Effects of Environment and Composition on Degradation of Guayule Rubber

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SYNOPSIS

Bales of antioxidant-stabilized guayule rubber underwent significant losses in bulk viscosity when stored under ambient conditions at an Arizona processing facility. Previous work implicated the unsaturated fatty acid esters present in entrained resin as promoters of such degradation. Aging studies as functions of storage temperature and unsaturated acid ester content were carried out on both bulk rubber and rubber–resin solution (miscella) for cultivar AZ-101. The rate of thermooxidative degradation, determined as a function of Mooney viscosity, was increased by the addition of unsaturated ester. Anaerobic degradation was not affected in this way. The activation energy of chain thermolysis was found to be 116 ± 6 kJ/mol (28 ± 1 kcal/mol). At temperatures above 60°C, chain recombination successfully competed with chain scission in lower viscosity rubber. The rate of thermooxidative degradation was substantially higher in a typical process miscella. A hindered amine antioxidant significantly reduces chain scission under these conditions. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

To provide guayule (*Parthenium argentatum* Gray) rubber (GR) for testing in tire compounds, Bridgestone/Firestone, Inc. recently operated a prototype processing facility in Sacaton, AZ. Rubber was extracted from the ground and flaked shrub by means of a simultaneous extraction and rubber fractionation (SERF) process using pentane–acetone as the solvent.[1] This approach permitted the selective isolation of a high molecular weight fraction with physical properties equivalent to that of grade 20 natural rubber (NR) from *Hevea brasiliensis* Muell. Arg. A low molecular weight coproduct (LGR) was isolated subsequently from fractionator overheads. During the initial period of operations, several bale lots of GR were found to have undergone significant losses in bulk viscosity, determined as Wallace plasticity (P_0) (Table I). These particular lots had been stored in an unventilated trailer for periods of up to 9 months at temperatures as high as 65°C. Viscosity changes were unexpected because all samples had been found to have high plasticity retention indices (PRI) and had been stabilized with Santoflex 134 (Monsanto), an effective antioxidant and antiozonant.

The geometry of the bales and their physical arrangement in the storage facility were such that little of the rubber mass was exposed to air. Nevertheless, unsaturated fatty acids present as triglycerides in baled GR have been implicated as potentiators of thermooxidative degradation.[2,3] A consequence of the partition process is that the nonrubber components (resin) entrained in both GR and LGR could be enriched in these triglycerides. An understanding of the effect of storage temperature and resin content on GR bulk viscosity would be an important tool in assuring product quality for polyisoprene from a variety of natural sources.

We report here the results of accelerated heat aging studies of GR and LGR as functions of temperature, unsaturated fatty acid residue concentration, and aging environment. These results allowed the prediction of thermal degradation rates under conventional storage conditions. We also report the ob-

Table I Bulk Viscosity Retention in SERF Process GR

	Plasticity (P_0)		Storage Period (days)	P_0 Retention (%)
Lot	Initial	Retest		
062488	41	34	228	83
081288	40	35	190	88
081588	42	39	190	93
081888	43	33	190	77
012789	37	33	37	89

servation of competitive chain-cleavage and cross-linking reactions in the bulk polymer.

EXPERIMENTAL

Analysis and Physical Testing

Bulk viscosities for production lots are reported as Wallace plasticities (P_0). Bulk viscosities for heat-aged samples are reported as Mooney viscosities (ML1 + 4) determined at 100°C with a Monsanto shearing disk viscometer. Molecular weights were determined by size exclusion chromatography in tetrahydrofuran (THF) as reported earlier.[4] Mark–Houwink constants were K = 1.91 × 10^{-4} dL/g, α = 0.74. Resin contents were determined by exhaustive acetone extraction of sheeted rubber samples in a Soxhlet extraction apparatus. Rubber samples were ashed at 600°C and the ash analyzed for zinc by atomic absorption spectroscopy on a Perkin–Elmer 1100B spectrometer. Zinc dibutyldithiocarbamate in LGR was calculated on the basis of zinc content. The linoleate content of sunflower seed oil was analyzed in $CDCl_3$ by ^{1}H-NMR (200 MHz) on a Varian Gemini-200 spectrometer. The area of the signal[5] at δ2.75 ppm (C=C—C$\underline{H_2}$—C=C) was compared to that of the signal at δ3.67 ppm (C$\underline{H_2}$—O) from a dioxane internal standard.

