

Effect of Resin Components on the Degradation of Guayule Rubber

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Synopsis

All natural rubbers are likely to contain some long chain fatty acids or their esters. The individual effect of the four C₁₈ fatty acids (stearic, oleic, linoleic, and linolenic acid) present in the guayule resin on the degradation of guayule rubber has been investigated concurrently by stress-relaxation of radiation cured rubber networks and by gel permeation chromatography studies on the raw rubber in the temperature zone 70–125°C. C₁₈ unsaturated fatty acids enhance the degradation of rubber several fold. The rate of degradation follows the order: rubber < rubber + stearic acid < rubber + oleic acid < rubber + linoleic acid < rubber + linolenic acid. The thermal degradation is slower than the thermooxidative. The rate of degradation monotonically increased with the number of conjugated double bonds and is first order with respect to acid concentration. The activation energy for the chain scission for both thermal and thermooxidative degradation has been found to be 95 ± 10 kJ/mol. The mechanism of degradation of guayule rubber in the presence of fatty acids is discussed.

INTRODUCTION

Guayule rubber (GR) containing a high concentration of its natural plant resin is known to have poor oxidative stability. These resins are mainly mixtures of α -pinene, β -pinene, cadinene, limonene, sesquiterpene alcohol, partheniol, and fatty acids in different proportions. Recent studies^{1,2} show that the effects of guayule resin on the degradation of hevea natural rubber (HR) are due to the presence of unsaturated fatty acids. The acids oxidize rapidly to form hydroperoxide and function as an initiator in the degradation of the rubber. The relative percentages of fatty acids reported in guayule resin are: palmitic acid, 6.9%; stearic acid, 5.6%; oleic acid, 5.3%; linoleic acid, 65.1%; linolenic acid, 17.1%. Though GR and HR are natural rubber, that is, both are identical in the backbone polymeric structure (of *cis*-1,4-polyisoprene), the gel content and amount and type of non-rubber ingredients in HR are different from those of GR. How all of these non-rubber ingredients protect HR in storage is not clearly understood. Moreover, there is very little systematic investigation of the effect of the resins in the long-term storage of bulk GR. It is important to know these to predict the storage stability of GR. Hence a systematic study has been undertaken to examine the effect of individual components of the fatty acid resins on the degradation behavior of bulk GR.

Polymers can degrade under many controlled environmental conditions, such as thermal, thermooxidative, and photooxidative. Degradation of HR has been reported by many authors.³⁻⁷ The initiation of oxidation by hy-

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droperoxide formation on the polymer chain has been reported to be a relatively rapid reaction for HR. Most of these studies are based on (1) heat or weight loss of volatile from the bulk polymer, (2) viscosity changes of HR solutions, or (3) extensive chemical studies of types and amount of volatile products during oxidation. It has been also reported³ that the thermal oxidation of rubber is different from the purely thermal (nonoxidative) degradation in the sense that the former yields a few low molecular weight compounds at each scission whereas in the latter many small molecules are obtained. Tobolsky and Mercurio⁸ studied the oxidative degradation of both gum uncrosslinked HR and HR networks. They determined the average number of chain scissions from M_n (number average molecular weight) measurement of the gum HR and also from the stress-relaxation measurements on the HR networks, assuming random scissions of the polymer chain. They concluded that scission occurs in the termination step of the free radical reaction and suggested a possible chemical mechanism for the oxidative scission of HR in the presence and absence of free radical initiators. Shelton and co-workers⁹ advanced the knowledge of the chemical mechanism of degradation of HR in recent years.

In this work, both the thermal and the oxidative degradation of unvulcanized bulk GR and GR networks have been studied with and without fatty acids containing 18 carbon atoms. The studies focus on early degradation manifested as chain scission. The degradation was followed by measuring the decrease in molecular weight of the uncrosslinked rubber using gel permeation chromatography (GPC) technique. The network degradation was followed by stress-relaxation measurements. Four fatty acids (stearic, oleic, linoleic, and linolenic), differing in the number of double bonds, were used. The structures are given in Table I. This study was carried out in the temperature range 70–125°C. Degradation studies at higher temperature are in progress.

EXPERIMENTAL

GR Network

Preparation of the Network. Guayule rubber ($M_n \approx 2.5 \times 10^6$, MWD = 1.4) was obtained from the Firestone Tire and Rubber Co. The fatty acids used were of technical grade.

The guayule rubber was exhaustively extracted with acetone to make it free of any residual resins and antioxidant. It was dried in vacuum. The

TABLE I
Frequency Factor of Rubber Degradation

Sample number and structure	Frequency factor A (min ⁻¹)
Rubber $\text{-(CH}_2\text{-C(CH}_3\text{)=CH-CH}_2\text{)}_n\text{-}$	6.17×10^9
Rubber + stearic acid $[\text{CH}_3(\text{CH}_2)_{16}\text{COOH}]$	1.00×10^{11}
Rubber + oleic acid $[\text{CH}_3(\text{CH}_2)_7\text{CH=CH(CH}_2)_7\text{COOH}]$	1.58×10^{11}
Rubber + linoleic acid $[\text{CH}_3(\text{CH}_2)_4\text{CH=CHCH}_2\text{CH=CH(CH}_2)_7\text{COOH}]$	3.39×10^{11}
Rubber + linolenic acid $[\text{CH}_3(\text{CH}_2)\text{CH=CHCH}_2\text{CH=CHCH}_2\text{CH=CH(CH}_2)_7\text{COOH}]$	6.76×10^{11}

rubber was then cold-milled with 5 phr of resin-acid for 25 passes. A thin sheet of ≈ 0.04 cm thickness was made at low temperature ($\approx 70^\circ\text{C}$) for 3 min. These sheets were then crosslinked by γ -radiation from a source at room temperature.

Stress-Relaxation Measurement. Continuous stress-relaxation was measured at three temperatures, 70°C , 90°C , and 110°C ($\pm 2^\circ\text{C}$ control near the sample) in both air and nitrogen in a small oven (Blue M). The amount of extension (50%) was determined by measuring the distances between two ink marks drawn on the tensile test piece initially. By means of a Statham force transducer, to which the upper clamp was attached, changes in tensile force at constant extension were followed with time.

Swelling Measurement. Weighed samples of rubber were swollen in benzene for 48 h at 25°C . The surface was quickly dried and the samples were then reweighed. The samples were kept in vacuum to constant deswelling weight. Volume fraction of rubber was calculated using the procedure of Ref. 10.

Uncrosslinked GR

Isolation of Rubber. Guayule rubber was obtained from whole shrub by removal of the resin with acetone in a Soxhlet extractor for 12 h in order to insure completely linear polymer. The deresinated plant was stirred with cold benzene in a beaker to extract the rubber. The solution was then centrifuged, filtered to remove all the impurities and dirt, and the rubber was precipitated by adding acetone.

Sample Preparation. The raw rubber, free of antioxidant and resin, was dissolved in benzene to make 2.5% solution. The fatty acids, obtained from Aldrich Chemical, Wisconsin, were of analytical grade and were used as supplied. One percent solution of fatty acid in benzene was prepared. Then an appropriate amount of fatty acid solution was added to the rubber solution and mixed thoroughly. A film was made by evaporating off the solvent and drying the rubber in vacuum. These films of ≈ 0.01 cm were used for the GPC study. All samples were degraded in an oven (Thelco Precision Model 20) in a constant flow of nitrogen or air with temperature control of $\pm 2^\circ\text{C}$.

Gel Study. The "macrogel" in the thermally degraded samples was determined gravimetrically by taking the difference in filter weight before and after passing through a $5\ \mu\text{m}$ Millipore filter.

