The Degradation of Guayule Rubber and the Effect of Resin Components on Degradation at High Temperature

A. K. BHOWMICK*, S. RAMPALLI, K. GALLAGHER†,
R. SEEGER, and D. MCINTYRE, *Institute of Polymer Science,
University of Akron, Akron, Ohio 44325, USA*

Synopsis

Degradation of pure guayule rubber and rubber in the presence of stearic, oleic, linoleic, and linolenic acid, has been studied at high temperatures (from 150° C to 600° C) using thermogravimetric analysis (TGA). On-line mass spectrometric analysis of the products of decomposition has also been done to understand the mechanism of degradation.

Degradation of rubber starts around 230° C in air and 330° C in nitrogen. Presence of acids changes the onset of degradation, because of low decomposition temperature of the acids. In the derivative curve, there is one T_{max} for degradation in nitrogen; two for rubber; and three for rubber containing acids are observed for degradation in air. The activation energy of degradation, as observed by isothermal kinetics, in the 1–10% weight loss region, is 225 kJ/mol in nitrogen and 167 kJ/mol in air. In the 10–100% region, however, the activation energy of degradation measured by the Freeman and Carroll method using dynamic thermogravimetry, is 239 kJ/mol in both nitrogen and air atmosphere. The main products of pyrolysis in inert atmosphere are propylene, propane, isobutylene, methyl butene, isoprene, 2,3-dimethyl cyclopentene, octene, 2,4-dimethylcyclohexene, dipentene, etc. Isoprene is found to be the most abundant. Fragments having m/e values of 136, 121, 107, 93, 79, and 53 are also produced in large quantities. The ratio of concentration of dipentene to isoprene increases marginally with temperature. The concentration of other fragments however increases drastically with temperature. The additives have no effect on the nature of products obtained. The conversion to different fragments depends upon the temperature of degradation and the stability of intermediate products. All smaller molecules are obtained from either dipentene or isoprene. A mechanism of formation of these products has been suggested.

INTRODUCTION

In our earlier communication,[1] the thermal and thermo-oxidative degradation of pure rubber and rubber in the presence of stearic, oleic, linoleic, and linolenic acid have been discussed over the temperature region 70–125° C. All unsaturated acids enhance degradation of rubber. It has also been observed that linolenic acid with three double bonds on the backbone has the most degradative effect on rubber. The above studies were carried out on cross-linked guayule rubber networks by stress relaxation and on degraded raw rubber by

---

*Present addresses: Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India.

†Sohio Research and Development Center, Warrensville Heights, Cleveland, Ohio, USA.

CCC 0021-8995/87/041125-15$04.00

gel permeation chromatography (GPC) measurement. In the low temperature zone, there were no volatile products upon heating. It is interesting and important to know the degradative influence of the acids on rubber above 125°C, because off-the-road tires using natural rubber frequently operate at high temperature. The thermal and thermo-oxidative degradation of pure guayule rubber (GR) in the presence or absence of simulated resin components have been studied in this paper by thermogravimetric analysis (TGA) and on-line mass spectrometer analysis of the products of decomposition.

Madorsky and co-workers[2,3] carried out systematic investigations on the thermal degradation of *cis*-polyisoprene and *trans*-polyisoprene. These studies indicate that monomer and dimer are formed as the main pyrolysis products. This was confirmed by Vacherot[4] from their flash pyrolysis studies at 500–600°C. In addition, 3,4-dimethyl, 4-vinyl cyclohexene, characteristic of 3,4 units, was obtained. Similar studies at 550–750°C were made by Jernejcie and Premru.[5] More recently Chien and Kiang[6] reported pyrolysis of polyisoprene in an inert atmosphere from 315°C to 384°C. They suggested β-chain scission of the polymer, leading to two allylic radicals.

Gelling and co-workers also reported pyrolysis products of polyisoprene.[7] Bevilacqua et al.,[8] and Voigt and Scheele[9] studied the oxidation products of polyisoprene at high temperatures. The oxidation of hevea and guayule was also studied earlier by Ponce-Velez and Campos-Lopez[10] by differential scanning calorimetry (DSC). They reported an activation energy of about 88-89 kJ/mol. Similar kinetic studies by DSC were made by Keller and Stephens.[11]

EXPERIMENTAL

Guayule rubber (GR) was obtained from the whole shrub by removal of the resin with acetone in a Soxhlet extractor for 12 hs. The rubber was extracted with cold benzene and the rubber solution was centrifuged and filtered. The rubber was precipitated with acetone.

SMR 5 (Hevea rubber, HR) was also used. After dissolving the rubber in benzene, the solution was filtered. The rubber was precipitated with acetone. Both GR and HR were dried in vacuum.

The fatty acids obtained from Aldrich Chemical, Wisconsin, were of analytical grade and were used as supplied. One percent solutions of fatty acids in benzene and a 2.5% solution of rubber in benzene were prepared. Just before use, an appropriate amount of fatty acid solution was added to the rubber solution and mixed thoroughly. A film of approximately 0.01 cm thickness was made by evaporating off the solvent from the mixture and drying the rubber in vacuum.

The guayule rubber used has 100% *cis*-1,4 microstructure, and the values of Mn, Mw and Mw/Mn are 2.25×10^6 g/g-mole, 3.6×10^6 g/g-mole, and 1.42, respectively. Mw of hevea natural rubber was 9.9×10^5 g/g-mole.

The pyrolysis study was carried out using a Dupont 1090 TGA instrument in nitrogen and in air at a flow rate of 60 mL/min and a heating rate of 10°C/min. For each experiment we used 10–15 mg of the sample. The products of degradation in helium were identified by a mass spectrometer fitted on line with the TGA instrument.

