INTRINSIC DEFECTS AND THE FAILURE PROPERTIES OF *cis*-1,4-POLYISOPRENES

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ABSTRACT

Inherent flaw sizes were determined from fatigue lifetimes, and from the crack length dependence of the strain energy to break, for four *cis*-1,4-polyisoprenes compounded to have the same crosslink density and low strain hysteresis. Both techniques indicated that the flaws intrinsic to guayule rubber (GR), and to a lesser extent conventional natural rubber, are larger than those found in deproteinized NR. This result may not be surprising; however, the failure properties of the elastomers, expected to depend on flaw size, were surprising. The guayule rubber and a natural rubber of relatively low purity (SMR-10) had the highest tensile strengths, tear strengths, breaking energies, and fatigue lifetimes, while DPNR exhibited the worst failure properties. Such an inverse correlation between flaw size and failure performance is due to the dominant effect of strain-induced crystallization. GR and SMR-10 have the highest propensity for strain-induced crystallization, while DPNR is the least strain-crystallizable. Interestingly, all rubbers exhibited the same isotropic crystallization behavior.

INTRODUCTION

The widespread use of natural rubber, and the long-standing interest in developing domestic equivalents such as guayule rubber, are mainly attributable to the outstanding failure properties unique to polyisoprenes having essentially 100% *cis*-1,4 chemical structure. Natural rubber is available in a variety of standardized "grades", differing in purity and viscosity, and can also be obtained in a deproteinized version. Some studies have been carried out on the relative performance of these materials. Given the well-developed state of fracture mechanics analysis, particularly with regard to elastomers, one would expect the failure performance of natural rubber to be thoroughly understood. However, the complexity and statistical variability of failure processes complicates the situation. Recently it was stated "*There have been no conclusive explanations on these characteristics (e.g., tear strength) of natural rubber on a rational basis. This is probably due to the lack of comprehensive studies on the relationship between structure and properties of natural rubber*".[1]

It is well known that elastomers, like most materials, have pre-existing, "naturally occurring", flaws.[2] By intensifying local stresses, presumably such flaws exert an influence on the failure properties of elastomers. Over the last decade, interest in these flaws has increased, due to concerns about their potential for reducing the barrier performance of rubber films. This performance is crucial in the use latex rubber products, such as surgical gloves and condoms, to block transmission of the sub-micron sized particles responsible for AIDS, hepatitis, and other viral diseases.[3]

The passage of viral-sized particles through ostensibly intact natural rubber films has been directly observed in the laboratory,[4,5] and indirectly observed in the field.[6] Evidence for such flaws in natural rubber comes from microscopic observations,[7] as well as water absorption measurements, wherein the initial rapid uptake suggests the existence of capillary channels [8]. In response to the inadequate barrier properties, and also due to concerns about allergic reactions to latex rubber, competing products based on polyurethane have been

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developed. However, preliminary results indicate that these polyurethane films have flaws comparable in size to those of natural rubber.[9]

The presence of intrinsic defects in rubber can also be deduced from its failure properties. The strength [2,10-13] and fatigue life[14-17] are influenced by the presence of defects having an apparent size in the range between 5 and 70 microns. Of course, these values represent effective sizes, reflecting a given degree of stress concentration.[17] This stress concentration also depends on the shape of a crack (*e.g.*, bluntness), as well as the dissipative capacity of the material itself.[18] The intrinsic flaw size is unaffected by temperature.[11] While compounding variables, in particular crosslink density and filler reinforcement, strongly affect the failure properties of rubber, they have less influence on the intrinsic defect size.[15,16] Some variation of flaw size with carbon black type[19] and with crosslink density[20] have been reported. The degree of dispersion of compounding ingredients influences the strength of rubber, apparently by a flaw-initiation mechanism [21]. The size of dispersed ingredients has special significance in the processing of latex rubber.[22]

The purpose of the present work was to systematically investigate the failure properties of two natural rubbers of different technical specifications, a deproteinized NR, and guayule rubber. From the results, an assessment was made of the intrinsic defects in *cis*-1,4-polyisoprene and their relationship to performance.

EXPERIMENTAL

The *cis*-1,4-polyisoprenes, listed in Table I, consisted of a high purity NR (SMR-L), a lower purity grade NR (SMR-10), a deproteinized natural rubber (DPNR-S from the H. A. Astlett Co.), and a guayule rubber. The GR (obtained from S. F. Thames of the Univ. of Southern Mississippi via the U.S. Dept. of Agriculture's Cooperative State, Research, Education and Extension Service) corresponded to an ASTM 2227 "grade 5", meaning it is intermediate between the SMR-L and SMR-10 in regard to contamination with debris. The nonpolymeric ingredients in the rubbers is about 6%,[23] with the exception of the DPNR, which is more than 96% polymer.[24,25]

The only compounding of the rubbers was the addition of an antioxidant and dicumyl peroxide (Varox Agerite-D and Varox DCP-R, respectively, from the R.T. Vanderbilt Co.). The quantity of the latter was adjusted to give the same equilibrium modulus (= 1.1 MPa at 30% elongation) for all four compounds (see Table I). Curing was carried out in a compression mold at 160°C for 60 minutes.