GPC Study. The GPC instrument in this work (Waters Associates 150 ALC) had four columns packed with styragel, with porosities of 1×10^6 , 1×10^5 , 1×10^4 , and 1×10^3 Å. THF was the solvent with a flow rate of 1 mL/min at 30°C . A differential refractometer was the concentration detector. An average pressure of 60 bar was maintained.

All solutions of samples of GR were prepared with THF at a concentration of 0.125% and were filtered first through $5\ \mu\text{m}$ Millipore filter and then a $0.45\ \mu\text{m}$ filter (Metricel membrane filter). The molecular weights were obtained from a calibration curve of molecular weight against peak elution volume using standard polyisoprene. The calibration curve is reported in Figure 1. From this curve the molecular weight of the GR is found to be 2.5×10^6 . This molecular weight is used as measured because (1) the con-

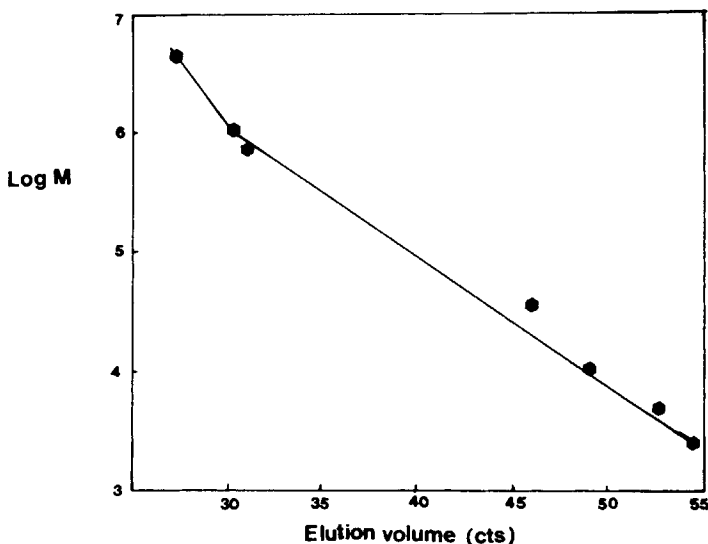


Fig. 1. GPC calibration curve for *cis*-1,4-polyisoprene. Plot of $\log M$ vs. elution volume.

centration-dependent term and shear degradation are partially compensating¹¹ and (2) the trend of molecular weights rather than absolute molecular weights is important in this study.

RESULTS AND DISCUSSION

Stress-Relaxation of Rubber Networks

Random Cleavage along the Network Chains vs. Cleavage at Crosslinks

It is well known from the theory of rubber elasticity that the tensile stress at zero time, $f(0)$, to deform a rubber to an extension ratio α will be given by

$$f(0) = n(0)RT(\alpha - \alpha^{-2}) = N(0)kT(\alpha - \alpha^{-2}) \quad (1)$$

where $n(0)$ and $N(0)$ are, respectively, the moles and the initial number of network chains per cubic centimeter of rubber and R , k and T are the gas constant, Boltzmann constant, and absolute temperature, respectively. Now at a time t , if the number of cleaved network chains per cc is $q(t)$ and the number of network chains per cc supporting the stress is $n(t)$, then

$$f(t) = n(t)RT(\alpha - \alpha^{-2}) = N(t)kT(\alpha - \alpha^{-2}) \quad (2)$$

or

$$\frac{f(t)}{f(0)} = \frac{n(t)}{n(0)} = \frac{N(t)}{N(0)} \quad (3)$$

Tobolsky⁸ first pointed out that when the scission is along the main chain and random, eq. (3) could be written as

$$\frac{f(t)}{f(0)} = \frac{N(t)}{N(0)} = \exp\left[\frac{-q(t)}{N(0)}\right] \quad (4)$$

or

$$q(t) = -N(0) \ln \frac{f(t)}{f(0)} \quad (5)$$

which is an expression for estimating $q(t)$ from the stress decay.

If the chain cleavage occurs randomly throughout the rubber network, $q(t)$ should be always the same, for a series of identical rubbers (having the same structure) crosslinked to different degrees. But if the cleavage occurs at or adjacent to the network junctions, $q(t)$ should be proportional to $N(0)$.

The stress-relaxation of guayule rubber and guayule rubber samples containing linolenic acid, having different initial chain densities, and prepared by varying the irradiation dose was measured in air at different temperatures. The rate of stress-relaxation increases with decrease in network chain density. Now the number of main chain scissions $q(t)$ is calculated using eq. (5) and has been plotted against time in Figure 2. It is observed that $q(t)$ is independent of $N(0)$, for both rubber and rubber containing acid. A similar observation has been made using radiation-cured hevea natural rubber which shows random cleavage of the links of the network chains as opposed to cleavage at the crosslinks.⁸ These results further show that, for natural rubber crosslinked to yield carbon-carbon crosslinks, scission occurs with practically no crosslinking reaction.

Temperature Dependence of Chemical Stress-Relaxation and Chain Cuts

Chemical stress-relaxation is a powerful physical method for measuring chemical bond cleavage in rubber networks. Stress relaxation data in air at 70°C of rubbers containing 5 phr of either stearic acid, or oleic acid, or linoleic acid or linolenic acid, and having comparable crosslink densities are shown in Figure 3. At longer times, the rate of degradation of rubber

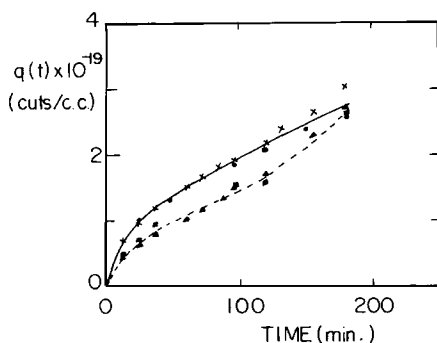


Fig. 2. Stress relaxation of rubbers containing different initial chain densities: (A) pure rubber at 90°C for: (X) $1.75 \times 10^{19}/\text{cc}$; (●) $3.21 \times 10^{19}/\text{cc}$; (B) rubber containing linolenic acid at 70°C (▲) $2.52 \times 10^{19}/\text{cc}$; (■) $1.56 \times 10^{19}/\text{cc}$.

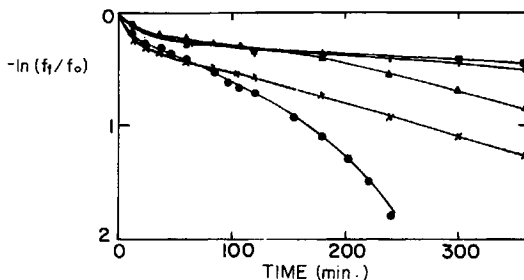


Fig. 3. Stress-relaxation of rubbers of similar crosslink density at 70°C: (■) rubber; (+) rubber + stearic acid; (▲) rubber + oleic acid; (X) rubber + linoleic acid; (●) rubber + linolenic acid.

containing linolenic acid seems to be the highest in the series, followed by linoleic acid and oleic acid. Similar observations have been made at higher temperatures. At higher temperatures the rate of relaxation increases, as shown in Figure 4. A few samples were examined to compare the relaxation behavior of GR in nitrogen and in air. In the former, the stress decay was slower, similar to the observations made before.¹² As shown in Figure 4, the degree of deviation from linear behavior, when $\ln[(f(t)/f(0))]$ is plotted against time is greater for relaxation at higher temperatures. Such deviations from a Maxwell decay for rubber vulcanizates has been shown for peroxide-cured gutta-percha (*trans*-1,4-polyisoprene).¹² It has also been observed that the stress-decay curves for purified samples show greater deviation from Maxwellian decay than those for unpurified ones.¹²