RESULTS AND DISCUSSION

Overall Weight Loss of Rubber

Degradation of Guayule Rubber in N_2 and Air

Figure 1 shows the weight loss of guayule rubber in N_2 and in air from room temperature to 600°C. The recording of the first derivative (% weight loss per minute) versus temperature is shown on the same plot. Degradation in N_2 starts at 330°C, while in air it starts at 230°C. No carbonaceous residues are left in the sample boat in either case. The derivative curve for degradation in N_2 shows one T_{max}, i.e., the temperature at which the degradation rate is a maximum, whereas two T_{max}s are observed in air (Table I). The value of T_{max} in a N_2 atmosphere is 400°C, and those in air are 360°C and 490°C. The occurrence of two T_{max}s in air indicates the formation of stable intermediate products along the course of the reaction. Similar observations are also made
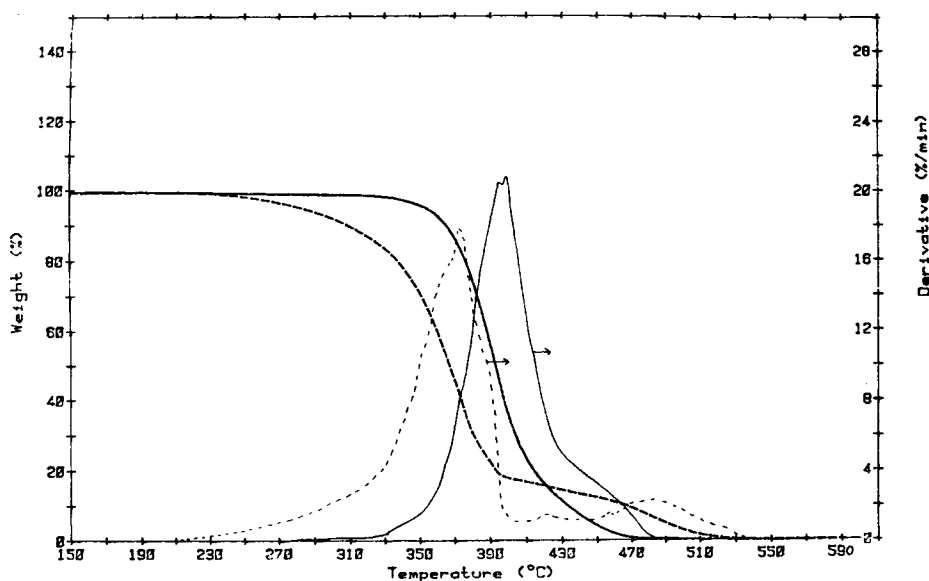

Fig. 1.   Degradation of guayule rubber in nitrogen (-) and in air (----).

TABLE I
Dynamic Thermogravimetry of Guayule Rubber in Nitrogen and in Air[a]

Sample	T_{max} in N_2, °C	T_{max} in air, °C
Control GR	400	360, 490
GR + stearic acid	390	360, 375, 490
GR + oleic acid	380	—
GR + linoleic acid	380	360, 380, 480
GR + linolenic acid	380	340, 375, 480

[a]Scan rate: 10°C/min.
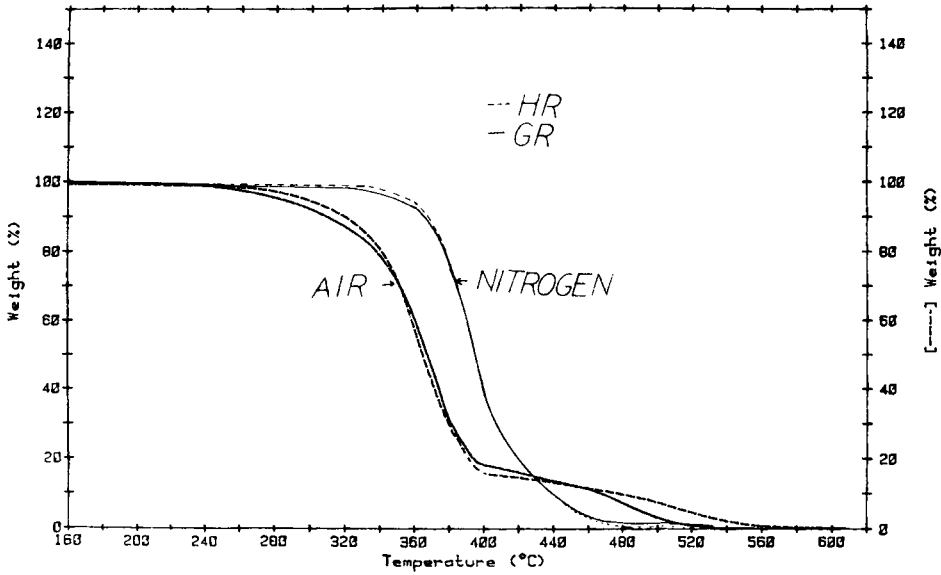 Gas flow: 60 mL/min.

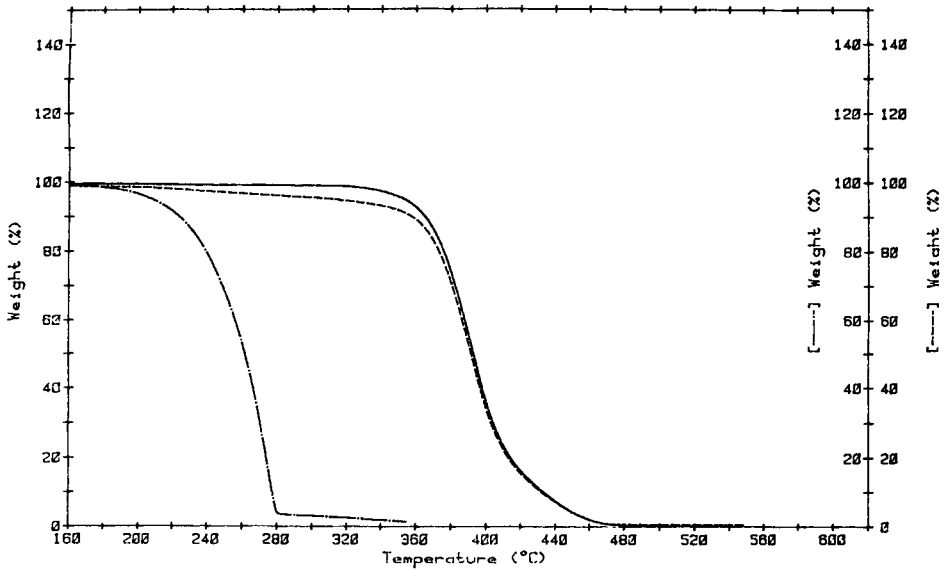Fig. 2.   Comparison of degradation of NR and GR in nitrogen and in air.

Fig. 3.   Effect of 5 phr linolenic acid on the degradation of guayule rubber in nitrogen. ——
Pure GR; - - - - GR + 5 phr linolenic acid; ···· Pure linolenic acid.

with hevea natural rubber degraded in nitrogen and in air (Fig. 2). Only at high temperatures in air are there any significant differences in the degradation of the two rubbers, probably due to residual plant tissues.

