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Investigation on the styrene-butadiene rubber cleavage with periodic acid under the influence of ultrasonic radiation

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SUMMARY

The cleavage of styrene-butadiene rubber (SBR) with periodic acid (H_5IO_6) and simultaneous injection of ultrasonic radiation has been performed. Two frequencies, 25 and 40 kHz, respectively, have been used. The results demonstrate clearly that 40 kHz ultrasound radiation accelerates significantly the cleavage reaction. The "Pearl String Model" theory had been used to elucidate this process.

INTRODUCTION

Oxidative degradation of elastomers such as SBR, NBR and natural rubber (Hevea Brasiliensis) with periodic acid (H_5IO_6) has been studied in order to obtain telechelic polymers with carbonyl end groups[1,2]. The molecular weight of the products obtained is a function of the reaction time but it reaches a limit after a certain time[2].

Studies of ultrasonic radiation show that they can be used as a tool for degradation of polymers[3,4]. The rate of polymer degradation under the influence of ultrasonic radiation has been associated to cavitation effects and they are related to the frequency and intensit of the radiaition[3].

This study focuses on the acceleration of the cleavage reaction of SBR with periodic acid under the influence of ultrasonic radiation. Two ultrasonic frequencies, 25 and 40 kHz, have been used. In order to rationalize the acceleration of the reaction, the pearl string model developed by Schoon and Riebber was applied[5] to explain the ultrasonic degradation of polymers and the limiting molecular weight obtained. According to this model the polymer molecules are built up like a necklace of so-called tertiary structural units resembling a string of pears and the chain is broken between its spherical units[5,6].

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EXPERIMENTAL

SBR-1502 (Petroflex SA) was purified by successive dissolution followed by precipitation in methanol. The degradation was performed in an ultrasonic bath with constant intensity and two different frequencies using 3% (w/v) SBR in toluene. A H_5IO_6 solution (H_5IO_6:SBR = 1:2 w/w) in ethanol and toluene (2/10, v/v) was added slowly to the rubber solution under magnetic stirring. The temperature was maintained at 34oC by a thermostatic bath. After determined intervals, samples of about 1.5ml were taken out from the reaction vessel. The samples were treated with water in order to separate the periodic acid and the cleaved SBR was precipitated in methanol.

The molecular weight of polymer was measured by gel permeation chromatography (GPC) using a CG-480C chromatograph equipped with four Waters Millipore ultra-styragel columns (105, 104, 103 and 500 oA) and a refractive index detector CG-46. The calibration curve was obtained by using a series of polystyrene standards of narrow distribution.

RESULTS AND DISCUSSION

The cleavage of elastomer by H_5IO_6 has been described in previous works[1,2]. The infrared spectrum of the cleavaged SBR shows a signal at 1753 cm^{-1} due to the carbonyl end group formed by the cleavage reaction.

In order to verify the effect of the ultrasonic radiation on the degradation reaction four different experiments have been done. First, ultrasonic degradation was used without periodic acid. In the second and third experiments ultrasonic waves of 40 and 25 kHz of frequency, respectively, and H_5IO_6 were used. Last, only H_5IO_6 was used as degradation agent. The effect of the degradation reactions on the molecular weight is shown in the Figures 1 and 2.