The chemical stress-relaxation depends very much on the network chain density $n(0)$. Hence the total number of cuts per cc that have occurred up to time t , designated by $q(t)$, has been calculated [eq. (5)] for all samples at three different temperatures. $q(t)$, being independent of $N(0)$ as shown in Figure 2, is a better parameter to compare different vulcanizates containing acids. All these measurements have been made with small initial crosslink density. It has been pointed out¹² that, at very large values of $n(0)$, the $q(t)$ values are very high presumably due to entanglement. It has been shown in Figures 5-7 that at all temperatures (70°-110°C), the number of cuts increases monotonically with time and increases with temperature also for all samples. All these curves can be described by an equation

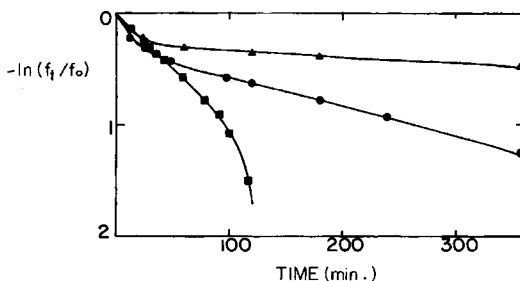


Fig. 4. Stress-relaxation of pure rubber at different temperatures: (▲) 70°C; (●) 90°C; (■) 110°C.

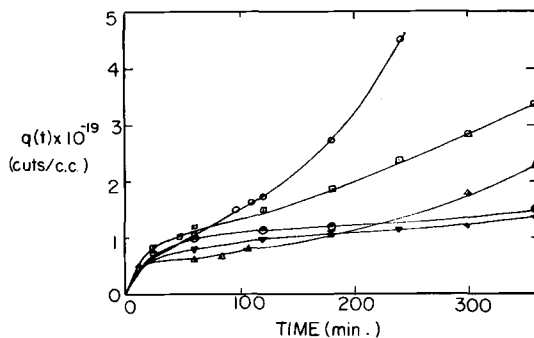


Fig. 5. Plot of $q(t)$ vs. time at 70°C in air: (●) pure rubber; (▼) stearic acid + rubber; (△) oleic acid + rubber; (□) linoleic acid + rubber; (○) linolenic acid + rubber.

$$q(t) = at + b \exp(ct)$$

where a , b , and c are constants. The exponential increase in the latter stage shows that the degradation process is autocatalytic, both for rubbers with and without acids. This effect was observed earlier for dicumyl peroxide-cured natural rubber (HR).¹² It is interesting to compare the curves obtained at different temperatures and longer times with acids. The behavior of pure rubber is different from the rest of the samples. The amount of degradation follows the order: rubber < rubber + stearic acid < rubber + oleic acid < rubber + linoleic acid < rubber + linolenic acid. Stearic acid shows some degrading effect on rubber presumably due to some very low level impurities in the technical grade acid. The trend in degradation corresponds to the number of double bonds present in the system. The mechanism for the involvement of the double bonds in the degradation of rubber is explained in the next section.

These results show that oxidative scission of pure GR takes place much

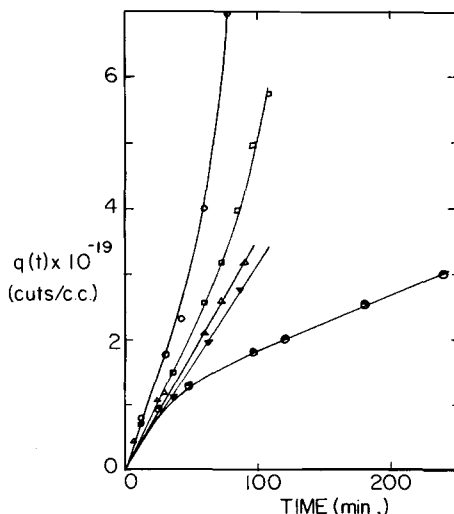


Fig. 6. Plot of $q(t)$ vs. time at 90°C in air: (●) pure rubber; (▼) stearic acid + rubber; (△) oleic acid + rubber; (□) linoleic acid + rubber; (○) linolenic acid + rubber.

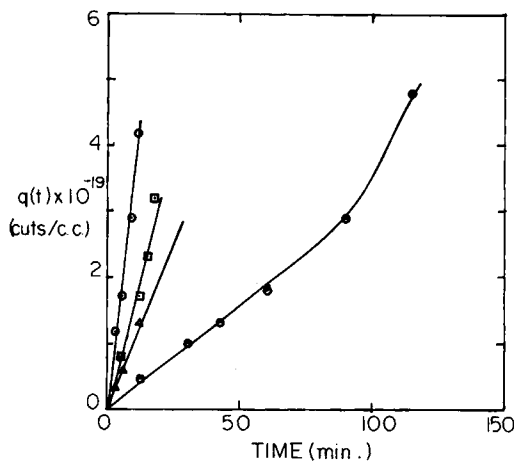


Fig. 7. Plot of $q(t)$ vs. time at 110°C in air: (●) pure rubber; (△) oleic acid + rubber; (□) linoleic acid + rubber; (○) linolenic acid + rubber.

faster than HR having the same crosslinking system. It is well known¹² that the oxidative degradation of a well-extracted sample of synthetic *cis*-1,4-polyisoprene cured by dicumyl peroxide (DCP) is much faster than that of HR-DCP. It has also been noted that the stress decay of synthetic *cis*-1,4-polyisoprene-DCP has an autocatalytic behavior while that of HR-DCP shows inhibited oxidation. This points out the inhibitory effect of the non-rubber ingredients in HR which cannot be extracted by organic solvents.

Further experiments were carried out to measure the swellability of the network after degradation. As shown in Figure 8, $(V_r' - V_r)/V_r'$, which is a measure of the amount of degradation, has been plotted against time where V_r' and V_r are volume fractions of rubber before and after degradation of rubber at 90°C . Though the relative order of resin components causing degradation is the same, the differences in the amount of degradation are not the same. Rubber-containing linoleic acid and linolenic acid show much higher rate of degradation than the pure rubber. At higher or lower temperatures similar behavior is observed, although the data are not reported here. It should be pointed out that part of the rubber forms gel or branched structures during degradation which are reflected in the equilibrium swelling measurements. But these structures do not support stress in the stress-

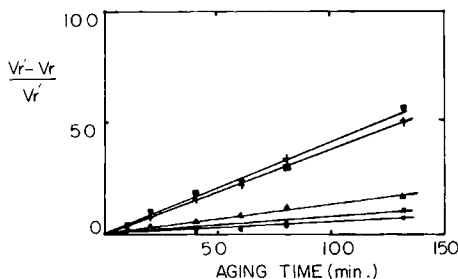


Fig. 8. Percent degradation in terms of volume fraction of rubber vs. time of aging: (●) rubber; (X) rubber + stearic acid; (▲) rubber + oleic acid; (+) rubber + linoleic acid; (■) rubber + linolenic acid.

relaxation measurement. Hence the swelling measurement only gives a rough estimate of the degradation of rubber.