Effect of Additives on Rubber Weight Loss

The saturated and unsaturated acids were added separately to the rubber at a level of 5 phr. The dynamic thermograms using these mixtures are recorded. As shown in Figure 3, the acids degrade at a much lower temperature than the rubber. This is probably due to the easy diffusion of low molecular weight molecules and radicals. The presence of acid in the rubber does not cause appreciable difference in the degradation behavior either in N_2 or in air at high temperature ($> 160°$) if the additivity of independent reactions is considered. The products of degradation in air are not identified and hence we do not have much information about the products. However, these results are in contrast to earlier observations[1] on low temperature degradation ($70–125°C$) in this laboratory when unsaturated acids enhance the degradation of rubber several fold. Values of T_{max} are reported in Table I. Three values of T_{max} are observed in air, whereas there is one in nitrogen atmosphere. The T_{max} values do not change with the nature of the acids.

Kinetics of Rubber Degradation

Isothermal Conditions: (1–10% Weight Loss) in Pure Rubber

Isothermal thermogravimetry, in which the weight loss is recorded for a sample heated to a predetermined constant temperature, is carried out at four different temperatures. Values of the rate constant, k_0, from degradation of control samples in nitrogen and in air are reported in Table II. These values are calculated from the slope of the plots (Figs. 4 and 5) of weight loss versus time as zero-order kinetics; rate of wt. loss = $k[GR]^0$. It must be noted that in the case of thermo-oxidative degradation there is a gentle curvature at the initial stages, $< 3\%$ degradation, so that the zero-order kinetics apparently do not apply. Therefore, the first-order rate constant, k_1, is calculated by the

TABLE II
Values of Rate Constants for Degradation of Guayule Rubber
in Nitrogen and in Air by Isothermal Thermogravimetry

Temperature, °C	Atmosphere	Rate constant, mg/min k_{0, N_2}	Apparent zero-order rate constant $k_{0, air}$ mg/min	First-order rate constant $k_{1, air}$, min^{-1}
270	Nitrogen	7.5×10^{-3}	—	—
295		5.3×10^{-2}	—	—
310		1.5×10^{-1}	—	—
320		3.9×10^{-1}	—	—
200	Air	—	2.2×10^{-3}	1.8×10^{-4}
235		—	1.5×10^{-3}	3.9×10^{-4}
250		—	2.3×10^{-3}	1.9×10^{-3}
265		—	6.6×10^{-2}	7.1×10^{-3}

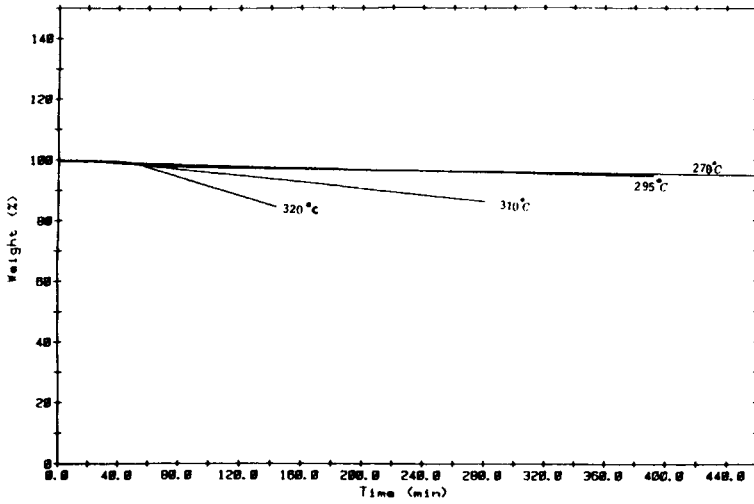Fig. 4. Plot of % weight loss vs time of degradation of GR in nitrogen at different temperatures.

following equation of Reich and co-workers,[12]

$$k_1 = \frac{2k_0}{2W_0 - k_0 t},$$ (1)

where k_0 = zero-order rate constant being the slope of the linear portion,
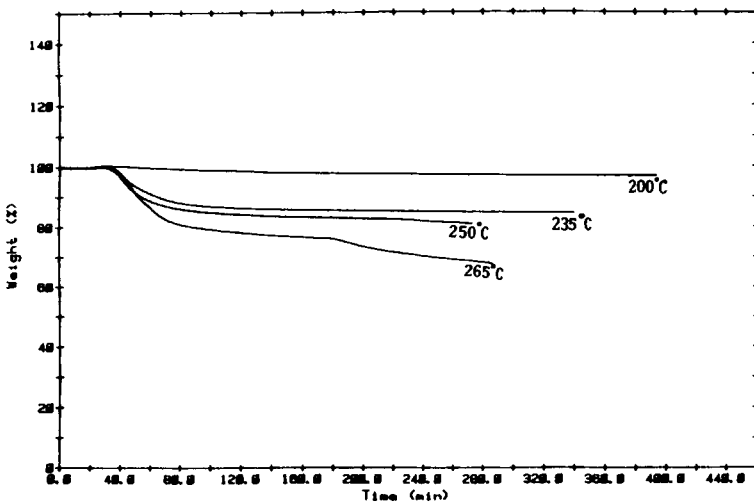W_0 = initial weight loss, and
t = time interval

Fig. 5. Plot of % weight loss vs time of degradation of guayule rubber in air at different temperatures.

As expected, the rate of degradation increases with temperature. Values of the zero-order rate constant, k_0 are higher in air than in a nitrogen atmosphere. The activation energy for degradation is calculated from the Arrhenius plot and found to be 225 ± 5 kJ/mol in nitrogen and 167 ± 5 kJ/mol in air. It must be mentioned here that the activation energy for the low temperature (75–125°C) degradation is 90 kJ/mol, found from both stress relaxation experiments of the rubber network and gel permeation chromatography studies of the degraded uncross-linked rubber.[1] In the low temperature degradation, mainly chain scission occurs, but in the former high temperature case, the volatilzates of low molecular weight species after bond breaking must be energized.

Non-isothermal Conditions in Acid-Rubber Mixture
(> 10% Weight Loss)

A true picture of the effect of the acid in the acid–rubber mixture is not determined easily, because of the much earlier degradation of only acid and not rubber in this region. Hence, temperature-scanning thermogravimetry has been performed to determine the effect of the acid in rubber degradation using the Freeman and Carroll method[13] of analysis.