All properties were measured at room temperature. Uniaxial extension data was obtained using an Instron 4206, in combination with a Wallace noncontacting optical extensometer (H. W. Wallace Co.). Strains were determined from displacement of fiducial marks on the test specimens. Tensile strength and energy to break were measured in accord with ASTM procedure D412, with 8 to 10 test specimens used for each compound. Trouser tear tests followed ASTM D624; 4 specimens each were tested at a cross-head speed equal to 25 cm/

TABLE I

ELASTOMERS

cis-1,4-polyisoprene	Symbol	Curative[a] (phr)	Antioxidant[b] (phr)	Modulus[c] (MPa)
NR	SMR-10	2.5	1	1.08 ± 0.05
NR	SMR-L	2.5	1	1.05 ± 0.05
Deproteinized NR	DPNR	2.8	1	1.10 ± 0.05
Guayule	GR	2.9	1	1.13 ± 0.05

[a] Dicumyl peroxide.

[b] Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ).

[c] Ratio of stress to strain at 30% extension.

min. Measurement of tensile fatigue lifetimes employed a Monsanto Fatigue To Failure Tester, following ASTM D4482-85. In order to avoid errors due to switch bounce, the counters in the instrument were replaced with a parallel interface board connected to a microcomputer. For every compound, 6 to 15 specimens were tested at each tearing energy.

Cut growth rates were obtained from precut specimens cyclically deformed using the Monsanto apparatus. For both this and strength measurements, flaws in the range of 0.06 mm to 3 mm were introduced using a heated knife edge. The actual flaw size, either initially or after cyclic deformation, was determined using an optical microscope.

Differential Scanning Calorimetry employed a Perkin-Elmer DSC-7 with an intercooler. Samples, preheated at 100°C for 10 min, were isothermally crystallized at -25°C for varying duration while in the calorimeter. The melting enthalpy was then measured by scanning at 10°/min.

RESULTS

Since tensile strength and other failure properties are strong functions of crosslink density, networks of the four elastomers were prepared having the same crosslink density, as seen from the equivalence of their elastic modulus (Table I). Assuming phantom-network behavior,[26] the molecular weight between crosslinks, M_c, is estimated to be about 2900 g/mole.

Chains in the network with free ends are not load-bearing at equilibrium, so that a network prepared from lower primary molecular weight chains can have reduced failure properties. Strain-crystallizing rubbers, in particular, have been shown to exhibit an inverse relationship between primary molecular weight and strength.[27] In principle, property differences among the four elastomers herein could arise from molecular weight differences. However, the primary molecular weights are so large (*ca.* one million or more in their initial "native" state, discounting branching[28]) that the fraction of elastically active chains exceeds 99%. This means that molecular weight differences are unimportant herein. In addition, any mastication of the chains during mixing would tend to equalize the respective molecular weights.[29]

In light of the above, we can interpret the relative performance of the four elastomers in terms of their intrinsic flaws and their behavior at high strains (that is, strains associated with orientational crystallization).

INTRINSIC FLAW SIZE

Since material failure corresponds to the propagation of existing damage to a catastrophic level, the intrinsic flaw size can be deduced from the degree of stress concentration through the application of fracture mechanics. Derived from the Griffith approach[30,31] relating propagation of cracks to the release of stored energy, fracture mechanics analysis is well-established in the field of rubber, enabling the description of the failure behavior over broad ranges of deformation type and severity. According to this approach, the driving force for failure is the strain energy release rate, G, which for the geometry considered herein, uniaxial extension, is given by[16,30,32]

$$G = 2\pi\lambda^{-1/2}Wc, \tag{1}$$

where λ is the stretch ratio, c the crack length, and W the strain energy density. The strength of rubber and its fatigue life reflect identical phenomena — the growth of flaws and concurrent (for uniaxial extension) increase in tearing energy up to the point of failure. For values of G above the limit for mechanical fatigue (*ca.* $> 10^2$ J/m^2), up to very large tearing energies (about 10^4 J/m^2), the failure properties of rubber can be characterized by the intrinsic flaw size, c_0, and two material parameters, a and b.[14,31]. In this regime, the change in crack size as a function of deformation cycles can be expressed as