GR

Rubber for the determination of molecular weights was isolated from the cultivar AZ-101 shrub maintained on land of the Gila River Indian Community. The shrub was defoliated, ground, flaked, and extracted with acetone–pentane azeotrope (21 : 79 w/w) at the Akron, OH pilot plant operated by Bridgestone/Firestone, Inc. GR was isolated from the resulting miscella by coagulation with acetone con-

taining Santoflex 13 (Monsanto) followed by drum drying of the swollen polymer.

Samples for aging studies were taken from a single bale produced at the Sacaton, AZ pilot plant (Table II). No zinc dibutyldithiocarbamate (Butyl Zimate, Vanderbilt) had been used in the course of the bale's manufacture. At the University of Akron's EPIC minipilot polymerization plant, 2.26 kg of GR were dissolved in sufficient hexane to produce a 5% (w/w) cement. The cement was passed through a filter cartridge fitted with a 100-mesh screen to remove particulates, primarily shrub fragments, then coagulated by pouring into acetone at a 6 : 1 (v/v) acetone–cement ratio. Desolventization of the swollen, coagulated polymer was carried out at 35°C in a vacuum oven to yield 2.15 kg (92%) of GR. The resin content of the GR was 0.24%.

LGR

A 2.28-kg sample of LGR was provided by the Engineering Biosciences Research Center of Texas A&M University (TAMU). This material, a composite of "secondary rubber" produced during operation of a guayule pilot processing facility,[1] had been stored at 5°C prior to shipment. A 2.15-kg sample of the LGR was homogenized and purified as described above. Desolventization of the swollen polymer yielded 1.97 kg (92%) of LGR. Table II summarizes bulk viscosity and resin content data for this material.

A low-resin, dithiocarbamate-free sample of low molecular weight polymer was prepared by placing 700 g of GR on a cold two-roll mill set to a 2.9-mm nip for 7.0 min.

Table II Guayule Rubber Characterization, Representative Samples

Sample	ML1 + 4 (100°C)	Acetone Extract (%)
GR	99.6[a]	2.2
LGR	39.2[b]	1.7
	43.0[c]	0.4

[a] Sample used in this study. Bale as produced at Sacaton, AZ pilot plant. Contained Santoflex 134.

[b] As received from TAMU. Material sampled from middle of polymer mass.

[c] TAMU material after recoagulation. Contained 0.03 phr zinc dibutyldithiocarbamate.

Table III   Effect of Linoleate on GR Bulk Viscosity and Thermolysis Rate (K) in a Forced-Air Oven at 60°C

Linoleate[a] (phr)	t (days)	ML1 + 4 (100°C)	DP_n	$K \times 10^{11}$ s^{-1}
0	0	100.0	4948	
	1	90.9	4383	
	2	97.0	4755	
	4	97.0	4755	
	8	97.0	4755	
	16	87.9	4204	
	23	90.9	4383	
	42	69.7	3234	
	60	60.6	2815	2.8 ± 0.3
2	0	97.0	4755	
	7	87.9	4204	
	14	75.8	3538	
	21	63.6	2950	
	28	54.5	2560	7.6 ± 0.5

[a] From sunflower seed oil.

Test Sample Preparation

Sunflower Seed Oil Spike

A hexane cement (4.4%) containing 2.10 kg of GR, 21.0 g of Santoflex 13 (Monsanto), and 54.0 g of sunflower seed oil was drum dried at the Central Research Laboratories of Bridgestone/Firestone, Inc., to yield five 360-g samples of rubber.

Linoleate Spike

Hexane cements (10.0% w/w) containing 230.0 g of GR, 2.3 g of Santoflex 134 (Monsanto), and 0.0, 4.6, and 9.2 g, respectively, of methyl linoleate were drum dried to yield samples for heat aging. Three batches of LGR both with and without methyl linoleate were also prepared. Rubber recoveries averaged 93%, based on cement charged to the dryer. Each sample was passed once through a two-roll mill to provide sheets with a uniform thickness of about 1 cm.