The Freeman and Carroll[13] method uses the expression

$$\Delta \log \frac{dW}{dt} = n\Delta \log W_r - \left(\frac{\Delta E}{2.3R} \right)\Delta(1/T), \qquad (2)$$
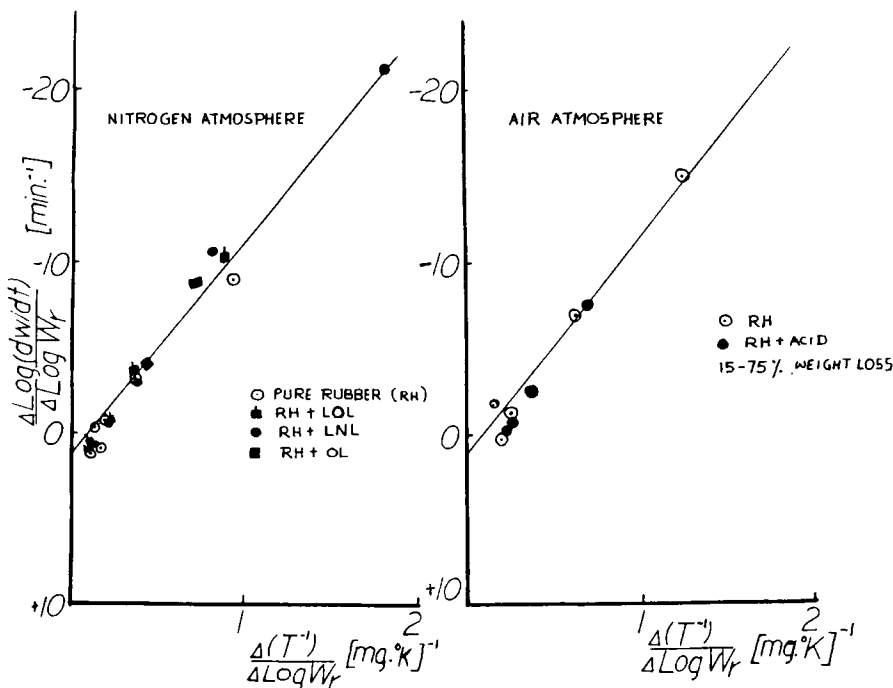

Fig. 6. Plot of $\dfrac{\Delta \log\left(\dfrac{dW}{dt} \right)}{\Delta \log W_r}$ vs. $\dfrac{\Delta(T^{-1})}{\Delta \log W_r}$ in nitrogen atmosphere and in air.

where dW/dt is the rate of reaction, n is the order of the reaction, R is a gas constant, T is the absolute temperature, and W_r is proportional to the amount of reactant remaining. Dividing Eq. (2) by $\Delta \log W_r$

$$\left(\Delta \log \frac{dW}{dt}\right) \bigg/ \Delta \log W_r = n - (\Delta E/2.3R)\Delta(1/T)/\Delta \log W_r \qquad (3)$$

Hence, a plot of the left-hand side of the equation versus $\Delta(1/T)/\Delta \log W_r$ gives the values of n and ΔE. Two plots are shown in Figures 6(a) and 6(b). An activation energy of 239 kJ/mol is found for degradation in both air and nitrogen atmosphere. The order of the reaction is unity both in the presence and in the absence of the acids at high levels of degradation ($> 10\%$). It was suggested that some of the unsaturated acids help to diffuse radicals and allow new products to be formed.[1] The volatilization rate of the products thus formed, however, seem to be almost same in the region 15–75% for which the activation energy is reported.

Products Formed During Degradation

The pyrolytic products of guayule rubber in helium at 385°C are determined by a mass spectrometer connected to the TGA apparatus. The mass spectra are given in Table III. The main products are underlined and are propylene, propane, isobutylene, butenes, methyl butene, isoprene, 2,3-dimethyl cyclopentene, octene, 2,4-dimethylcyclohexene, 1-methyl-4-ethyl cyclohexene, 1,5-dimethyl-5-vinyl cyclohexene, dipentene, etc. in order of increasing mass. All the smaller fragments can be accounted for, if they are assumed to be generated from dipentene and isoprene, as suggested later in the mechanistic discussion. The decomposition of each of the secondary products gives new products. Chien and Liang[6] suggest that dipentene alone will break down to give masses of 136, 119, 107, 93, 68, 67, 53, 41, 39, 27. Similarly, isoprene breakdown gives 68, 67, 53, 41, 40, 39, 27. Propylene gives 42, 41, 39, 27. As a result, the intensity of the smaller fragments becomes higher.

Similar pyrolysis experiments have been conducted over a wide range of temperatures and their products have been analyzed. Relative ion currents are plotted against temperature in Figure 7 for isoprene, dipentene, and mass 204. Both the isoprene and dipentene pass through a maximum near 367°C. The concentration of different fragments at 360°C is shown in Figure 8. The isoprene fragment concentration is greater at all temperatures. The higher concentration of isoprene is suggested later in the discussion to be due to the thermodynamic stability of the product. In contrast to the work on commercial polyisoprene (Natsyn),[6] higher amounts of isoprene compared to amounts of dipentene are found. The increase in isoprene may be due to the fact that guayule rubber has a more regular microstructure (100% cis) than commercial polyisoprene which contains 3,4, and 1,2 units.

The relative mass/charge (m/e) areas of major products of m/e values of 136, 121, 107, 93, 79, and 53 with respect to isoprene 68 as 100% is plotted against temperature in Figure 9. The dipentene (136) to isoprene ratio increases marginally with temperature and then plateaus off, while the fragments 121 and 107 gradually increase with temperature. But the increase here is not

