{\frac{\frac{1}{M_{no}} - \frac{1}{x_l}}{\frac{1}{M_n} - \frac{1}{x_l}}\right\} = \ln Y = k_o \frac{x_l}{cm_o} t \qquad (5)$$

The difference between the above equations is the dependence of scission rate on the solution concentration. For this reason '$k_o t/c$' is dimensionless instead of 'kt'.

Similarly, Harrington and Zimm proposed that their experimental rate could be characterized by the expression [18]

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{M_t}\right) = k_H\left(\frac{1}{M_{\lim}} - \frac{1}{M_t}\right) \qquad (6)$$

This in integral form is equivalent Eq. (5) and Eq. (4) with 'k_H' from Eq. (6) taking the place of 'kx_l' (Madras model) in Eq. (4) and '$k_o x_l/cm_o$' (Ovenall model) in Eq. (5). These three models were called as OHM model as the phenomenon behind the model development is the same with the only difference being in the rate constant. Based on the extensive work by Giz and coworkers [18], it was concluded that the OHM (Ovenall/Harrington/Madras) model best represents the experimental data compared to all the other theoretical models available.

3. Results and discussion

The ultrasonic degradation of polystyrene copolymers and polybutadiene copolymer rubbers were studied by performing the degradation process in o-dichlorobenzene at 30 °C and the data obtained was fitted by Eq. (4) to obtain the degradation rate coefficient. Fig. 1a shows the evolution of the number-average molecular weight. Fig. 1b and c shows the linearity indicated by Eq. (4). The rate coefficient for the ultrasonic degradation of polymers was determined from the slope of the linearly regressed lines of Fig. 1b and c. Fig. 1b compares the variation of ln(Y) with sonication time for the polybutadiene copolymer rubbers (SBR, NBR), with polybutadiene rubber. The degradation rate coefficient, k ($\times 10^{10}$ mol g^{-1} s^{-1}), obtained for polybutadiene homopolymer is 13.1 while that of copolymers such as SBR and NBR are 5.8 and 3.7, respectively. Fig. 2 shows the comparison of the degradation rate coefficients of these copolymers with their respective homopolymers. The results indicate that the order of the degradation for polybutadiene copolymers follows the order PB > SBR > NBR. The cause for the lower degradation for NBR compared to SBR
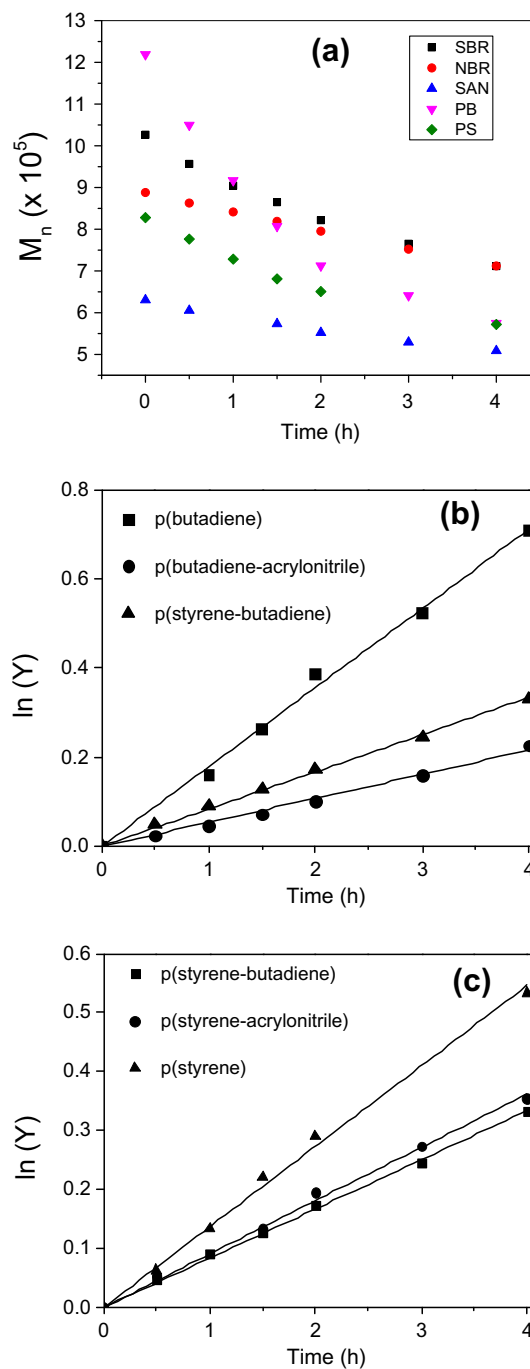