Accelerated Oven Aging

Forced-Air Oven

GR samples weighing 360–450 g each were placed in aluminum pans (2 × 20 × 5 cm). A second pan was stapled over each to prevent direct exposure to the air flow. The covered samples were placed in a Blue M forced-air oven maintained at 60 ± 2°C. Duplicate samples for bulk viscosity determination were removed from random positions within the

oven. Controls stored at room temperature were tested on days 0 and 60. Table III summarizes Mooney viscosity data for unaged and aged samples.

Nitrogen Atmosphere

GR and LGR samples, approximately 4 × 4 × 1 cm (14 g) each, were placed in aluminum pans in a Napco Model 5831 vacuum oven fitted with a door latch for operation at ambient pressure and preheated to the desired temperature (±2°C). The oven was evacuated, then vented to ambient pressure with nitrogen. When samples were removed for analysis, this evacuation-venting sequence was used to restore the inert atmosphere. Tables IV–VI summarize Mooney viscosity data for unaged and aged samples.

Resin Component Partition During Coagulation

A model miscella was prepared from 10.00 g of antioxidant-free GR, 5.00 g of sunflower seed oil, and 5.00 g of resin saponification neutrals[6] in 80.00 g of 21 : 79 acetone : pentane (w/w). A 70.00-g sample of the miscella was slowly poured into 385 g of acetone in a 500-mL capacity centrifuge bottle. The bottle was sealed and placed on a Glas-Col labora-

Table IV   Effect of Temperature on GR Bulk Viscosity and Thermolysis Rate (K) in N$_2$ Atmosphere

T (°C)	t (days)	ML1 + 4 (100°C)	DP_n	$K \times 10^{11}$ s^{-1}
60	0	97.8	4807	
	7	94.6	4607	
	14	91.4	4412	
	35	87.3	4171	
	56	74.0	3448	
	77	62.5	2899	2.0 ± 0.2[a]
75	0	97.8	4807	
	3	87.8	4200	
	5	74.2	3458	
	7	75.6	3530	14 ± 4[b]
	14	72.5	3373	
	21	74.5	3474	
90	0	97.8	4807	
	1	80.0	3763	
	2	62.4	2894	
	3	46.2	2240	
	4	54.2	2546	64 ± 17[c]
	5	49.0	2343	
	6	50.6	2404	

[a] Days 0–77.
[b] Days 0–7.
[c] Days 0–4.

Table V   Effect of Linoleate on GR Bulk Viscosity and Thermolysis Rate (K) at 60°C in N_2 Atmosphere

Linoleate[a] (phr)	t (days)	ML1 + 4 (100°C)	DP_n	$K \times 10^{11}$ s^{-1}
0	0	97.8	4807	
	7	94.6	4607	
	14	91.4	4412	
	35	87.3	4171	
	56	74.0	3448	
	77	62.5	2899	2.0 ± 0.2
2	0	92.6	4485	
	7	87.6	4188	
	14	83.6	3960	
	21	82.0	3872	
	35	77.2	3613	
	49	71.7	3333	
	63	64.0	3967	1.9 ± 0.1
4	0	84.3	4000	
	7	78.8	3698	
	14	73.5	3423	
	21	71.0	3298	
	35	69.5	3225	
	49	63.5	2944	
	63	55.9	2615	2.2 ± 0.2

[a] From methyl linoleate.

tory rotator for 60 min to equilibrate the phases. The bottle was then centrifuged at 1500 rpm for 20 min and the overheads decanted. Vacuum desolventization of the overheads yielded 6.67 g of residue. The proton signal at $\delta 5.30$ ppm ($\underline{HC}\!=\!\underline{CH}$ and $\underline{CH}\!-\!OOC$) was quantified by comparison with known oil–neutrals mixtures. On this basis, the overhead residue was found to contain 3.24 g of triglycerides and 3.43 g of neutrals. By difference, the coagulated rubber contained 0.26 g of triglycerides and 0.07 g of neutrals.