TABLE III
Mass List of Pyrolysis Products of Guayule Rubber in Helium at 385° C

Conds.: TGA			Base m/e: 68			RIC: 2207740.		
35	0.00	0.00		0. Minima		Min inten: 37.		
190			*	0 Maxima				
Mass	%RA	% RIC	Inten.	Mass	%RA	%RIC	Inten.
36.70?F	2.96	0.31	6808.	91.08F	23.78	2.48	54656.
37.74?F	6.70	0.70	15408.	92.10F	15.76	1.64	36224.
38.82?F	89.64	9.33	206080.	93.10F	46.99	4.89	108032.
39.88?F	27.78	2.89	63872.	94.12F	18.68	1.95	42944.
40.90?F	86.75	9.03	199424.	95.12F	11.39	1.19	26176.
41.94?F	17.93	1.87	41216.	96.12F	2.37	0.25	5448.
42.98?F	11.78	1.23	27072.	97.14F	0.68	0.07	1574.
43.94F	7.60	0.79	17472.	98.14F	0.14	0.01	324.
45.02F	0.58	0.06	1326.	99.14	0.02	0.00	40.
46.04F	0.30	0.03	686.	101.08F	0.02	0.00	43.
48.02F	0.05	0.00	106.	102.08F	0.22	0.02	501.
49.00F	0.66	0.07	1526.	103.08F	1.30	0.13	2980.
50.08F	8.00	0.83	18400.	104.10F	0.48	0.05	1114.
51.08F	18.12	1.89	41664.	105.10F	6.80	0.71	15632.
52.06F	8.16	0.85	18752.	106.12F	2.42	0.25	5560.
53.08F	57.46	5.98	132096.	107.12F	14.87	1.55	34176.
54.10F	5.67	0.59	13024.	108.14F	4.23	0.44	9728.
55.10F	32.74	3.41	75264.	109.14F	1.74	0.18	4004.
56.14F	4.33	0.45	9952.	110.14F	0.65	0.07	1500.
57.18F	1.85	0.19	4264.	111.16F	0.11	0.01	250.
58.10F	1.34	0.14	3084.	112.16F	0.13	0.01	299.
59.08F	0.59	0.06	1366.	113.32M	0.02	0.00	37.
60.78F	1.09	0.11	2516.	115.08F	0.74	0.08	1696.
62.08F	2.06	0.21	4736.	116.12F	0.16	0.02	371.
63.06F	5.16	0.54	11872.	117.10F	0.68	0.07	1572.
64.06F	1.05	0.11	2420.	118.12F	0.10	0.01	238.
65.04F	15.12	1.57	34752.	119.12F	2.60	0.27	5968.
66.04F	5.11	0.53	11744.	120.14F	0.88	0.09	2026.
67.08F	88.31	9.20	203008.	121.14F	10.87	1.13	24992.
68.08F	100.00	10.41	229888.	122.16F	1.53	0.16	3520.
69.10F	15.81	1.65	36352.	123.16F	0.98	0.10	2260.
70.10F	5.24	0.55	12048.	124.18F	0.30	0.03	700.
71.10F	0.49	0.05	1126.	125.18	0.02	0.00	38.
72.10F	0.05	0.00	106.	128.10	0.04	0.00	85.
73.04F	0.05	0.00	109.	129.10	0.02	0.00	56.
74.02F	0.49	0.05	1118.	131.14F	0.07	0.01	160.
75.04F	0.41	0.04	951.	132.14F	0.06	0.01	145.
76.04F	0.33	0.03	755.	133.14F	0.38	0.04	873.
77.04F	24.16	2.52	55552.	134.14F	0.95	0.10	2188.
78.06F	5.40	0.56	12416.	135.16F	0.59	0.06	1366.
79.06F	39.14	4.08	89984.	136.16F	9.42	0.98	21664.
80.08F	12.92	1.35	29696.	137.18F	1.06	0.11	2444.
81.08F	17.07	1.78	39232.	138.18F	0.58	0.06	1338.
82.10F	5.92	0.62	13600.	139.18F	0.03	0.00	79.
83.10F	1.14	0.12	2628.	147.16F	0.08	0.01	176.
84.10F	0.70	0.07	1620.	148.18F	0.20	0.02	462.
85.12F	0.11	0.01	246.	149.20F	0.06	0.01	128.
86.06F	0.12	0.01	269.	150.20F	0.18	0.02	407.
87.08F	0.16	0.02	363.	152.22	0.04	0.00	84.
89.04F	0.68	0.07	1568.	162.20	0.04	0.00	81.
90.06F	0.14	0.01	319.	163.20	0.02	0.00	40.

RIC + MASS CHROMATOGRAMS   SCANS   1 TO 1732

CONDS.: TGA
RANGE: G 1.1732 LABEL N 0. 4.0 QUAN: A 0. 1.0 J 0 BASE: U 20. 3

100.0   342520.

68   68.020
                                                                      ± 0.500

0.0   30720.

136   136.041
                                                                      ± 0.500

0.0   168.

204   204.061
                                                                      ± 0.500

802.4   2748410.

RIC

          167   235   299   367   435   499   Temperature(°C)
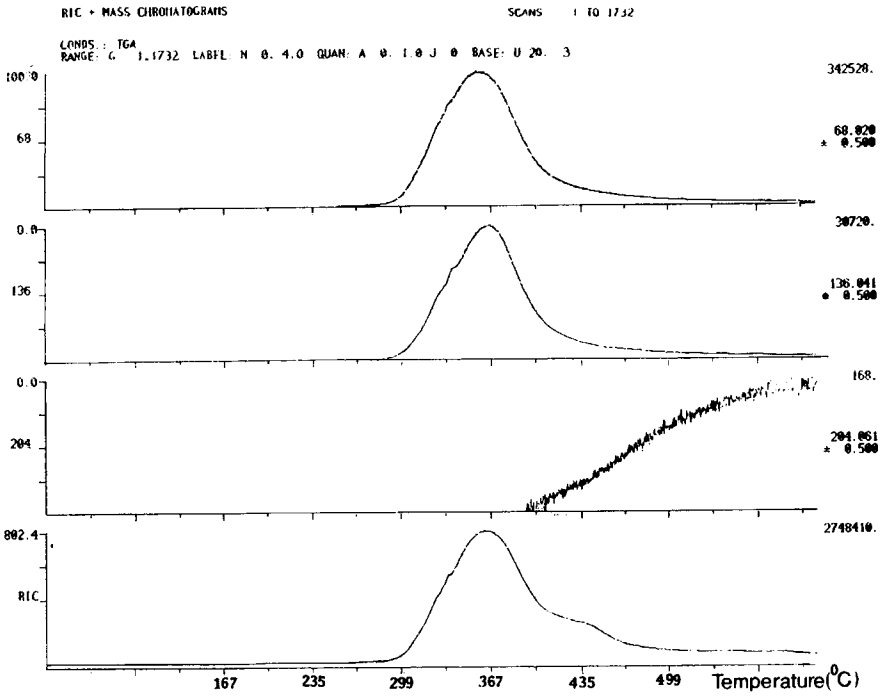
Fig. 7. Variation of the ion current of individual fragments in mass spectroscopy with temperature.

MASS SPECTRUM   BASE M/E: 68
                                                   RIC: 2781180.
CONDS.: TGA   68.1

100.0   340992.