Fig. 1. Variation of (a) number average molecular weight (b) ln Y of butadiene and butadiene copolymer rubbers (c) Y of styrene and styrene copolymers with sonication time for the ultrasonic degradation in o-dichlorobenzene at 30 °C and intensity of 175 J/min.

may be due to the hydrogen bonding in NBR, which provides a resistance to the cleavage of the polymer though the hydrogen bonding forces are weak compared to intermolecular forces.

Fig. 1c compares the variation of ln Y with sonication time for the polystyrene copolymers (SBR, SAN) with polystyrene homopolymer. The degradation rate coefficient, k ($\times 10^{10}$ mol g^{-1} s^{-1}), obtained for polystyrene homopolymer is 9.6, which matches with the reported values [25], while the rate coefficient for the copolymers such as SAN and SBR rubbers are 7.2 and 5.8, respectively. The degradation trend for these group of polymers follows the order PS > SAN > SBR. Though intermolecular forces in acrylonitrile
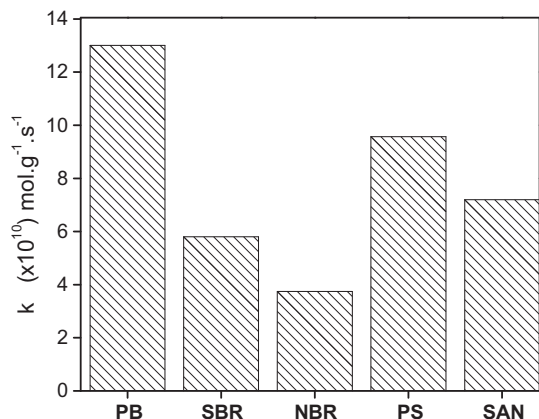
Fig. 2. Comparison of degradation rate coefficients for polystyrene and polybutadiene copolymers with its homopolymers.

may decrease the energy available for degradation, the degradation rate for SAN polymer is higher than that of the SBR polymer. The possible factor for this observation is due to the lesser amount of acrylonitrile in the SAN polymer (30 wt%). The degradation rate coefficients of polystyrene copolymers, SAN (70 wt% styrene) and SBR (45 wt% styrene), are lower than that of polystyrene. The observed results indicate that the rate of degradation is not completely dependent on the styrene content [25] but also depend on the arrangement of two monomer units in the polymer backbone.

4. Effect of solvent

The effect of solvent on the ultrasonic degradation of SBR rubber was studied using various solvents of varying volatility such as o-dichlorobenzene, p-xylene, chlorobenzene, toluene, benzene at 30 °C and intensity of 175 J/min. The results for the degradation
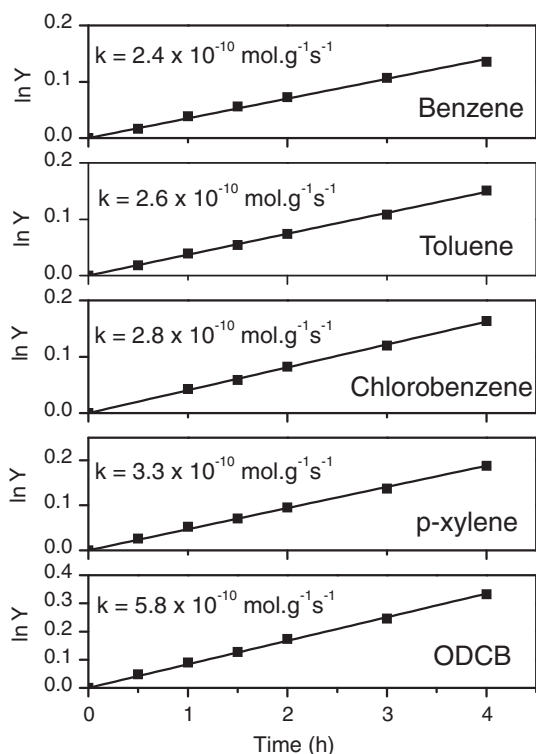
of SBR in various solvents are shown in Fig. 3 as the variation of ln Y with sonication time. To understand the effect of solvent properties (other than vapor pressure) on the degradation, studies were carried out with different solvents (pure and mixed) at different temperatures such that the vapor pressure of the solvent remains constant. Fig. 4 shows the variation of ln Y with sonication time for the degradation of SBR rubber in chlorobenzene at 46 °C, p-xylene at 53 °C and a mixture of chlorobenzene(80%)–o-dichlorobenzene (20%) solvent at 50 °C. For all these experiments with different solvents and temperatures, the vapor pressure was 4.96 kPa, which is the vapor pressure of toluene at 30 °C.

The effect of solvent on the degradation rate coefficient is observed from the variation of k values in Fig. 3 where the k value is highest with o-dichlorobenzene and lowest with benzene. The relationship between the ultrasonic degradation rate coefficient for SBR polymer and solvents of different vapor pressure at constant temperature (o-dichlorobenzene, p-xylene, chlorobenzene, toluene, benzene at 30 °C) and with solvents of constant vapor pressure (chlorobenzene at 46 °C, p-xylene at 53 °C and a mixture of chlorobenzene (80%)–o-dichlorobenzene (20%) at 50 °C) is shown in Fig. 5a. The observed effect can be explained by the influence of solvent on the cavitational behavior during the ultrasonic process. When the solvent volatility is high (high vapor pressure), more solvent vapor will enter the cavitation bubble providing more cushioning effect during bubble collapse which reduces the shock and shear forces [1,7,8] resulting in a decrease in the overall degradation rate coefficient. Therefore, the degradation will be less efficient in high volatile solvents with low heat of vaporization. Therefore, the variation of rate coefficient with different solvents is attributed to their cavitation, bubble growth and its collapse, which is consistent with other studies [3,7].

The variation of rate coefficients with solvents of increasing vapor pressure shows a near exponential decrease and shows the important role of vapor pressure on the rate of degradation. However, when experiments were conducted with the solvents at different temperatures but the same vapor pressure, the
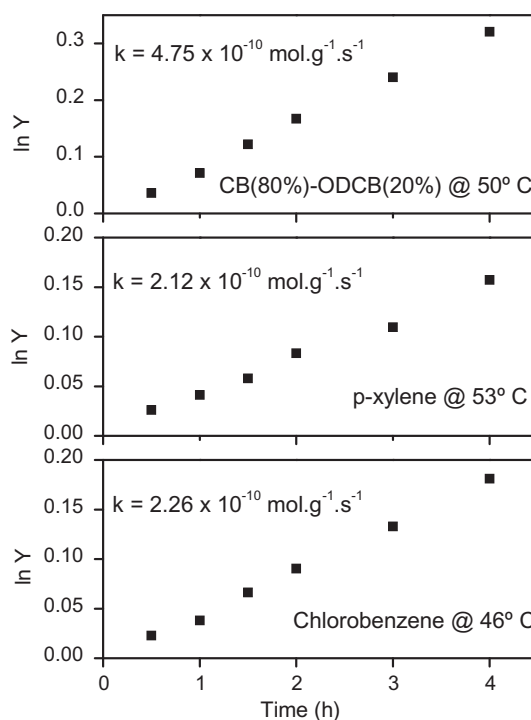

Fig. 3. Variation of ln Y with sonication time for ultrasonic degradation of SBR in different solvents at 30 °C and intensity of 175 J/min.

Fig. 4. Variation of ln Y with sonication time for ultrasonic degradation of SBR in different solvents at different temperatures with same vapor pressure (4.96 kPa) and intensity of 175 J/min.
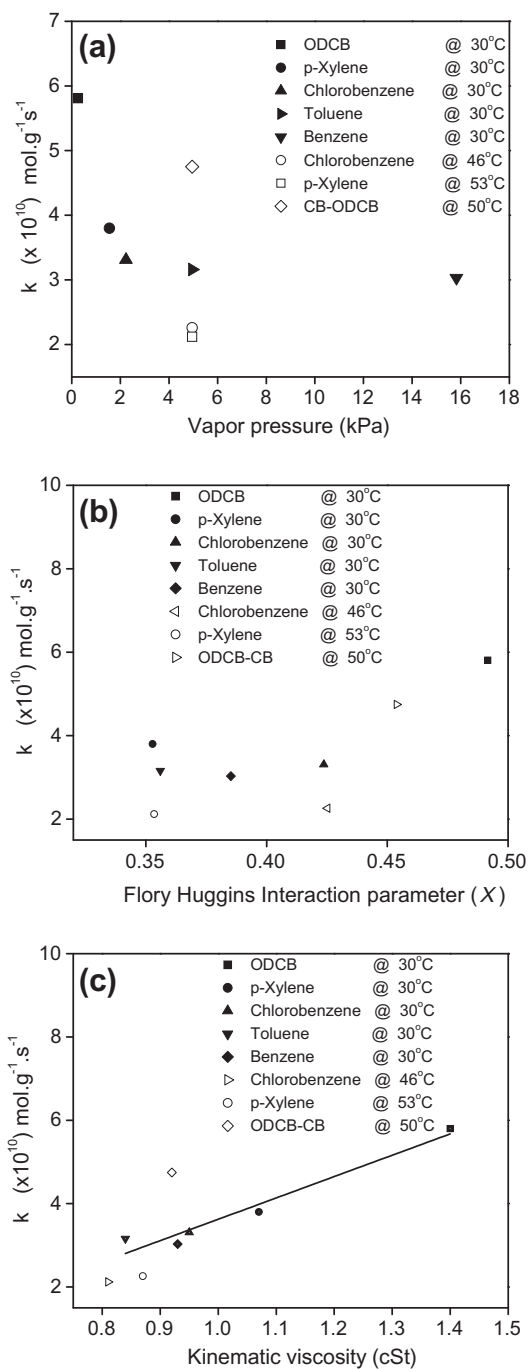
Fig. 5. Variation of degradation rate coefficient of SBR with (a) vapor pressure of solvent, (b) Flory Huggins interaction parameter (χ) of solution and (c) kinematic viscosity of solution at an intensity of 175 J/min.

Fig. 6. (a) Variation of ln Y with sonication time in o-dichlorobenzene at 30 °C for ultrasonic degradation of SBR at different intensities. (b) Variation of degradation rate constant with absorbed ultrasound intensity.

degradation rate coefficient varies from 2.12 to 4.75 ($\times 10^{10}$ mol g^{-1} s^{-1}), as seen from Fig. 5a. This variation of degradation rate coefficient clearly shows that parameters other than vapor pressure of solvent also have an influence on the ultrasonic degradation process of the polymer.

The degradation parameters can be influenced by the thermodynamic property of the interaction between the solvent and the polymer such as the Flory–Huggins interaction parameter [3]. The Flory-interaction parameter (χ) for the polymer–solvent system was calculated by the following expression [26]

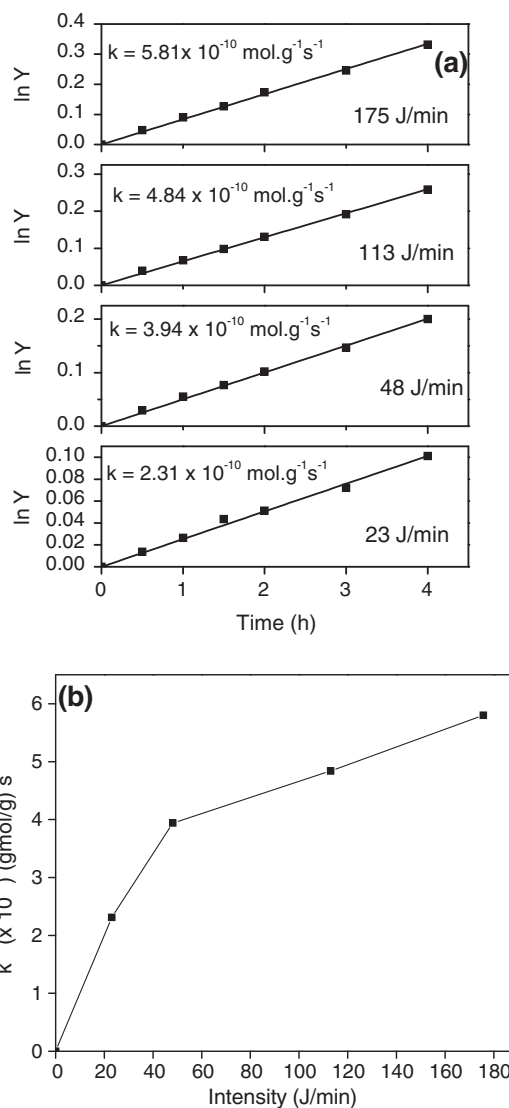$$\chi = 0.34 + \frac{V_s}{RT}(\delta_p - \delta_s)^2 \qquad (7)$$

where V_s is the molar volume of the solvent (cm^3 mol^{-1}), R is the gas constant (cal mol^{-1} K^{-1}), T is the temperature in K, δ_p and δ_s are the solubility parameters for the polymer and solvent respectively (cal cm^{-3})$^{1/2}$. The solubility parameter for various solvents and the polymers was obtained from the literature [27]. The Flory interaction parameter obtained with the solvents matches closely with the reported values [28]. Fig. 5b shows the relation between the degradation rate constant for the SBR polymer and the Flory–Huggins interaction parameter (χ) calculated for different solvent-SBR system. It has been hypothesized that lower the value of χ, higher is the degradation rate [3,8]. This can be explained as the polymer is in uncoiled condition, it experiences a greater force as it pulled towards the collapsing bubble than a chain of same length of coiled polymer. Hence the polymers in good solvents, which have low χ value, degrades faster than in poor solvents [3]. It can be seen from Fig. 5b that a similar trend is observed for p-xylene, toluene and benzene solvents. Even though toluene and p-xylene have low χ value, the rate constant is lower than o-dichlorobenzene which has a high χ value. This indicates that the Flory Higgins interaction parameter only has a weak relationship with the degradation rate coefficient and other parameters such as vapor pressure may be more important in determining the degradation rate.

Studies were carried out to understand the effect of kinematic viscosity of the solution in the degradation of the polymer. This is because kinematic viscosity is a major factor in shearing flows and the ultrasonic degradation is a fluid mechanical process that can be influenced by the kinematic viscosity [8]. The kinematic viscosity of the solution with different solvents at 30 °C was determined experimentally. Fig. 5c shows the relation between the degradation rate and the kinematic viscosity of the solution. The variation of degradation rate follows a close linear relationship with kinematic viscosity of the solution for all the solvents except for benzene. These studies indicate that kinematic viscosity and vapor pressure of the solution have a significant influence on the degradation process.

5. Effect of ultrasound intensity

The effect of ultrasound intensity on the degradation rate was studied on SBR rubber at 30 °C in *o*-dichlorobenzene solvent by varying the intensity. Fig. 6a shows the variation of ln Y with sonication time for the ultrasonic degradation of SBR rubber for different ultrasonic intensities. The results depict an increase in the degradation process for an increase in the absorbed ultrasonic intensity. The relation between the change in degradation rate coefficient, k, and the ultrasound intensity is shown in Fig. 6b. A number of systems which shows similar rise in k on increasing the intensity have been described [1,4]. It was shown that [1], above the cavitation threshold, the maximum radius of the bubble is proportional to the square root of the intensity. Therefore an increase in intensity creates bigger bubbles which on collapse induce high shear forces [1]. Further, a large number of cavitation bubbles per unit volume are formed that increase the shear field increasing the rate of degradation.

6. Conclusions

In the present work, the degradation of commercially important copolymers SBR, NBR rubbers and SAN copolymer were investigated using ultrasound. A continuous distribution kinetics model was used to model the degradation process and the experimental data were fitted with the model. The data for the copolymers were compared with their respective homopolymers and the results shows that the homopolymer has a higher degradation rate coefficient than its copolymers. The variation in degradation rate coefficient, k, for the copolymers and their respective homopolymers were described in terms of the intermolecular forces induced by acrylonitrile and the weight ratio of monomer quantities. The effect of solution properties, such as vapor pressure of solvent, kinematic viscosity of the solution and Flory–Huggins interaction parameter, was studied and it was found that the vapor pressure and kinematic viscosity of the solution provides a trend in the degradation rate whereas no clear trend is observed with the interaction parameter. The effect of intensity on the degradation shows that the increase in the rate of degradation process is not linear with intensity. The study on the effect of solvent and ultrasound intensity on the degradation process for SBR rubber shows that by careful manipulation of conditions, the polymer degradation can be varied and controlled.

Acknowledgments

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