Miscella Aging and Stabilization

To a 45-L jacketed reactor fitted with a Rushton turbine agitator was charged 550 g of resin-free GR and the appropriate quantity of antioxidant. To remove oxygen, the reactor was sealed, pressurized with nitrogen to 345 kPa, then vented to 35 kPa. This process was repeated nine times. Using nitrogen pressure, 5.90 kg of 21 : 79 acetone : pentane (w/w) was charged to the reactor. The reactor contents were agitated at 52°C for 12 h to dissolve the rubber. A mixture of 1.10 kg of resin in 900 g of acetone-pentane was charged to the reactor using nitrogen pressure. The reactor was then pressurized

to an additional 138 kPa with air introduced through the reactor bottom. Initial miscella samples were taken at this time. Agitation at 52°C was continued until sampling was completed. Miscella samples were transferred into a 1.5-L sampling cylinder containing 5.0 g of Santoflex 13 dissolved in 250 mL of acetone–pentane. Rubber was coagulated from the sample by slowly emptying the cylinder contents into about 13.5 L of acetone containing 25.0 g of Santoflex 13. The resulting swollen rubber was desolventized on a drum dryer. Mooney viscosity data for GR recovered from unstabilized and stabilized miscellas are summarized in Tables VII and VIII.

RESULTS AND DISCUSSION

Resin Composition

Guayule resin is a complex and variable mixture of secondary metabolites, including various terpenoids and fatty acid triglycerides.[6] These triglycerides contain a high proportion of unsaturated fatty acid residues, with an overall triglyceride composition similar to that of soybean or sunflower seed oils. Triglycerides can constitute as much as 51% of the resin by weight.[7]

The resin extracted from the intact shrub was not necessarily the same as the resin that ended up

Table VI   Effect of Linoleate on LGR Bulk at 75°C in N_2 Atmosphere

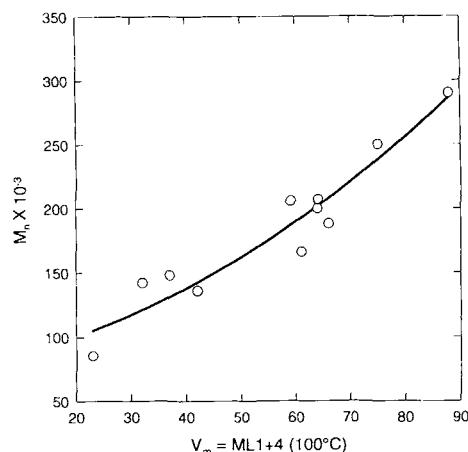| Origin	Linoleate[a] (phr)	t (days)	ML1 + 4 (100°C)
Secondary rubber, TAMU pilot plant	0	0	43.0
		3	41.9
		7	41.8
		17	40.5
		27	45.0
		37	49.0
Milled GR	0	0	92.6
		7	87.6
		14	83.6
		21	82.0
	2	0	31.1
		7	28.1
		14	29.4
		21	31.1
	4	0	28.5
		7	24.9
		14	25.8
		21	26.2

[a] From methyl linoleate.

Table VII   Effect of Santoflex 13 on GR Bulk Viscosity and Degradation Rate (K) at 52°C in Air Atmosphere

Antioxidant (% Miscella Solids)	t (h)	ML1 + 4 (100°C)	DP_n	$K \times 10^{10} \ s^{-1}$
0.0	0	72.5	3373	
	2	70.5	3274	
	5	68.5	3177	
	21	57.5	2682	
	36	49.0	2343	
	75	39.0	1994	7.7 ± 0.6
0.5	0	76.5	3577	
	3	75.5	3525	
	8	76.5	3577	
	26	72.0	3348	
	48	66.5	3082	
	96	56.0	2619	3.0 ± 0.2
1.0	0	75.5	3525	
	3	76.0	3551	
	8	76.0	3551	
	24	66.0	3059	
	48	63.5	2944	
	96	61.0	2832	2.2 ± 0.5
2.0	0	75.5	3525	
	3	76.0	3551	
	8	76.0	3551	
	23	66.0	3059	
	48	63.5	2944	
	98	61.0	2832	2.2 ± 0.5