        39.0

        53.0

50.0   93.1

                        79.0

        29.1

                               107.1
                                      121.1   136.1
                                                      148.1 162.1   190.2
M/E   40   60   80   100   120   140   160   180
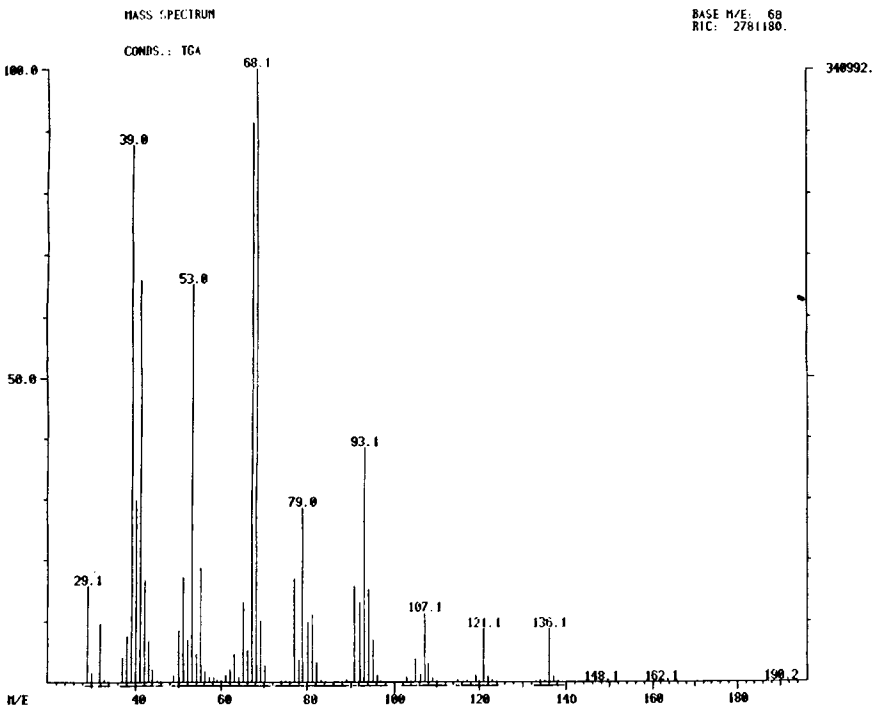
Fig. 8. The concentration of different fragments obtained in mass spectra analysis of pyrolyzed products of guayule rubber at 360° C.
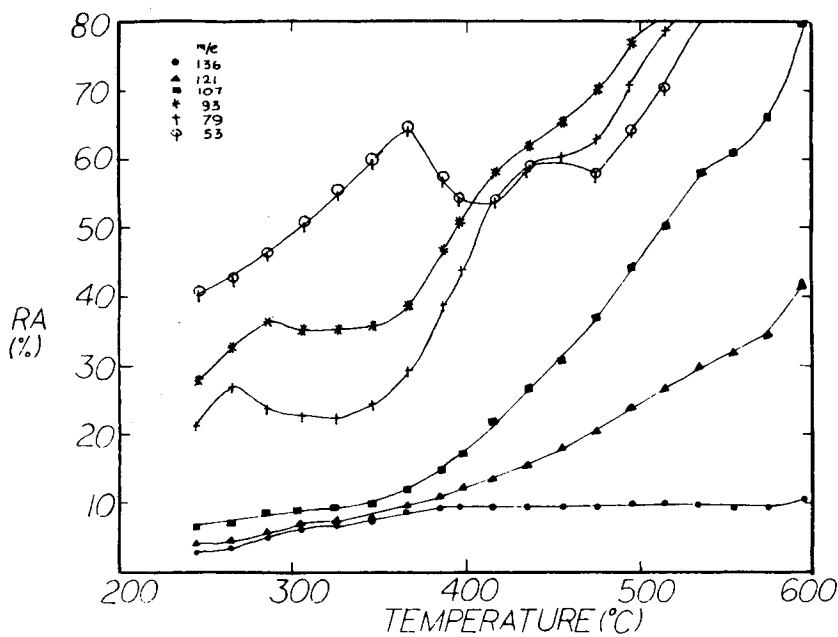
Fig. 9. Concentration of major products of m/e 136, 121, 107, 93, 79, and 53 relative to the amount of isoprene, plotted against temperature of degradation of pure guayule rubber.
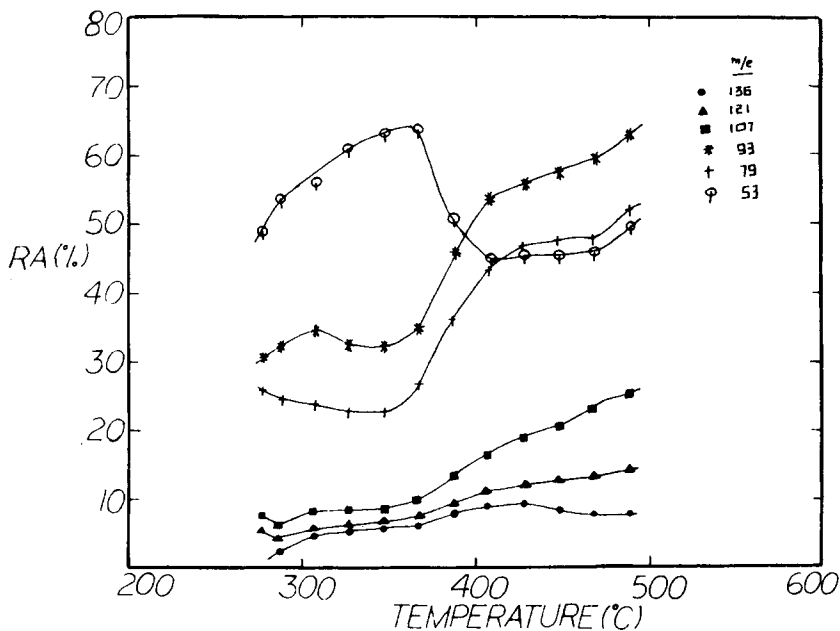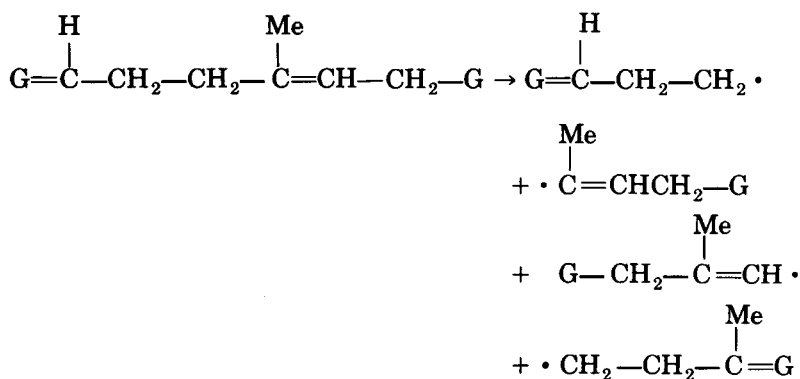