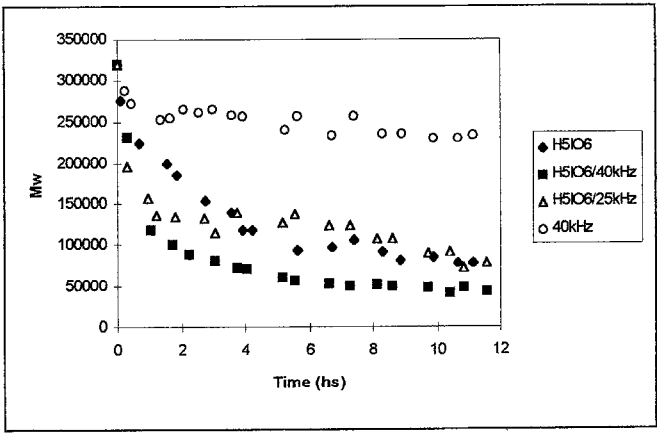

Figure 1 - Effect of reaction time on $\overline{M}w$

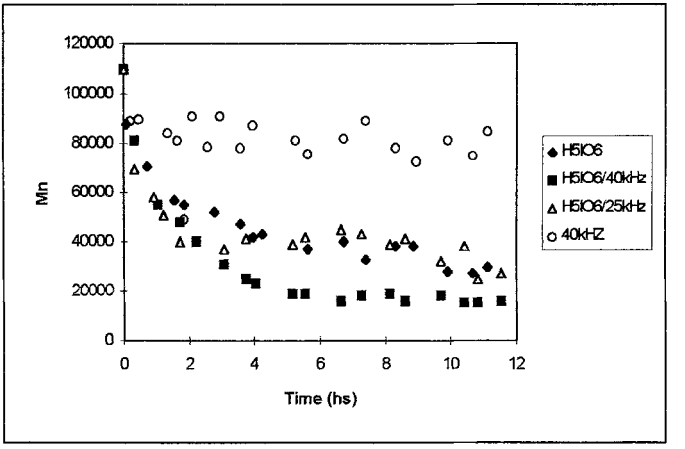

Figure 2 - Effect of reaction time on $\overline{M}n$

One can observe that the periodic acid is much more efficient than ultrasonic radiaton alone for degradation. Furthermore, the comparison between two differen ultrasonic frequencies, 40 and 25kHz, in the polymer solution with periodic acid demonstrated that degradation with 40kHz is more efficient than with 25 kHz. In the first case, acceleration and a decrease in the limiting MW is observed. The 25 kHz ultrasonic radiation accelerates the reaction but does not decrease the limiting molecular weight.

A more fundamental treatment of the results offers some insight into the mechanism of ultrasonic cleavage acceleration and the structural characteristics of the polymer. According to the pearl string model[5,6] the average molecular weight Mi of the polymer after ultrasonic radiation during "i" time intervals would be

$$\overline{M}_i = \frac{\overline{M}_o \cdot \overline{M}_\alpha}{\overline{M}_o - (\overline{M}_o - \overline{M}_\alpha)(1 - \pi)^i} \qquad (1)$$

where M_o is the initial molecular weight, M_α is the lowest or limiting molecular weight, or in other words, the "pearl weight", and π is the degradation constant and can be described as the number of molecules in "i" time divided by the number of molecules in (i-1) time. The π can be calculated by the rearrangement of equation (1)

$$\pi = 1 - \left[\frac{\overline{M}_o - (\overline{M}_i - \overline{M}_\alpha)}{\overline{M} \cdot (\overline{M}_o - \overline{M}_\alpha)} \right]^{1/i} \qquad (2)$$

According to this model a change in the π values during the degradation process is considered to be fragmentary, that is the polymer chain is cleaved between its structural units in several steps. The system is considered to be stepless if π is constant and the pearlstring molecule is broken within a single step into all its units[5].

The Figures 3 and 4 show the variation of π with the reaction time. The degradation process seems to be stepless for H_5IO_6/40kHz ultrasonic radiation system and for all other systems, the degradation process is fragmentary. The small increase in the values of π after 8 hours of reaction is possibly due to recombination of chains.

Table 1: Limiting molecular weights obtained after degradation reaction using H_5IO_6 and/or ultrasonic radiation*.

Limiting MW (M_α)	Degradation system			
	H_5IO_6	H_5IO_6/40kHz	H_5IO_6/25kHz	40kHz
$\overline{M}w_\alpha$	80 000	40 000	80 000	230 000
$\overline{M}n_a$	30 000	15 000	30 000	80 000

* The values were taken from the plot (Figures 1 and 2, respectively)

Table 1 shows the limiting molecular weights obtained from the various systems. The limiting MW is smaller for H_5IO_6/40kHz ultrasonic radiation system than for the others systems. The pearl size is formed by the entanglement of polymer chains and ultrasonic radiation causes reorganization of the conformational state of the chains decreasing the size of the pearl. As a result, smaller limiting MW are obtained.