Table VIII   Effect of BHT on GR Bulk Viscosity and Degradation Rate (K) at 52°C in Air Atmosphere

Antioxidant (% Miscella Solids)	t (h)	ML1 + 4 (100°C)	DP_n	$K \times 10^{10} \ s^{-1}$
0.0	0	72.5	3373	
	2	70.5	3274	
	5	68.5	3177	
	21	57.5	2682	
	36	49.0	2343	
	75	39.0	1994	7.7 ± 0.6
1.0	0	75.0	3499	
	4	75.5	3525	
	8	74.5	3474	
	24	65.0	3012	
	48	63.0	2921	
	96	54.0	2538	3.2 ± 0.4
3.0	0	73.5	3423	
	3	75.5	3525	
	8	71.5	3323	
	24	65.5	3035	
	48	59.0	2746	
	96	48.5	2325	4.2 ± 0.2

Figure 1 GR number-average molecular weight (M_n) as a function of Mooney viscosity (V_m).

in the rubber bale. Coagulation of GR from a typical GR-resin miscella (triglyceride content of the resin: 50% w/w) yielded a rubber phase containing entrained resin (resin content of the rubber: 4.5%) with a triglyceride content of 79%. The resin left in GR was enriched in those components that enhance oxidative degradation.

Thermolysis Mechanism

Thermal degradation involves an initial break in the polymer chain to form free radicals. The change in polymer composition under anaerobic conditions, expressed as the change in the concentration of intact polymer chains (P), is a first-order process[3]

$$\frac{d[\mathrm{P}]}{dt} = -\frac{k_i k_d}{k_d + k_r}[\mathrm{P}] \tag{1}$$

where k_i is the rate of initiation (chain cleavage),

$$\mathrm{P} \rightarrow \mathrm{R}\cdot + \mathrm{R}'\cdot, \tag{2}$$

k_d is the rate of disproportionation (electron transfer between chain fragments to form stable nonradicals),

$$\mathrm{R}\cdot + \mathrm{R}'\cdot \rightarrow \mathrm{R} + \mathrm{R}', \tag{3}$$
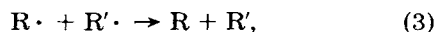
and k_r is the rate of termination (chain fragment recombination),

$$\mathrm{R}\cdot + \mathrm{R}'\cdot \rightarrow \mathrm{P}. \tag{4}$$
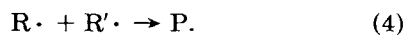
Initiation is very slow in comparison to chain fragment recombination ($k_i \ll k_r$).[8] Adding unsaturated

fatty acid triglyceride (linoleate, linolenate) provides a pathway for chain transfer (electron transfer from chain fragment to triglyceride ester molecule, L):

$$\mathrm{R}\cdot + \mathrm{L} \rightarrow \mathrm{R} + \mathrm{L}\cdot. \tag{5}$$

The chain fragments terminate and can no longer combine to reform intact polymer chains. A substantial increase in the apparent rate of the overall reaction would be anticipated as the triglyceride level is increased.[3]

For a first-order chain cleavage process, the number-average degree of polymerization (DP_n = the number-average molecular weight, M_n, divided by the molecular weight of the isoprene repeat unit) is described by[9]

$$\ln[DP_n/(DP_n - 1)]$$
$$= Kt + \ln[DP_{n_0}/(DP_{n_0} - 1)] \tag{6}$$

where the initial degree of polymerization is DP_{n_0}.