Fig. 10. Effect of linoleic acid on the concentration of major products relative to that of isoprene at different temperatures.

linear throughout. The dipentene as soon as it is generated is converted to lower fragments including isoprene. Hence, intensity of lower fragments increases. The conversion to different fragments is dependent on temperature and the stability of the intermediate products. Jernejcie and Premru[5] have observed a decrease in mole% of dipentene with increase in temperature in their work at 550°C and 750°C.
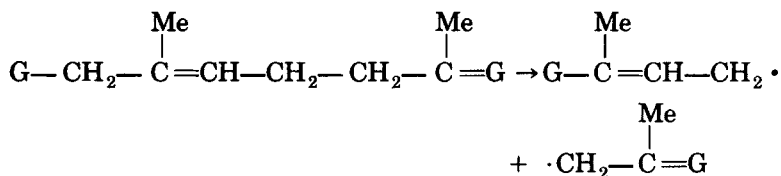
The effect of additive (for example linoleic acid) is shown in Figure 10. The products that are formed during pyrolysis are similar to those for pure natural rubber. The relative trend of the products with decomposition temperature is the same as described earlier. But the %RAs of the different fragments (136, 121, 107, 93, 79, 53) are lower than those of the original rubber after the maximum in isoprene or dipentene concentration (around 360°C). Below this maximum temperature, the trend is not regular. For comparison, the products formed at 385°C are given in Table IV. The products are formed at much lower concentration. It has been observed[1] that below 125°C the rubber degrades by forming smaller molecules which do not volatilize and that the degradation is enhanced in the presence of linoleic acid or unsaturated acids containing double bonds.

The initiation of rubber decomposition follows from radical generation as suggested by Madorsky[2,3] and later authors[6] where α and β are relative to the methyl group.

α chain scission

$$
\begin{array}{c}
\overset{H}{\underset{|}{G=C}}-CH_2-CH_2-\overset{Me}{\underset{|}{C}}=CH-CH_2-G \rightarrow G=\overset{H}{\underset{|}{C}}-CH_2-CH_2 \cdot
\end{array}
$$

$$+ \cdot \overset{Me}{\underset{|}{C}}=CHCH_2-G$$

$$+ \quad G-CH_2-\overset{Me}{\underset{|}{C}}=CH \cdot$$

$$+ \cdot CH_2-CH_2-\overset{Me}{\underset{|}{C}}=G$$

β chain scission

$$G-CH_2-\overset{Me}{\underset{|}{C}}=CH-CH_2-CH_2-\overset{Me}{\underset{|}{C}}=G \rightarrow G-\overset{Me}{\underset{|}{C}}=CH-CH_2 \cdot$$

$$+ \cdot CH_2-\overset{Me}{\underset{|}{C}}=G$$

methyl scission

$$G-CH_2-\overset{Me}{\underset{|}{C}}=CH-CH_2-G \rightarrow Me \cdot + G-CH_2-\overset{\cdot}{C}=CH-CH_2-G$$
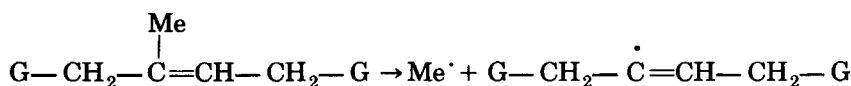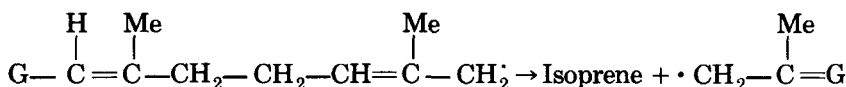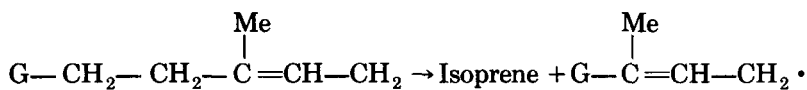
TABLE IV
Mass List of Pyrolysis Products of Linoleic Acid-Rubber Mixture at 385° C in Helium

Conds.: TGA			Base m/e: 68			RIC: 607232.		
35	0.00	0.00		0. Minima		Min Inten: 0.		
150			* 0 Maxima					
Mass	%RA	%RIC	Inten.	Mass	%RA	%RIC	Inten.
36.70?F	2.28	0.25	1508.	91.06F	21.13	2.30	13984.
37.72?F	5.34	0.58	3536.	92.06F	15.28	1.67	10112.
38.82?F	76.50	8.34	50624.	93.08F	45.99	5.01	30432.
39.86?F	26.50	2.89	17536.	94.08F	18.04	1.97	11936.
40.88?F	70.12	7.64	46400.	95.10F	10.00	1.09	6616.
41.92?F	14.31	1.56	9472.	96.10F	1.78	0.19	1176.
42.96?F	9.73	1.06	6440.	97.12F	0.49	0.05	324.
43.92F	12.77	1.39	8448.	98.14	0.08	0.01	53.
45.00F	0.49	0.05	327.	99.26	0.02	0.00	13.
45.98F	0.14	0.02	94.	101.18	0.01	0.00	9.
49.04F	0.48	0.05	320.	102.06	0.11	0.01	74.
50.06F	6.52	0.71	4312.	103.08F	1.03	0.11	680.
51.08F	16.20	1.77	10720.	104.06F	0.34	0.04	225.
52.08F	7.41	0.81	4904.	105.08F	5.68	0.62	3760.
53.08F	50.77	5.53	33600.	106.08F	1.88	0.20	1242.
54.12F	4.83	0.53	3196.	107.10F	13.54	1.48	8960.
55.10F	24.71	2.69	16352.	108.10F	3.72	0.41	2460.
56.10F	3.38	0.37	2240.	109.10F	1.17	0.13	777.
57.16F	1.41	0.15	932.	110.10F	0.38	0.04	254.
58.06F	1.22	0.13	805.	111.10	0.05	0.01	36.
59.04F	0.52	0.06	341.	112.08	0.07	0.01	45.
60.02F	0.15	0.02	100.	115.08	0.52	0.06	346.
61.02F	0.63	0.07	420.	116.06	0.08	0.01	50.
62.04F	1.65	0.18	1090.	117.10	0.45	0.05	296.
63.04F	4.55	0.50	3008.	118.14F	0.05	0.01	35.
64.06F	0.91	0.10	605.	119.10F	1.95	0.21	1290.
65.04F	13.64	1.49	9024.	120.12F	0.53	0.06	352.
66.02F	5.07	0.55	3356.	121.12F	9.72	1.06	6432.
67.06F	85.40	9.31	56512.	122.14F	1.21	0.13	804.
68.06F	100.00	10.90	66176.	123.14F	0.59	0.06	390.
69.06F	13.71	1.49	9072.	124.16	0.15	0.02	98.
70.08F	3.92	0.43	2596.	128.16	0.01	0.00	9.
71.08F	0.28	0.03	183.	131.08	0.03	0.00	19.
72.28	0.02	0.00	16.	132.04	0.02	0.00	16.
73.98F	0.35	0.04	230.	133.12	0.15	0.02	99.
75.02F	0.27	0.03	178.	134.12	0.59	0.06	388.
76.00F	0.19	0.02	125.	135.14F	0.25	0.03	167.
77.04F	22.44	2.45	14848.	136.14F	8.15	0.89	5392.
78.04F	5.04	0.55	3332.	137.14F	0.83	0.09	549.
79.04F	36.32	3.96	24032.	138.16F	0.32	0.03	210.
80.06F	12.02	1.31	7952.	147.24	0.01	0.00	9.
81.06F	14.51	1.58	9600.	148.14	0.06	0.01	39.
82.08F	4.88	0.53	3232.	149.22	0.02	0.00	11.
83.08F	0.76	0.08	504.	150.18	0.06	0.01	41.
84.08F	0.38	0.04	250.				
85.08	0.05	0.01	33.				
86.02	0.07	0.01	44.				
87.04F	0.09	0.01	60.				
88.00F	0.08	0.01	56.				
89.04	0.49	0.05	326.				
89.98F	0.07	0.01	44.				