Activation Energy and Frequency Factor

The temperature dependence of the rate of stress-relaxation of rubbers has been discussed above. The slopes of the curves plotting $-\ln[f(t)/f(0)]$ against time are calculated following a method of Tamura and Murakami.¹³ A representative plot has been given in Figure 9. The slopes of these curves are the rate constants for main chain scission, k . The calculated rate constants for all samples are then plotted against $1/T$ in Figure 10. Assuming the Arrhenius equation

$$k = A \exp(-E/RT) \quad (6)$$

where A is the frequency factor and R and T are the gas constants and temperature, respectively, one can calculate E , the apparent activation energy for the main chain scission. These values are 90 ± 4 kJ/mol for all of the samples. This value indicates that, though the acids are causing degradation at a faster rate, the activation energy for the rubber degradation step is the same. This value of the activation energy is quite consistent with the value reported in the literature from other measurements and on HR.¹²

To investigate the faster and more extensive degradation of rubber by acids containing double bonds, the frequency factor A was analyzed. The frequency factor (A) is reported in Table I. The frequency factor in simple systems is a relative measure of the frequency of reactive collisions in a given system. The value of A for rubber containing linolenic acid is about 100 times higher than that of pure rubber. Since the rate determining step of the overall oxidation mechanism is the initiation step by the radical from the hydroperoxide decomposition, it can be inferred that an increasing number of double bonds in the acid molecule increases the frequency of hydroperoxide decomposition in the chain scission mechanism and hence causes higher degradation rates.

GPC Study of Uncrosslinked GR

In the preceding part, the stress-relaxation of rubber to show network degradation in the presence of the fatty acids was discussed. Further in-

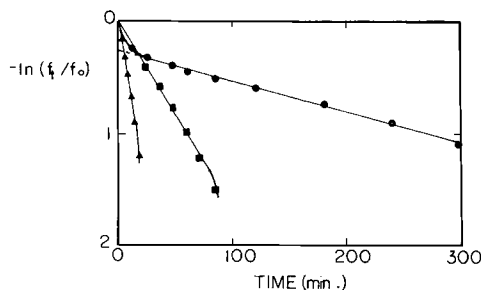


Fig. 9. Stress-relaxation of rubber containing linoleic acid at different temperatures; (●) 70°C; (■) 90°C; (▲) 110°C.

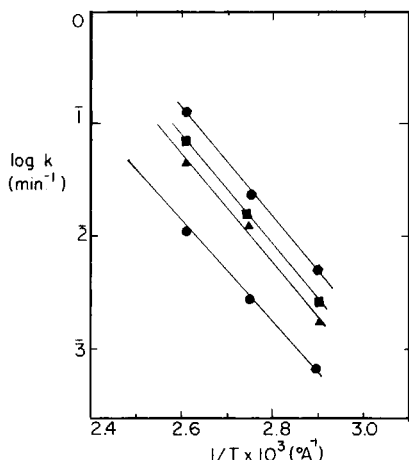


Fig. 10. Plot of $\log k$ vs. $1/T$ according to eq. (6): (●) rubber; (▲) rubber + oleic acid; (■) rubber + linoleic acid; (●) rubber + linolenic acid.

vestigations were carried out using uncrosslinked rubber and the GPC technique to suggest a mechanism for the degradative effect of the fatty acids on rubber.

Initial experiments were performed up to a high degradation temperature (300°C). But at these high temperatures rubber becomes completely gelled and hence prohibits GPC measurements. Therefore this study involves degradation at lower temperatures (75–125°C). It is also very important to note that the rubber begins to degrade much earlier than volatile fragments appear. Hence the thermogravimetric analysis technique (weight loss) could not be applied in this temperature region.

Representative GPC traces showing the effect of degradation of rubber on the molecular weight and weight distribution both in nitrogen and in air are given in Figures 11 and 12. As the degradation proceeds, the peak

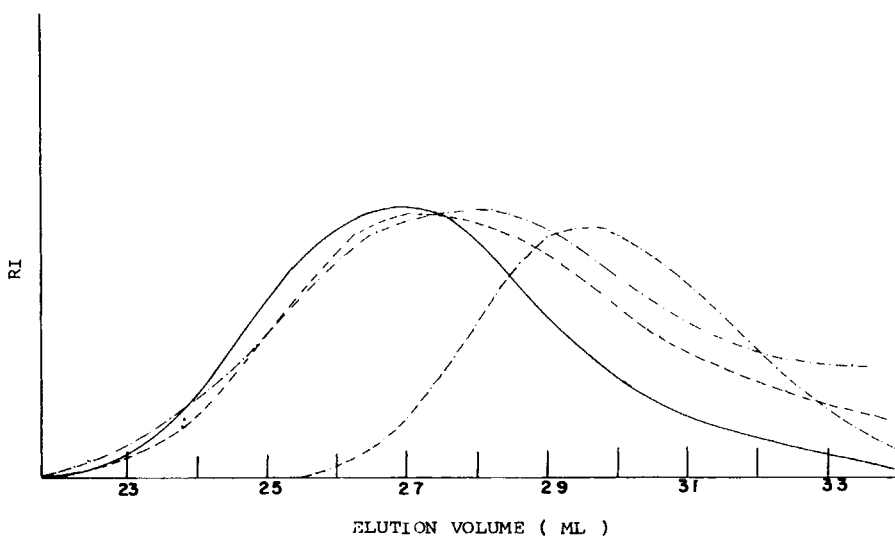


Fig. 11. GPC traces for degradation of rubber at 110°C in nitrogen atmosphere: (—) control; (---) 10 min; (-·-) 20 min; (····) 30 min.

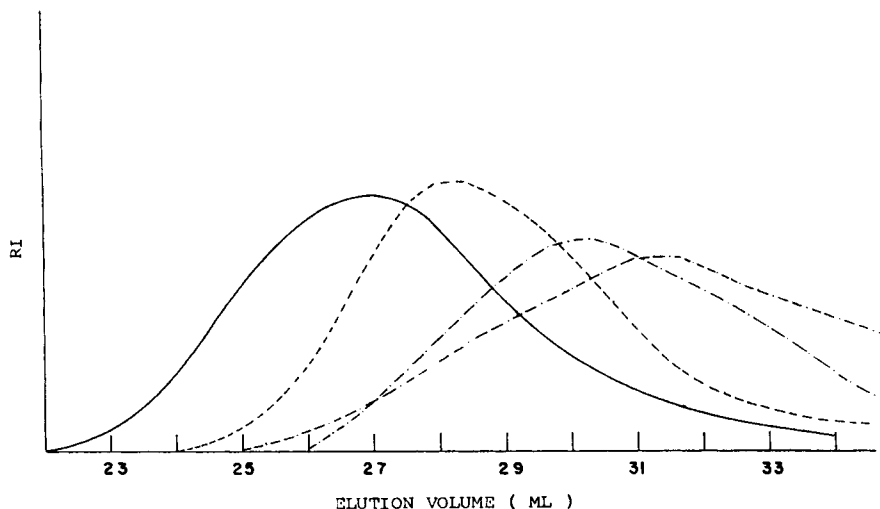


Fig. 12. GPC traces for degradation of rubber at 110°C in air: (—) control; (---) 10 min; (- · - ·) 20 min; (· · · ·) 30 min.

count shifts towards higher elution volumes and hence lower molecular weight. The molecular weight distribution also broadens with degradation. It must be mentioned here that, even in this temperature region (75–125°C), the rubber forms amounts of gel ranging from 3% to 16% depending on the degradation temperature. At 110°C the amount of gel was 3% for the pure rubber and the gel increased to 5%, 8%, and 10% for rubber containing 5 phr of oleic, linoleic, and linolenic acid, respectively. Hence the GPC investigation was restricted to the study of the separated sol.

A thin film of rubber is degraded first. The portion of degraded sample that goes into the solution is termed as sol. This is separated from the gel by filtration and the GPC study is carried out on the sol.

Molecular Weight and Molecular Weight Distribution of Degraded Sols

The number average molecular weight (M_n) and also the molecular weight distribution (MWD) of GR after degradation in the presence of different amount of acids were measured as a function of time. The data at 95°C are reported in Table II. All the experiments have been carried out in nitrogen and in air. Representative plots of decrease of molecular weight of rubber degraded in nitrogen and in air at 75°C have been shown in Figures 13 and 14.