Nair[10] reports that a curvilinear relationship exists between M_n and the Mooney viscosity of NR. As illustrated in Figure 1, the Mooney viscosity (V_m) of GR from the cultivar used in this study is related ($r^2 = 0.913$) to M_n in accordance with

$$M_n = 1.80 \times 10^1 \cdot V_m^2 + 7.94$$
$$\times 10^2 \cdot V_m + 7.75 \times 10^4. \tag{7}$$

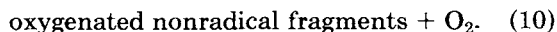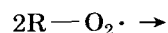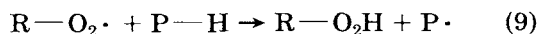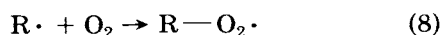Bulk viscosity can therefore serve as an indirect probe of polymer chain cleavage.
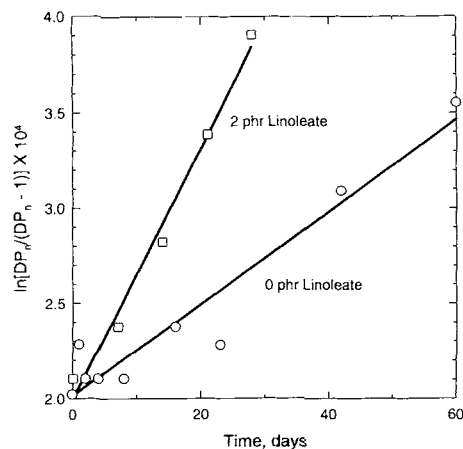
Figure 2 Effect of linoleate on GR number-average degree of polymerization (DP_n) in a forced-air oven at 60°C.
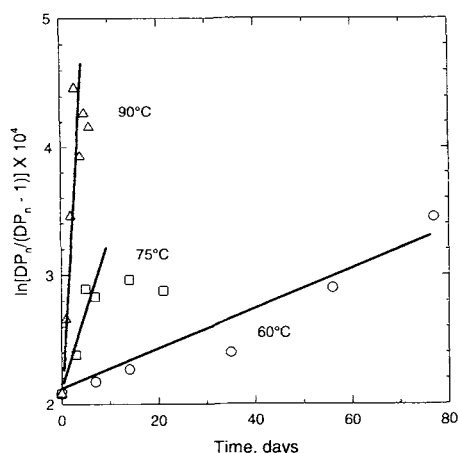
Figure 3 Effect of temperature on GR number-average degree of polymerization (DP_n) in N_2 atmosphere.

Bulk GR Aging

When large-volume (300–400 g) samples were aged at 60°C in a forced-air oven (Table III), plots of $\ln[DP_n/(DP_n - 1)]$ versus time (Fig. 2) yielded linear relationships from which the pseudo zero-order rate constants K were determined. The rate of decrease in bulk viscosity showed a significant dependence on the level of unsaturated fatty acid triglycerides. How much of the rate increase was due to the triglycerides was not clear, because the oxygen in air served as a chain propagation agent. In so doing, it competed for chain fragments:

$$R\cdot + O_2 \to R-O_2\cdot \qquad (8)$$

$$R-O_2\cdot + P-H \to R-O_2H + P\cdot \qquad (9)$$

$$2R-O_2\cdot \to$$

$$\text{oxygenated nonradical fragments} + O_2. \qquad (10)$$

The surface–volume ratio for a typical rubber bale is much smaller than that of the test pieces used here. The overwhelming proportion of the polymer in a bale has little contact with oxygen, at least in the short term. Consequently, the aging process was reevaluated under anaerobic conditions (Table IV). As with the samples aged in air, there was an initial loss in viscosity consistent with random chain cleavage. At temperatures above 60°C, however, this reduction in viscosity eventually stopped. The interval between the onset of viscosity reduction and the onset of apparent viscosity stabilization decreased as the temperature increased. Such changes can be the result of competition between chain cleavage and crosslink formation.
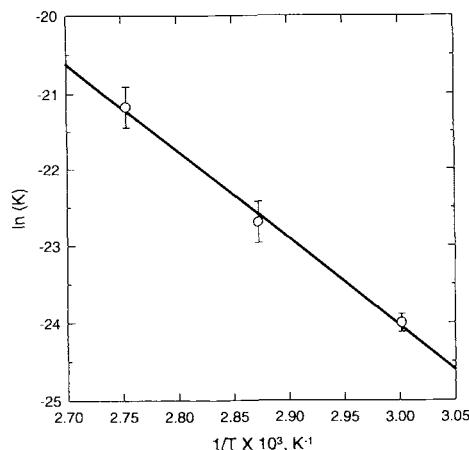
Figure 4 GR degradation rate (K) as a function of temperature.