The formation of isoprene and dipentene can be visualized in terms of the following general depolymerization reactions of chain radicals into monomer (isoprene) and dimer (dipentene), or smaller fragments.

(i) *Unzipping to monomer*

$$G-CH_2-CH_2-\underset{\underset{Me}{|}}{C}=CH-CH_2 \rightarrow \text{Isoprene} + G-\underset{\underset{Me}{|}}{C}=CH-CH_2 \cdot$$

$$G-\underset{\underset{H}{|}}{C}=\underset{\underset{Me}{|}}{C}-CH_2-CH_2-CH=\underset{\underset{Me}{|}}{C}-CH_2^{\cdot} \rightarrow \text{Isoprene} + \cdot CH_2-\underset{\underset{Me}{|}}{C}=G$$

(ii) *Dimer formation*
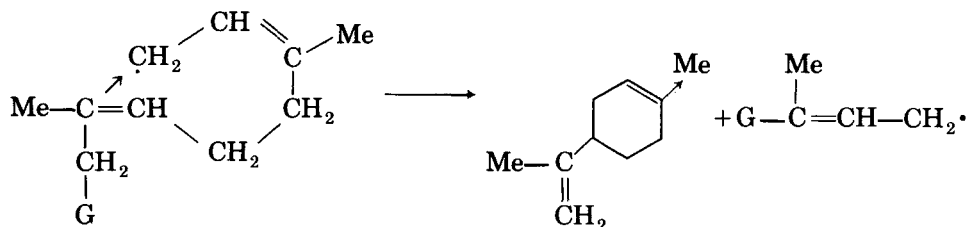
The abundance of dipentene relative to 1,5-dimethyl-5-vinyl cyclohexene suggests the greater stability of dipentene due to its hyperconjugation of the accompanying radical and steric hindrance of methyl groups in the latter.

(iii) *Fragment formation*

The smaller products (C_3, C_4 and C_2) obtained here are the result of the less likely pyrolysis of the original chain at different position or the more likely decomposition of intermediate products at higher temperatures. For example,

$$G-\underset{\underset{Me}{|}}{C}=\underset{\underset{H}{|}}{C}-CH_2-CH_2^{\cdot} \longrightarrow C_2H_4 + CH_3-CH=CH_2$$

136   121
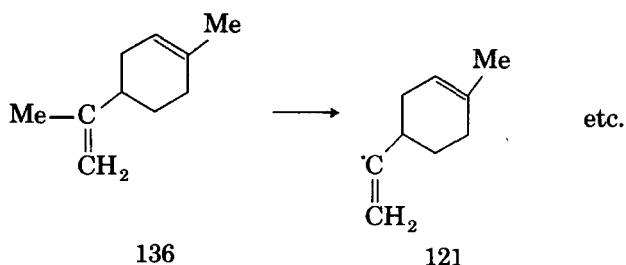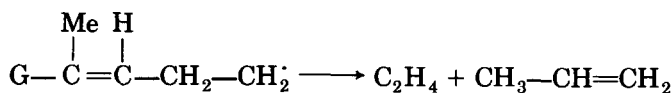
Acids thus neither increase the overall rate of degradation or the degradation product.

This small effect of the acids on the mechanism of high temperature degradation is surprising. Presumably the radical chains are either stabilized in the presence of the acids or transferred to the acids and terminated. Since the acid is only present in a 5% concentration, the same products and rates are measured.

References

1. A. K. Bhowmick, S. Rampalli, and D. McIntyre, *J. Appl. Polym. Sci.*, **30**, 2367 (1985).
2. S. L. Madorsky, S. Strauss, D. Thompson, and L. Williamson, *J. Res. Natl. Bur. Std.* **42**, 499 (1949).
3. S. Strauss and S. L. Madorsky, *Ind. Eng. Chem.*, **43**, 1212 (1956).
4. M. G. Vacherot, *Eur. Polym. J.*, **7**, 1455 (1971).
5. M. Jernejcie and L. Premru, *Rubber Chem. Technol.*, **41**, 411 (1968).
6. J. C. W. Chien and J. K. Y. Kiang, *Eur. Polym. J.*, **15**, 1059 (1979).
7. I. R. Gelling, M. J. Loadman, and B. D. Sidek, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 1383 (1979).
8. E. M. Bevilacqua, E. S. English, J. S. Gall, and P. M. Norling, *J. Appl. Polym. Sci.*, **8**, 1029 (1964).
9. J. U. Voigt and W. Scheele, *Kaut. Gummi Kunststoffe*, **22**, 467 (1969).
10. M. A. Ponce-Velez and E. Campos-Lopez, *J. Appl. Polym. Sci.*, **22**, 2485 (1978).
11. R. W. Keller and H. L. Stephens, *Rubber Chem. Technol.*, **54**, 161 (1982).
12. L. Reich, H. T. Lee, and D. W. Levi, *Polym. Letter*, **1**, 535 (1963).
13. E. S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).