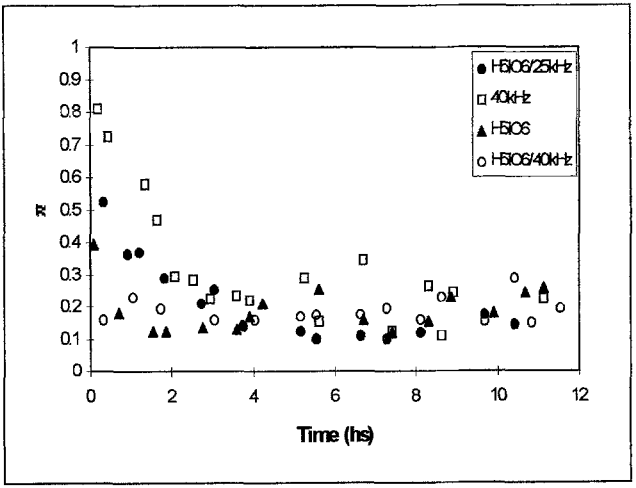

Figure 3: The behaviour of π for $\overline{M}w$ with reaction time

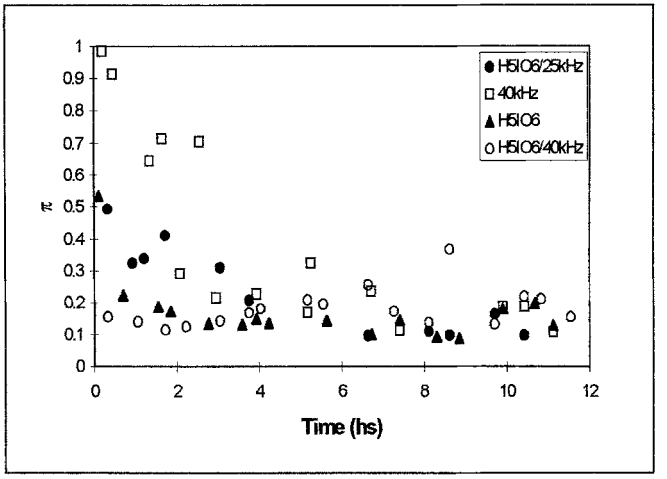

Figure 4: The behaviour of π for Mn with reaction time

Considering the π values for H_5IO_6/40kHz ultrasonic radiation system as constant, the equation (1) can be rewritten

$$\ln (Mi - M\alpha)/M\alpha Mi = \ln (Mo - M\alpha)/MoM\alpha + i \ln (1 - \pi) \qquad (3)$$

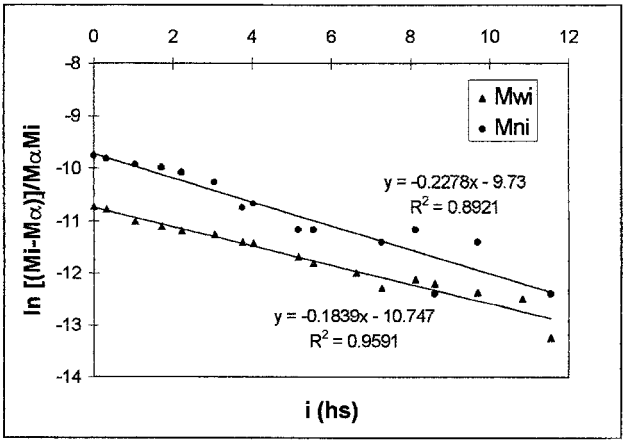

Figure 5: Plot for equation (3).

Figure 5 illustrates graphically equation 3 for this system. The values of π may be calculated from the slope of the lines. In table 2 the values of π obtained as the average of all values of π for the Mi are compared with the ones obtained by equation 3.

Both procedures result in a satisfatory agreement of the π. Small differences between the two methods are probably due to recombination reactions at large reaction times producing a dispersion of the values.

Table 2: Degradation constants for the H_5IO_6/40kHz ultrasonic radiation system

	$\pi^{(a)}$	$\pi^{(b)}$
$\overline{M}w$	0.1680	0.1796
$\overline{M}n$	0.2037	0.1805

[a] calculated from equation (3)

[b] average of values of π for all the Mi

CONCLUSION

The degradation reaction of the SBR by periodic acid was accelerated under the influence of 25 and 40 kHz ultrasonic radiation frequencies. The 40kHz/H_5IO_6 system is characterized by a lower limiting molecular weight compared to the other systems. The pearl string model is able to explain the mechanism of the degradation and the limiting molecular weight obtained after a certain reaction time. The cleavage of SBR in the H_5IO_6/40kHz system behaves like a pearl string degradation process in one step, however the degradation using only H_5IO_6 or H_5IO_6 in combination with 25 kHz radiation is fragmentary.

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