It is observed that the M_n of pure GR decreases in 8 h at 95°C from 2.5×10^6 to 1.45×10^6 (42% decrease) in nitrogen and to 0.16×10^6 (94% decrease) in air. At 75°C in 8 h the decrease is 14% in nitrogen and 65% in air. At 125°C, the degradation is increased from 95°C (about 92% in nitrogen). In all cases the presence of oxygen (in air) increases the degradation several fold over the values for nitrogen atmospheres. The degradation in both air and nitrogen is, however, severely increased in the presence of the unsaturated fatty acids resin (Table II and Figs. 13 and 14). For example, in the presence of 5 phr linoleic acid containing two double bonds, the rubber at 95°C degrades about 20% from the initial M_n after 2

TABLE II
Values of M_n , MWD, Q , and D of GR at 95°C in Nitrogen and in Air

Sample no.	Acid level (phr)	Time of exposure (h)	$M_n \times 10^{-5}$		MWD		$Q \times 10^{-16}$		$D = \frac{[M_n(o) - M_n(t)]}{M_n(o)}$	
			N	Air	N	Air	N	Air	N	Air
			Rubber	0	2	22.5	6.8	1.53	2.75	2.46
		4	19.7	2.7	1.60	3.30	5.96	182.97	21.2	89.2
		8	14.5	1.6	2.03	3.97	16.04	323.99	42.0	93.6
Rubber + stearic acid	2	2	22.0	6.8	1.54	2.77	3.02	59.29	12.0	72.8
		4	18.6	2.7	1.66	3.34	7.62	182.97	25.6	89.2
		8	14.1	1.6	2.05	4.04	17.12	323.99	43.6	93.6
	5	2	21.8	6.6	1.54	2.79	3.25	61.76	12.8	73.6
		4	17.9	2.5	1.70	3.38	8.79	199.38	28.4	90.0
		8	13.0	1.4	2.20	4.10	20.45	373.44	48.0	94.4
Rubber + oleic acid	2	2	22.1	6.7	1.55	2.75	2.91	60.51	11.6	73.2
		4	19.1	2.5	1.62	3.35	6.84	199.38	23.6	90.0
		8	13.2	1.6	2.19	4.03	19.80	323.99	47.2	93.6
	5	2	21.6	6.7	1.58	2.79	3.49	60.51	13.6	73.2
		4	18.7	2.4	1.63	3.41	7.46	208.61	25.2	90.4
		8	13.0	1.5	2.20	4.20	20.45	347.07	48.0	94.0
	8	2	21.0	6.6	1.60	2.93	4.22	61.76	16.0	73.6
		4	17.0	2.3	1.76	3.44	10.42	218.64	32.0	90.8
		8	10.0	1.9	2.27	4.41	33.23	373.44	60.0	94.4
Rubber + linoleic acid	2	2	21.2	6.7	1.57	2.76	3.97	60.51	15.2	73.2
		4	18.0	2.4	1.64	3.38	8.61	208.61	28.0	90.4
		8	10.7	1.4	2.31	4.37	29.61	373.44	57.2	94.4
	5	2	20.0	6.0	1.62	3.06	5.54	70.15	20.0	76.0
		4	14.5	2.2	1.98	3.71	16.04	229.59	42.0	91.2
		8	3.7	1.1	3.54	4.86	127.53	481.33	85.2	95.6
	8	2	15.7	5.2	2.03	3.20	13.12	84.35	37.2	79.2
		4	7.0	2.0	2.78	3.96	56.97	254.76	72.0	92.0
		8	2.3	0.9	3.83	5.20	218.6	567.0	90.8	96.2
Rubber + linolenic acid	2	2	20.6	6.1	1.60	2.94	4.73	68.64	17.6	75.6
		4	16.7	2.3	1.67	3.50	11.01	218.64	33.2	90.8
		8	8.7	1.2	2.88	4.66	41.51	439.38	65.2	95.2
	5	2	19.0	4.5	1.77	3.34	6.99	100.92	24.0	82.0
		4	12.3	2.0	2.16	3.95	22.87	254.77	50.8	92.0
		8	2.5	0.6	3.88	5.49	199.38	843.0	90.0	97.4
	8	2	13.7	3.0	1.75	3.80	18.27	162.46	45.2	88.0
		4	6.8	1.8	2.81	4.33	59.29	285.53	72.8	92.8
		8	1.4	0.5	4.00	5.8	373.44	1209.00	94.4	98.2

h under nitrogen in contrast to only 10% degradation for the pure rubber under the same condition. Similar observations have been made at other temperatures. The decrease of M_n due to degradation at 75°C for 2 h in air for rubber containing 5 phr linoleic acid is 60% compared to a decrease of 20% for the pure rubber. The decrease is, however, most severe in the case

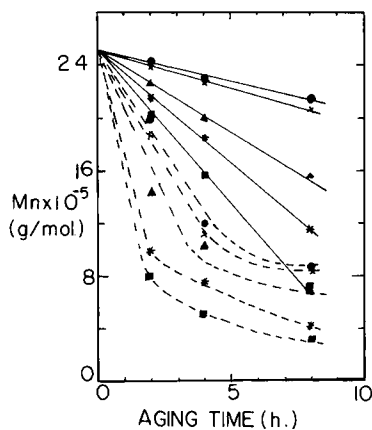


Fig. 13. Plot of M_n vs. time at 75°C for: (●) pure rubber; (X) rubber + 5 phr stearic acid; (▲) rubber + 5 phr oleic acid; (*) rubber + 5 phr linoleic acid; (□) rubber + 5 phr linolenic acid; (—) in nitrogen; (---) in air.

of linolenic acid (Fig. 13 and Table II). The percentage decrease in molecular weight, defined as $[M_n(0) - M_n(t)]/M_n(0)$, where $M_n(0)$ is the initial molecular weight and $M_n(t)$ that at a time t and degradation temperature T has been plotted in Figure 15. The degradation of rubber with and without acids in nitrogen seems to vary linearly with time up to 8 h. With saturated fatty acids (stearic acid) the amount of degradation is comparable to that of pure rubber.

The rubber degradation, however, is dependent on the amount of acid added. As shown in Figure 14 and Table II, a higher dosage of acid causes faster degradation. It was observed before² in capillary rheometer study that the apparent melt viscosity of GR decreased in the presence of higher amounts of whole resin. Even with 2 phr of unsaturated fatty acid there is increased molecular breakdown. The degradation of rubber is always increased by the addition of acids to GR in not only a nitrogen atmosphere

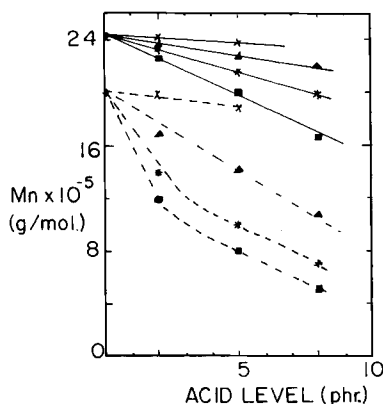


Fig. 14. Plot of M_n of rubber vs. acid level added for 2 h degradation at 75°C: (●) pure rubber; (X) rubber + stearic acid; (▲) rubber + oleic acid; (*) rubber + linoleic acid; (■) rubber + linolenic acid; solid lines for samples degraded in nitrogen atm, and dotted lines for degradation in air.