Values of K were determined from the initial slopes of plots of $\ln[DP_n/(DP_n - 1)]$ versus time over the intervals where random chain cleavage would be expected (Fig. 3). The Arrhenius plot of these data (Fig. 4) is consistent with an activation energy of 116 ± 6 kJ/mol (28 ± 1 kcal/mol). These results may be compared to the values of 95 ± 10 kJ/mol for GR and 90 ± 4 kJ/mol for NR determined by GPC on the sol fractions of aged polymer films.[3]

Table V summarizes the effect of added methyl linoleate on bulk viscosity at 60°C. Differences in the initial bulk viscosities of the GR samples were consequences of the ester's plasticizing effect. The actual rate of chain cleavage determined from bulk viscosity measurements exhibited no dependence on the concentration of linoleate (Fig. 5). Previous studies of the effect of resin components on GR degradation[2,3,11] reported that the rate of chain
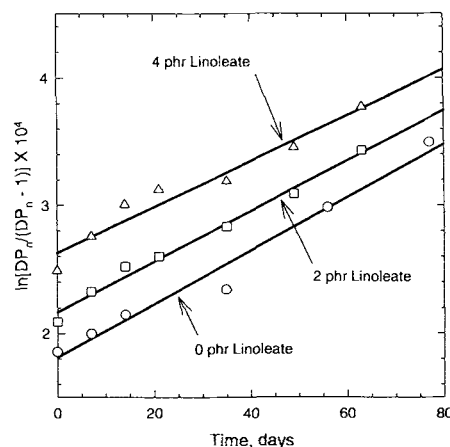
Figure 5 Effect of linoleate on GR number-average degree of polymerization (DP_n) at 75°C in N_2 atmosphere.

cleavage is dependent on the level of fatty acid unsaturation. Therefore, we conclude that chain termination by transfer of hydrogen from the polymer to the unsaturated ester [eq. (5)] competes with both recombination of chain fragments [eq. (4)] and chain fragment addition to undegraded polymer chain [eq. (11)].[12]

$$R\cdot + P \rightarrow RP\cdot. \tag{11}$$

Chain fragment recombination is diffusion controlled.[13] In the bulk polymer, relatively few radical fragments diffuse out of their polymer chain cages to encounter other chains or unsaturated esters. The rate of diffusion would increase as the average chain length decreases. Therefore, at very high conversions the overall rate of degradation would accelerate. Another way to increase the rate of chain end diffusion would be to increase chain mobility by increasing the temperature. However, higher aging temperatures actually lead to conditions where viscosity reduction effectively stops. In this case, chain end mobility is sufficiently high so that addition to intact chains becomes competitive with all other degradative processes.

Bulk LGR Aging

In accordance with the chain cleavage mechanism described above, the initial rate of decrease in the Mooney viscosity at 60°C would be about 0.7 units/day for polymer with an initial viscosity of 100. The corresponding rate of decrease for polymer with an initial Mooney viscosity of 30–40 units (in other words, a typical LGR sample) would be about 0.2 unit/day. This rate increases to 1.3 unit/day at 75°C. Overall, bulk LGR would not be expected to undergo large losses in bulk viscosity under typical storage conditions.

LGR was actually found to have little or no significant long-term loss in viscosity at 75°C (Table VI). There appeared to be some dependence of the initial rate of degradation on the level of linoleate. The initial drop-off in viscosity increased from 0.9 units/day with no added linoleate to 3.0 units/day with 2 phr linoleate, and to 3.6 units/day with 4 phr linoleate. In these instances, the bulk viscosity is sufficiently low so that radical chain ends more easily migrate out of the polymer cage and encounter fatty acid ester. However, linoleate-free LGR actually underwent a 19% net *increase* in Mooney viscosity after 21 days.

When we observed a 14% increase in Mooney viscosity for LGR that contained 0.03 phr of Butyl

Zimate, we were concerned that this particular antidegradant may have somehow effected polymer chain crosslinking. The results obtained with dithiocarbamate-free LGR are consistent with the explanation that the increase was due, at least in part, to thermally induced gel formation. Chain fragment diffusion and subsequent addition to intact polymer [eq. (11)] are more likely in LGR. We anticipate that adequately stabilized LGR should exhibit excellent storage properties after recovery from the rubber–resin miscella.