$$\frac{dc}{dn} = aG^b. \tag{2}$$

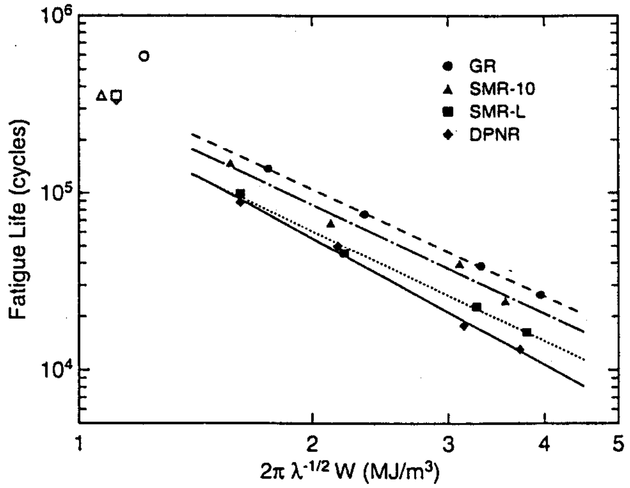

FIG. 1. — Fatigue lifetimes measured at various strains for the four elastomers. Each point represents the average of 6 to 15 measurements. The lines are best-fits of Equation (3) to the data (solid symbols) obtained at tearing energies for which mechanical fatigue dominates; the slope yields the parameter b listed in Table II. At lower tearing energies (hollow symbols), crack propagation occurs at a slower rate than that given by Equation (2).

Integration gives the number of cycles required for a flaw to increase from its initial size to a macroscopic dimension[14,31]:

$$N = [a(b-1)\lambda^{-b/2}(2\pi W)^b c_0^{b-1}]^{-1}. \tag{3}$$

Equation (3) indicates that a double logarithmic plot of fatigue life versus the quantity ($\lambda^{-1/2}W$) will be a straight line of slope equal to the material constant b. In Figure 1 the fatigue lifetimes measured at various strains for the four elastomers are displayed in this form. The values of b obtained are listed in Table II, where it can be seen that all are close to the value of 2 reported in the literature for natural rubber,[14] although DPNR has somewhat different behavior.

To determine the cut growth parameter a in Equation (2), small (< 1 mm) flaws were introduced into test specimens, followed by deformation for hundreds to a few thousand cycles. From the resulting crack growth, a was calculated, using the values of b determined from Figure 1. Note that a for DPNR differs substantially from the values for other rubbers.

Since the fatigue lifetime for uncut specimens is determined in part by the intrinsic flaw size, c_0 could be deduced for each of the elastomers from their measured N, using Equation

TABLE II

FAILURE PROPERTIES

cis-1,4-polyisoprene	a[a]	b[a]	σ_B[b]	W_B[c]	G_C[d]
SMR-10	0.31 ± 0.15	2.08 ± 0.09	13.5 ± 0.7	15.7 ± 0.5	4380 ± 180
SMR-L	0.48 ± 0.16	2.08 ± 0.12	10.3 ± 1.5	11.6 ± 1.2	2800 ± 180
DPNR	22 ± 10	2.39 ± 0.12	8.1 ± 1.3	9.1 ± 0.8	2450 ± 180
GR	0.12 ± 0.02	2.03 ± 0.08	15.1 ± 1.2	17.7 ± 1.2	4380 ± 180

[a] From Equation (3) (with W and c_0 in units of MJ/m³ and m, respectively).
[b] Tensile strength (MPa).
[c] Energy to break (MJ/m³).
[d] Tear strength measured at 250 mm/min (J/m²).

(3) and the parameters a and b listed in Table II. These results (Table III) indicate that the intrinsic flaw size of the rubbers are in the order: **GR > SMR-10 > SMR-L > DPNR**. The two "purified" forms of natural rubber, DPNR and SMR-L, have smaller intrinsic flaws than do SMR-10
and GR.

To corroborate this result, we obtain an alternate measure of c_0 from the elastomers' strengths. The tensile strength of rubber is a measure of the tearing energy necessary to reduce N to unity. When the tip radius of a crack is much smaller than its length, the stress concentration in a perfectly elastic material is directly proportional to the square root of the flaw size,[33] so that breaking stress is inversely proportional to flaw size[12]:

$$\sigma_B \propto c^{1/2}. \tag{4}$$

Thomas and coworkers[34] have extended this analysis to nonlinearly elastic materials such as rubber. For large precuts, the breaking energy is low due to an absence of strain-induced crystallization.[35] For smaller initial cuts, the attained strains are sufficient to cause the bulk rubber to crystallize; in this circumstance, the energy to break depends on crack size according to[34]

$$W_B = kc^{-1/2}, \tag{5}$$

where k is a constant. The change in W_B with crack length was measured for the four rubbers (Figure 2). The high strength region, where proportionality between W_B and the square root of c is observed, was extrapolated to the value of the breaking energy measured in the absence of any intentionally introduced flaws. This yields a second measure of the intrinsic flaw size. These results, also listed in Table III, indicate that **GR, SMR-10 > SMR-L, DPNR**. Consistent with the fatigue life determinations of c_0, the purified rubbers have smaller intrinsic flaws.

FAILURE PROPERTIES

The tensile strength, σ_B, and energy to break were measured on uncut specimens of the four rubbers. