

Ultrasonic Degradation of Sol Rubber in Solution

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Synopsis

Sol rubber dissolved in three solvents—cyclohexane, petroleum ether (40–60°C. fraction), and toluene—was degraded by ultrasonic waves, the degradation kinetics being followed by measuring spectrophotometrically the consumption of the free radical scavenger α, α' -diphenyl- β -picryl hydrazyl. The kinetic data have been examined by the rate equations developed from two different approaches: one by Jellinek and the other by Ovenall. It has been observed that the number of bonds broken as a function of time can be fitted equally well by both equations in the initial stage, but as the time of degradation increases, especially when the number-average degree of polymerization attains a value less than $3P_e/2$, the rate can be described better by Jellinek's equation than that of Ovenall. The rate constants K and the final degree of polymerization for rubber are found to depend on the nature of the solvent.

Introduction

Natural rubber is very susceptible to degradation by such agents as heat, light, and air, and several investigators have studied the resulting degradation behavior. Ultrasonic degradation, which has some resemblance to the mechanical degradation, e.g., mastication, seems not to have been reported so far. In the present paper we deal with the results on the kinetics of the ultrasonic degradation of natural rubber (sol fraction) in three inert solvents. The progress of degradation has been followed by measuring the consumption of the free radical scavenger, α, α' -diphenyl- β -picryl hydrazyl (DPPH).

The exact form of the rate equation representing ultrasonic degradation kinetics has been the subject of some controversy.¹⁻⁶ It is generally agreed that the rate of degradation increases with degree of polymerization (DP) of the polymer, and there exists a limiting DP (P_e) below which a molecule does not degrade.

Assuming that all bonds in a degradable molecule are equally likely to break and that after infinite time of degradation the system would contain molecules with DP lying between unity and P_e , Jellinek et al.² proposed a rate equation which may be written in a simplified form as

$$\begin{aligned} dB_i/dt &= K(P_i - 1)n_i && \text{For } P_i > P_e \\ dB_i/dt &= 0 && \text{For } P_i \leq P_e \end{aligned} \quad (1)$$

where dB_i/dt is the rate of breakage of molecules of degree of polymerization P_i of which there are n_i such molecules present, and K is the rate

constant of reaction, independent of P_i and n_i but dependent on both the polymer-solvent system and on the experimental conditions.

On the other hand, Ovenall et al.,⁵ on the basis of the assumption that all bonds in a chain are equally likely to break except those within $P_e/2$ monomer units of each end and the molecules which do not degrade further have DP's in the range $(P_e/2)-P_e$, have given the rate equation as

$$\begin{aligned} dB_i/dt &= K(P_i - P_e)n_i && \text{For } P_i > P_e \\ dB_i/dt &= 0 && \text{For } P_i \leq P_e \end{aligned} \quad (2)$$

Our kinetic data have been examined in order to compare the fit to the two equations developed from the two different approaches.

Experimental

A Mullard ultrasonic generator (Type E 7562) fitted with a 1 Mcycle quartz transducer was used as an irradiation source. The transducer was fixed into a water bath, the temperature of the bath being controlled to within 5°C. during the experiment. Degradations were carried out at room temperature ($\sim 28^\circ\text{C}$). The horizontal ultrasonic beam was allowed to enter into the reaction cell through a thin aluminum window and after passing through the cell, was reflected upwards by means of a suitable reflector placed on the other side of the cell so that chance of standing wave formation was avoided. The 0.075% rubber solutions in 22-cc. portions were used in the cell.

Sol rubber was prepared from the rubber latex supplied by the Swastik Rubber Products Ltd., Poona, in the following way. To free it from proteins, the rubber latex was hydrolyzed with 2% caustic soda at 55°C. with constant stirring for 5 hr. and subsequently centrifuged, washed, and coagulated with dilute acetic acid. The resin was removed by refluxing with acetone (Soxhlet) for three days. This was then put into petroleum ether (40–60°C. fraction), and the sol fraction was fractionally precipitated by acetone at controlled temperature, dried *in vacuo*, and stored under nitrogen in the cold. Throughout the experiments care was taken to exclude light. The weight-average molecular weight of this sample as determined with Brice-Phoenix light scattering photometer was 2.887×10^6 . Since we used a well fractionated sample, we assumed that the weight-average and number-average molecular weights were nearly the same.

Solvents used were dried with metallic sodium. Degradations were carried out in an atmosphere of nitrogen. All experimental conditions, such as intensity of radiation and geometry of the systems, were maintained constant for all sets of experiments. The rate of degradation was determined by estimating spectrophotometrically the consumption of DPPH added to the rubber solution as a free radical scavenger. Two molecules of DPPH would be consumed for a single rupture of a polymer molecule and this assumption was followed for all calculations made. The concentration of DPPH used was nearly $5.0 \times 10^{-5} M$.

DPPH used for this purpose was prepared in this laboratory by the method of Poirier et al.⁷ and recrystallized from a benzene–ligroin solvent mixture (2:1 by volume). Lyons and Watson⁸ observed that 1:1 DPPH–benzene complex is formed on crystallization from a benzene–ligroin mixture,

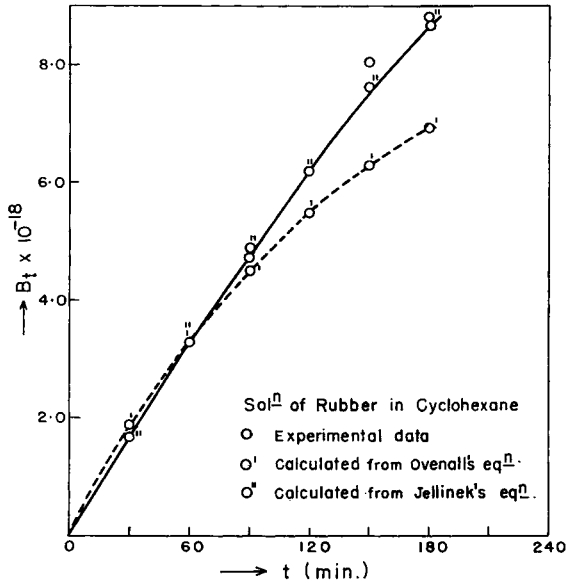


Figure 1.

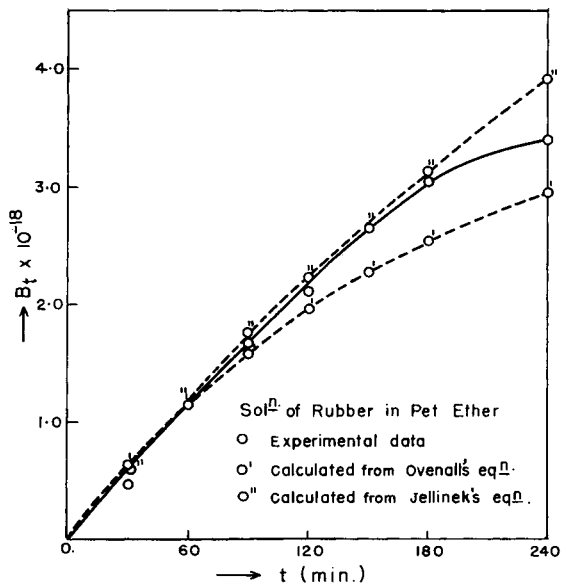


Figure 2.

and the correct value would be obtained when the apparent rates of radical production is multiplied by weight fraction (0.835) of DPPH. Corrections for this were made for all calculations.

All spectrophotometric measurements were carried out in a Hilger spectrophotometer (Model H 700.307) with 1-cm. glass cells; the slit width was kept at 0.1 mm. Absorption maxima for DPPH in solutions of cyclohexane, petroleum ether (40–60°C. fraction), and toluene were found at 5130, 5060, and 5190 Å., respectively. The DPPH concentrations of the irradiated solutions were determined by comparing the absorption-concentration curves made with standard solutions of DPPH.

Results and Discussion

The sol rubber dissolved in three different solvents, i.e., cyclohexane, petroleum ether (40–60°C. fraction) and toluene, was degraded; the results are shown by the solid curves in Figures 1–3. The degradation parameters P_e and K were so chosen as to give the best fit to these curves. The number B_t of bonds broken in a polymer after irradiation time t may be obtained by integrating the rate equations (1) and (2) along with their respective, postulated boundary conditions.^{5,6}

Thus from eq. (1) we have

$$B_t = n_0 \{ [(2P_n/P_e) - 1] - [(2P_n/P_e) - 1 + K(P_n - P_e)t] \exp \{-KP_e t\} \} \quad (3)$$

and from equation (2)

$$B_t = n_0 \{ (4P_n/3P_e - 1) - (P_n/3P_e - 0.5) \exp \{-3KP_e t/2\} - (P_n/P_e - 0.5) \exp \{-KP_e t/2\} \} \quad (4)$$

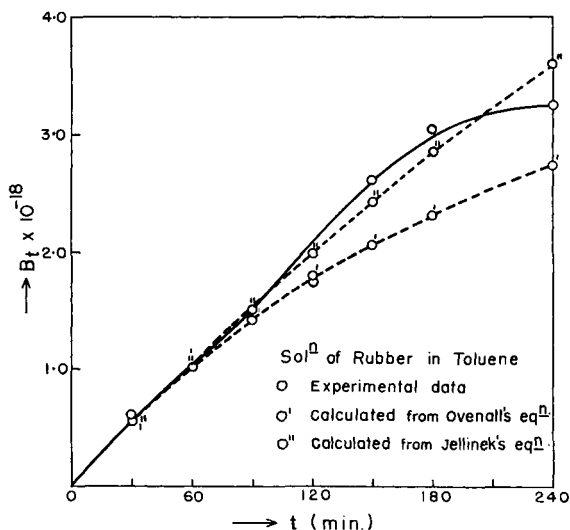


Figure 3.

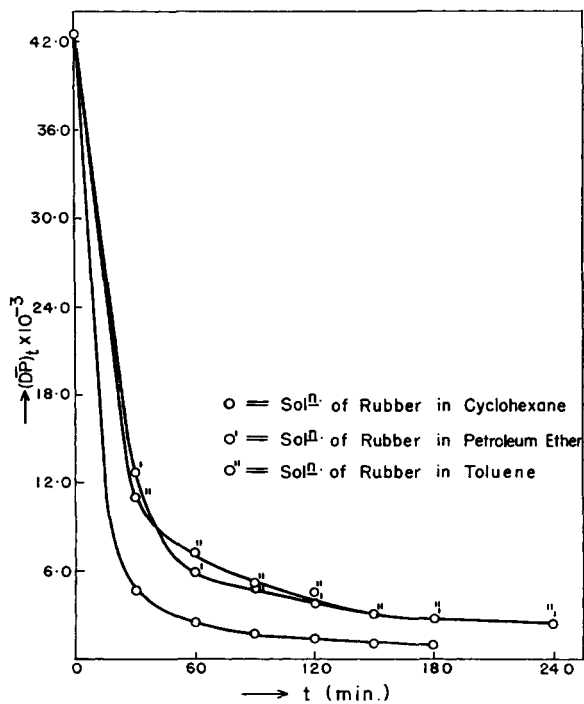


Figure 4.

These equations are valid for molecules with original number-average degree of polymerization P_n greater than $3P_e/2$, and n_0 molecules are initially present.

The values of B_t calculated according to eqs. (3) and (4) and plotted against t , are shown by the broken curves in Figures 1-3.

The progress of degradation during irradiation in terms of the number-average $(\overline{DP})_t$ has been calculated by the relationship

$$(\overline{DP})_t = (\overline{DP})_0 n_0 / (n_0 + B_t)$$

where $(\overline{DP})_0$ is the initial number-average degree of polymerization. It is seen in Figure 4 that the number-average degree of polymerization decreases sharply at the beginning, slows down as the degradation progresses, and ultimately tends to a constant value. This attainment of rather sharp molecular weight distribution in the last stage has been a noteworthy characteristic of degradation of a chain molecule by ultrasonic irradiation. The degree of polymerization $(\overline{DP})_\infty$ after infinite time of irradiation was determined by extrapolation of the $(\overline{DP})_t$ versus t curves to infinite time.

In Table I values of P_e , K , and other relevant data are listed. The $(\overline{DP})_\infty$ values and constants K for rubber are found to depend on the nature of the solvent. K is higher (~ 3 times) in cyclohexane than that

TABLE I
 Degradation Parameters

Solution	Initial number of molecules present/g. of sample taken $\times 10^{-18a}$	$(\overline{DP})_0$	P_e	$(\overline{DP})_\infty$	$K \times 10^6, \text{min.}^{-1}$	
					Jellinek's eq.	Ovenall's eq.
Rubber- cyclohexane	0.2069	42390	1017	950	6.5	8.1
Rubber- petroleum ether	0.2069	42390	2414	2000	2.25	2.8
Rubber- toluene	0.2069	42390	2520	2200	2.0	2.5
Polystyrene- benzene ^b		3650	1780	1330		5.3
Polystyrene- toluene ^b		3650	1740	1310		13.3

^a A 22-cc. portion of 0.075% rubber solution used.

^b Data from Ovenall et al.⁹

in petroleum ether and toluene, and the values obtained from eqs. (3) and (4) differ by about 25%. $(\overline{DP})_\infty$ is lowest (~ 950) in cyclohexane, being 2000 and 2200 for the other two systems, respectively. It may be mentioned that, in a similar study⁹ on polystyrene in benzene and toluene, K was found to be about 2.5 times higher in the latter solvent. $(\overline{DP})_\infty$ was nearly the same and seemed to lie in the range 1000–2000. Our values also appear to be in agreement with the above except in cyclohexane. However, lower values of $(\overline{DP})_\infty$, around 200–500, have been reported,¹⁰ and no definite conclusion regarding the lower limit can be made at this stage because it may be dependent on some unknown experimental parameters.

On comparing the curves in Figures 1–3, it will be observed that the number of bonds broken as function of time can be fitted equally well by eqs. (3) and (4) in the initial stage and therefore it is not possible to decide which rate equation is to be preferred. However, as the time of degradation increases, especially when the number-average degree of polymerization attains a value less than $3P_e/2$, the rate is better described by eq. (3) than by eq. (4), even though the deviations from observed values are not large.

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Résumé

On a dégradé le caoutchouc soluble dissous dans trois solvants: le cyclohexane, l'éther de pétrole (fraction 40–60°C) et le toluène, par des ondes ultrasoniques et les cinétiques de dégradation ont été suivies en mesurant d'une façon spectrophotométrique la consommation du capteur de radicaux libres, le α, α' -diphényl- β -picryl-hydrazyl. On a examiné les données cinétiques pour les deux équations de vitesses développées à partir de deux différentes approximations, l'une par Jellinek et l'autre par Ovenall. On a observé que le nombre de liaisons cassées en fonction du temps peut très bien être prévu par les deux équations à l'état initial; quand le temps de dégradation augmente, surtout quand le D.P. moyen en nombre atteint une valeur en-dessous de $3 P_e/2$, la vitesse peut être mieux décrite par l'équation de Jellinek que par celle de Ovenall. On a trouvé que les constantes de vitesse K et la valeur finale du D.P. du caoutchouc dépendent de la nature du solvant.

Zusammenfassung

In drei Lösungsmitteln—Cyklohexan, Petroläther (40–60°C Fraktion) und Toluol—gelöster Solkautschuk wurde durch Ultraschall abgebaut und die Abbaukinetik durch spektrophotometrische Messung des Verbrauchs des Radikalabfängers α, α' -Diphenyl- β -Picrylhydrazyl verfolgt. Die kinetischen Ergebnisse wurden anhand der beiden auf verschiedener Grundlage einerseits von Jellinek und andererseits von Ovenall entwickelten Geschwindigkeitsgleichungen überprüft. Die Zahl der gelösten Bindungen als Funktion der Zeit genügt in der Anfangsphase beiden Gleichungen gleich gut; mit zunehmender Abbaudauer, insbesondere wenn das Zahlenmittel von D.P. einen Wert geringer als $3 P_e/2$ erreicht, kann die Geschwindigkeit besser durch die Gleichung von Jellinek als die von Ovenall beschrieben werden. Die Geschwindigkeitskonstante K und der Endwert von D.P. für Kautschuk sind von der Natur des Lösungsmittels abhängig.

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