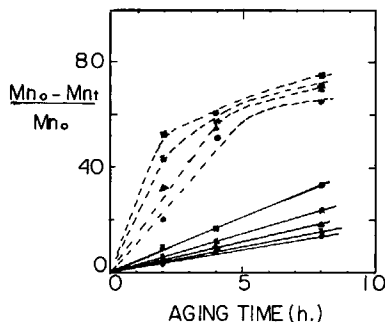


Fig. 15. Plot of $[M_n(t) - M_n(0)]/M_n(0)$ vs. time of aging at 75°C in nitrogen (—) and in air (- - -) for: (●) pure rubber; (X) rubber + 2 phr stearic acid; (▲) rubber + 2 phr oleic acid; (*) rubber + 2 phr linoleic acid; (■) rubber + 2 phr linolenic acid.

but even more so in an air atmosphere. At constant concentrations the different acids do not change their relative order in causing degradation, namely, stearic acid < oleic acid < linoleic acid < linolenic acid. As shown in Figure 16, the amount of degradation is always monotonically increasing with the number of double bonds in the acids. This order is also independent of the temperature of degradation. It is interesting to note here that higher amount of less degradative acids causes the equivalent amount of degradation of rubber in the presence of a lower dosage of most degradative acids. This is also important in the sense that, in actual resin, linolenic acid, though present in a small amount, can be most harmful in storage stability of GR. In all cases, the degradative effect in nitrogen atmosphere is always less than that in air. For example, at a 5 phr level of linolenic acid the M_n decreases from 85% in nitrogen to 96% in air under the same conditions.

The width of the molecular weight distribution (MWD) of the original rubber is generally 1.4. Degradation broadens the GPC curve (Figs. 11 and 12) and hence the MWD values become higher. The highest value of the MWD is 5.85 obtained for samples degraded in air for 8 h at 125°C. The corresponding MWD for GR degraded in nitrogen atmosphere is narrower (Fig. 17). Acid level, degradation time, and concentration of acid double

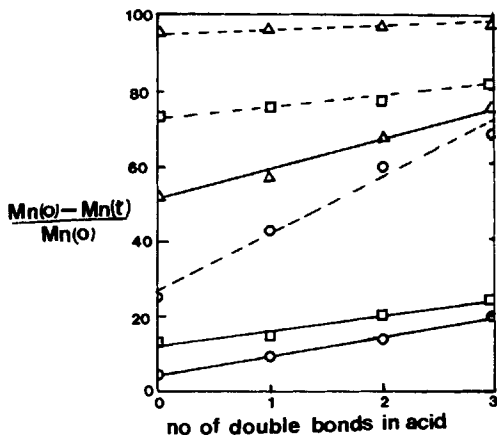


Fig. 16. Plot of percent decrease in M_n vs. number of double bonds, aging time, 2h; temperatures: (○) 75°C; (□) 95°C; (△) 125°C; (—) in nitrogen and (- - -) in air.

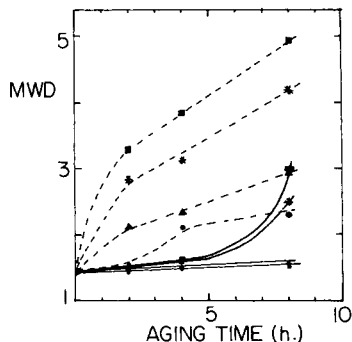


Fig. 17. Molecular weight distribution (MWD) of rubber after degradation at 75°C in nitrogen (—) and in air (- -) vs. aging time, for rubber and rubber containing 8 phr of acid: (●) pure rubber; (▲) rubber + oleic acid; (*) rubber + linoleic acid; (■) rubber + linolenic acid.

bonds broadens the MWD. The polydispersity index, however, is not linear. It must be remembered that the MWD given here is representative value of the *sol* part of the GR and not the overall sample of GR.

Studies on Scission Rates

The decrease of M_n discussed above and the broadening of the MWD are due to scission of the rubber chain in the degradative environment. The number of scission per cc denoted by $Q(t)$ has been calculated from the following relation⁸:

$$Q(t) = \rho N_A [M_n(t)^{-1} - M_n(0)^{-1}] \quad (7)$$

where ρ = density of rubber, N_A = Avogadro's number, $M_n(t) = M_n$ of degraded sample in time t , and $M_n(0) =$ initial M_n of the sample. The number of chain scissions is reported in Table II and Figure 18 for degradation at 75°C in nitrogen and in air. The decrease in M_n is proportional to the number of chain scissions, which are greater for degradation at higher temperatures or in the presence of acids containing an increased number of double bonds. There are more chain scissions for degradation in air than in nitrogen. In

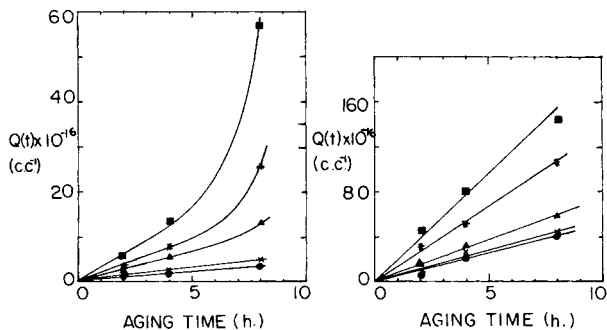


Fig. 18. Plot of $Q(t)$ vs. aging time at 75°C in (a) nitrogen and (b) air for pure rubber and rubber containing 5 phr of acids; (●) pure rubber; (X) rubber + stearic acid; (▲) rubber + oleic acid; (*) rubber + linoleic acid; (■) rubber + linolenic acid.

fact, the chain scissions at constant temperature increase up to a factor of 20 by varying atmospheric gas and acid concentration up to 8 phr.

$Q(t)$ is essentially a concentration term, its unit being scission/cc. The plot of $Q(t)$ vs. time in the initial stage is linear, and indicates a zero-order (or pseudozero) kinetics in GR concentrations. The upturn in $Q(t)$ in air in the long time region is due to a sudden increase in the hydroperoxide concentration, because the scission rates are either first or second order with respect to the concentration of peroxy compound.¹ A similar upturn has been observed in the oxygen absorption of tetralin as a function of time.¹⁴

The rate of degradation is better understood in terms of the rate constant k_d . These values are calculated from the initial slope of the $Q(t)$ vs. time curve (Fig. 18) and have been reported in Table III. The rate of degradation increases with temperature, acid level, and in air. From the values of k_d at different temperatures, a plot of $\log k_d$ vs. $1/T$ has been made [eq. (6)]. The data show scatter in the plot. The scatter may be due to (1) an incomplete separation of the gel or (2) a low molecular tail at higher temperatures that is very close to the baseline resolution. The activation energy has been estimated from the slope and is reported in Table III. It is interesting to note that the activation energy does not change and is independent of the nature of the acids or the acid level. The value obtained 95 ± 10 kJ/mol

TABLE III
Values of Rate Constant and Activation Energy

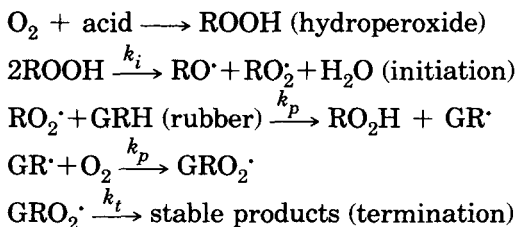
Sample no.	Acid level (phr)	Atmosphere	Rate constant $k_d \times 10^{-14}$ (min ⁻¹)				Activation Energy ΔE (kJ/mol)
			75°C	95°C	110°C	125°C	
Rubber	0	N	0.8	2.7	43.0	54.0	95 ± 10
		Air	8.3	62.0	67.0	492.0	95 ± 10
Rubber + stearic acid	2	N	1.0	3.3	55.0	60.5	95 ± 10
		Air	8.3	62.0	73.0	492.5	95 ± 10
	5	N	1.0	4.2	60.0	64.2	95 ± 10
		Air	8.9	77.0	80.0	515.0	95 ± 10
Rubber + oleic acid	2	N	1.0	3.7	—	—	—
		Air	10.3	68.0	80.0	540.0	95 ± 10
	5	N	2.7	4.2	75.0	—	95 ± 10
		Air	12.3	77.0	100.0	631.7	95 ± 10
		8	N	4.0	4.7	100.0	—
Air	16.0		78.0	100.0	786.2	95 ± 10	
Rubber + linoleic acid	2	N	1.6	4.2	—	—	—
		Air	11.7	78.0	100.0	597.9	95 ± 10
	5	N	3.2	6.2	100.0	115.0	95 ± 10
		Air	21.0	93.0	140.0	1145.0	95 ± 10
		8	N	6.7	11.7	160.0	—
Air	37.0		98.0	150.0	1433.0	95 ± 10	
Rubber + linolenic acid	2	N	2.5	4.6	100.0	143.0	95 ± 10
		Air	14.0	88.0	120.0	1144.0	95 ± 10
	5	N	5.2	8.7	120.0	234.0	95 ± 10
		Air	33.0	102.0	160.0	2298.0	95 ± 10
		8	N	15.3	23.0	210.0	397.0
Air	70.0		122.0	200.0	11529.0	95 ± 10	

is in fair agreement with the stress-relaxation measurements reported here and previous experiments.¹ k_d values are also plotted against the concentration of the acids (Fig. 19). For all acids, both in thermal and thermooxidative degradation, the reaction seems to be first order with respect to the acid concentration.

MECHANISM

Oxidative Degradation

The mechanism of rubber oxidation has been firmly established.^{15,16} This was discussed by previous workers^{1,9} by fitting the oxidation scheme into the Bolland-Gee mechanism.¹⁵ The basic sequence of oxidation of rubber-acid mixtures could be summarized as follows:



Simultaneously, natural rubber is also expected to generate hydroperoxide radicals upon oxidation as follows:

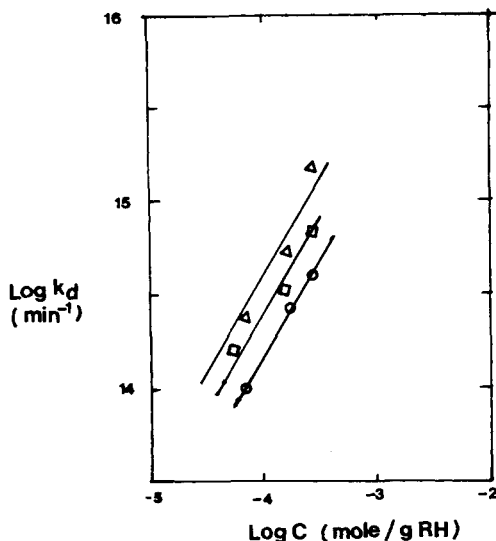
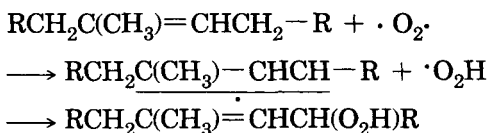
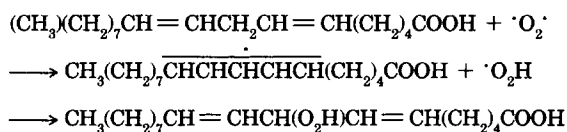
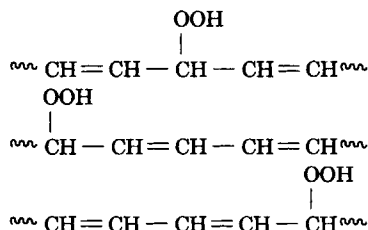


Fig. 19. Plot of rate constant k_d for degradation in nitrogen at 75°C vs. the concentration of acid: (○) oleic acid; (◻) linoleic acid; (△) linolenic acid.

The rate of oxidation, though zero order with respect to natural rubber in the initial stages, is a function of hydroperoxide concentration and independent of oxygen concentration in ordinary air atmosphere.¹ Since the rate of reaction is first or second order with respect to peroxide content,^{1,8,15} the degradation would increase with the formation of hydroperoxide. Actually, the hydroperoxide formed by the reaction of labile hydrogen atoms (α -hydrogen atoms) are very unstable and decomposes to give secondary products. The stability of the peroxides formed depends on the structure of the fatty acids and rubber. It can be argued that linoleic acid and linolenic acid with two and three double bonds, respectively, are expected to stabilize the radicals more through delocalization than the three carbon delocalization formed during the oxidation of rubber. The delocalization of a radical in linoleic acid can be expressed as follows:



It has been reported that there is a shift in the double bond in the oxidation of methyl linoleate^{17,18} and methyl oleate.^{19,20} The shift may occur by a free radical mechanism. In the case of methyl linoleate, three isomeric linoleate hydroperoxides are postulated with two of the isomers having conjugated diene structures:



It was found that even methyl stearate produces dehydropolymers with *tert*-butyl peroxide, indicating the reaction of the saturated fatty acid itself.¹⁷

It has been also observed that the rate of absorption of oxygen by methyl linoleate is roughly 10 times faster than that of methyl oleate.²¹ The absorption of oxygen could easily be understood in terms of the delocalization of the double bonds. The data reported in the present research also supports this view in form but not in magnitude. That is, higher numbers of double bonds per acid are equivalent to higher amounts of acids (from 2 to 8 phr), because they supply higher amounts of hydroperoxide. The hydroperoxide then acts as an initiator forming free radicals and enhancing the rate of oxidative degradation of rubber several fold.

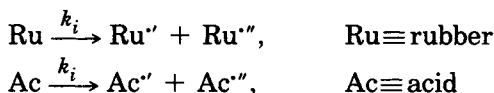
Thermal Degradation

The degradation of rubber in nitrogen is slower than in air, as evident from the values of the rate constants (Table III). The free energy of acti-

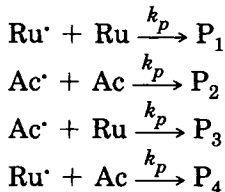
vation for degradation seems to be surprisingly low and the same as that in air. The lower activation energy of degradation of rubber can be explained in terms of weak links,²² though the nature of these is still largely speculative. The concept of weak links was put forward in order to explain the unusual rapid decrease in molecular weight of vinyl polymers. The weak links in natural rubber could arise from small head-to-head or tail-to-tail configurations, strained bonds in folded chain parts, or unusual groups like carbonyl type, peroxide, or epoxy groups²² in the rubber as it leaves the tree or is being introduced during processing operations. Similar results were obtained by Sarfara et al.²³ from their studies on the light scattering of purified hevea rubber degraded in solutions in cyclohexane and in decalin. It is believed that these weak links are broken by free radical mechanism. Once these free radicals are generated, they are stabilized by the acids, and then follow the same mechanism of the oxidation of rubber in the presence of fatty acids. This explains the relative order of the acids found for the thermal degradation of rubber.

Thermal degradation could be understood through the very simple reaction schemes as presented below:

Initiation:

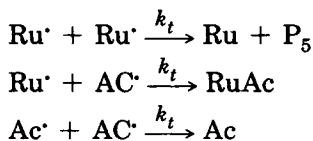


Propagation:



P_1 , P_2 , P_3 , and P_4 are the products here. For simplicity all rubber radicals and acid radicals are represented by Ru' and Ac' , respectively. In actual practice, the structure of the radicals may be different. Furthermore, it has been assumed that the rubber and the acid decompose at the same rate at the initiation step.