GR Miscella Aging

The time that the rubber spent in solution during processing is brief in comparison to the time spent in storage after processing. Nevertheless, a low concentration of polymer in the miscella, contact with air and resin, and an elevated processing temperature (52°C) provide conditions favorable to degradation once the rubber is extracted.

GR maintained at 52°C in a model SERF process miscella (1 : 2 GR : resin in acetone-pentane, GR content 6.5% w/w) underwent rapid degradation (Table VII). As with bulk GR, the change in Mooney viscosity followed pseudo first-order kinetics (Figs. 6, 7). The observed rate $(7.7 \times 10^{-10} \text{ s}^{-1})$ for antioxidant-free rubber was 50 times faster than the rate $(1.6 \times 10^{-11} \text{ s}^{-1})$ calculated for bulk polymer from Arrhenius plot data. In solution, chain fragments rapidly diffuse out of polymer chain cages, decreasing the likelihood of recombination or gel formation. Air present in the reactor head space accelerates the overall rate of degradation. Under typical processing conditions where recycled miscella is used as the
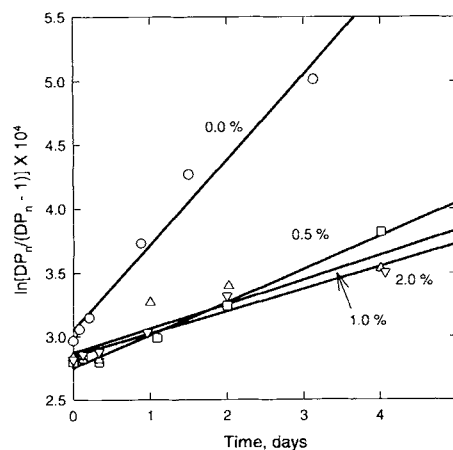
Figure 6 Effect of Santoflex 13 on GR number-average degree of polymerization (DP_n) in miscella at 52°C in N_2 atmosphere.
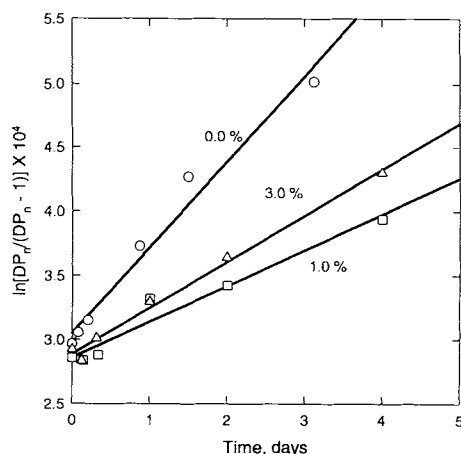
Figure 7 Effect of BHT on GR number-average degree of polymerization (DP_n) in miscella at 52°C in N_2 atmosphere.

extraction solvent, stabilization with effective antidegradants becomes crucial.[14]

Amine and phenolic antioxidants are effective in decreasing the rate of degradation (Tables VII, VIII). Santoflex 13, a representative alkylated p-phenylenediamine, provides a significant rate reduction at levels as low as 0.5% of miscella solids (Fig. 6). BHT (di-t-butyl-p-cresol), a representative monohydric hindered phenol, is somewhat less effective at the same level (Fig. 7). Nevertheless, BHT has an important processing advantage: it can be recovered from desolventized, rubber-free miscella.[15]

CONCLUSION

Anaerobic thermal degradation of bulk GR, while leading to significant viscosity losses over time, is insensitive to the level of unsaturated fatty acid triglycerides in entrained resin. Chain recombination successfully competes with chain cleavage at higher temperatures ($\geq$75°C). This is especially true for the low-viscosity coproduct rubber. Oxidative degradation does show a sensitivity to triglyceride level, however. In solution prior to coagulation and baling, GR is especially susceptible to chain cleavage. The use of a hindered amine antioxidant significantly reduces degradation under these conditions.

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