Termination:



It has been assumed here that all the radicals in proximity terminate very fast and therefore are represented by a single rate constant, k_t . Under steady state conditions,

$$\text{rate of initiation} = \text{rate of termination}$$

Hence,

$$k_i[\text{Ac}] = k_t[\text{Ru}][\text{Ac}] \quad (8)$$

$$k_i[\text{Ru}] = k_t[\text{Ru}]^2 + k_i[\text{Ru}][\text{Ac}] \quad (9)$$

where [] represents concentration. Since a very small amount of the acid is added, interaction of an acid radical with another acid radical is neglected.

Combining eq. (8) and (9), we obtain

$$k_i[\text{Ru}] = k_t[\text{Ru}]^2 + k_i[\text{Ac}] \quad (10)$$

$$[\text{Ru}]^2 = \frac{k_i[\text{Ru}] - k_i[\text{Ac}]}{k_t}$$

and

$$[\text{Ac}] = \frac{k_i[\text{Ac}]}{k_i[\text{Ru}]} = \frac{k_i[\text{Ac}]}{k_t} \cdot \left[\frac{k_t}{k_i[\text{Ru}] - k_i[\text{Ac}]} \right]^{1/2} \simeq \frac{k_i[\text{Ac}]}{k_t} \cdot \left[\frac{k_t}{k_i[\text{Ru}]} \right]^{1/2} \quad (11)$$

assuming $[\text{Ru}] \gg [\text{Ac}]$. Now, the rate of rubber decomposition is empirically defined as

$$R = -\frac{d[\text{Ru}]}{dt}$$

or

$$\begin{aligned} R &= k_p[\text{Ru}][\text{Ru}] + k_p[\text{Ru}][\text{Ac}] \\ &= k_p[\text{Ru}] \left[\frac{k_i[\text{Ru}] - k_i[\text{Ac}]}{k_t} \right]^{1/2} \\ &\quad + k_p[\text{Ru}] \frac{k_i[\text{Ac}]}{k_t} \cdot \left[\frac{k_t}{k_i[\text{Ru}]} \right]^{1/2} \\ &\simeq k_p[\text{Ru}] \left[\frac{k_i[\text{Ru}]}{k_t} \right]^{1/2} + k_p[\text{Ru}]^{1/2} \frac{k_i[\text{Ac}]}{k_t} \cdot \left[\frac{k_t}{k_i} \right]^{1/2} \\ &= k'_1[\text{Ru}]^{3/2} + k'_1[\text{Ac}][\text{Ru}]^{1/2} \end{aligned}$$

where $k'_1 = k_p [k_t/k_i]^{1/2}$. Now, assuming $[\text{Ru}]$ is constant at the initial stage, we obtain

$$R = -\frac{d[\text{Ru}]}{dt} = k_1 + k_1[\text{Ac}] \quad (12)$$

This has been verified and given in Figure 19. Higher concentration of acid causes higher degradation. After the initial stage of the reaction, the molecular weight (MW) becomes smaller and smaller and the viscosity (η) of the rubber is reduced according to $\eta \simeq M^{3.4}$. The diffusion (D) of the species

containing radical becomes easier, since $D \propto 1/\frac{1}{2}$ and decreases the cage effect for rubber recombination. Hence, there would be the auto acceleration, which is observed in the present study.

CONCLUSIONS

The degradative effect of resin components on guayule rubber both in air and in nitrogen atmosphere has been studied concurrently by stress-relaxation of radiation-cured rubber and by following the average molecular weight of unvulcanized raw rubber after degradation in the temperature zone 70–125°C. In general, the rate of degradation is faster in air than in nitrogen atmosphere. The C₁₈ unsaturated fatty acids enhance the degradation of rubber several fold compared to the corresponding saturated fatty acid, stearic acid. The rate of degradation caused by the fatty acids increases in the order linolenic acid > linoleic acid > oleic acid ≥ stearic acid and is first order with respect to the acid concentration. This has been observed in both stress-relaxation experiment and GPC studies. The effect of these acids on degradation of rubber is directly proportional to the number of double bonds. The activation energy for both oxidative and thermal degradation has been found to be 95 ± 10 kJ/mol, similar to that for the oxidation of hevea natural rubber. Mechanism of increased degradation of rubber in presence of unsaturated fatty acids in air and in nitrogen is believed to be due to stabilization of the free radicals through delocalization over more than three carbon atoms.

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References

1. R. W. Keller and H. L. Stephens, *Rubber Chem. Technol.*, **55**, 161 (1982).
2. R. W. Keller, D. S. Winkler, and H. L. Stephens, *Rubber Chem. Technol.*, **54**, 115 (1981).
3. E. M. Bevilacqua, in *Thermal Stability of Polymers*, R. T. Conley, Ed., Marcel Dekker, New York, 1970.
4. J. Hrivikova, A. Blazkova, and L. Lapcik, *J. Appl. Polym. Sci.*, **25**, 761 (1980).
5. V. V. Voronenkov, G. Blykina, Y. E. Shapiro, and E. H. Lazurin, *Vysokomol. Soedin., Ser. B*, **20**, 742 (1978).
6. M. A. Ponce-Valez and E. Campos-Lopez, *J. Appl. Polym. Sci.*, **22**, 2485 (1978).
7. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Wiley-Interscience, New York, 1964.
8. A. V. Tobolsky, *Properties and Structure of Polymers*, Wiley, New York, 1960; A. V. Tobolsky and A. Mercurio, *J. Am. Chem. Soc.*, **81**, 5539 (1959).
9. J. R. Shelton, in *Stabilization and Degradation of Polymers*, D. L. Allara and W. L. Hawkins, Eds., Adv. Chem. Ser. 169, American Chemical Society, Washington, D. C., 1978.
10. P. K. Pal, A. K. Bhowmick, and S. K. De, *Rubber Chem. Technol.*, **55**, 23 (1982).
11. D. McIntyre, A. L. Shih, J. Savoca, R. Seeger, and A. MacArthur, *Org. Coat. Appl. Polym. Sci., Proc.*, **48**, 612 (1983).
12. K. Murakami and K. Ono, *Chemorheology of Polymers*, Elsevier, New York, 1979.
13. S. Tamura and K. Murakami, *Rubber Chem. Technol.*, **48**, 141 (1975).
14. A. Robertson and W. A. Waters, *Trans. Faraday Soc.*, **42**, 201 (1946).
15. J. L. Bolland and G. Gee, *Trans. Faraday Soc.*, **42**, 236 (1946).
16. E. H. Farmer and A. Sundralingham, *J. Chem. Soc.*, **147**, 121 (1942).
17. A. L. Clingman and D. A. Sutton, *J. Am. Oil. Chem. Soc.*, **30**, 53 (1953).

18. W. O. Lundberg and J. R. Chipault, *J. Am. Chem. Soc.*, **69**, 833 (1947).
19. E. H. Farmer, H. P. Koch, and D. A. Sutton, *J. Chem. Soc.*, 541 (1943).
20. J. Ross, A. I. Gebhart, and J. F. Gerech, *J. Am. Chem. Soc.*, **71**, 282 (1949).
21. A. J. Stirton, J. Turer, and R. W. Riemenschneider, *Oil Soap, Egypt*, **22**, 81 (1945).
22. H. H. G. Jellinek, in *Aspects of Degradation and Stabilization of Polymers*, H. H. G. Jellinek, Ed., Elsevier, New York, 1978.
23. P. S. Sarfara, H. L. Bhatnagar, and A. B. Biswas, *J. Appl. Polym. Sci.*, **7**, 2199 (1963).

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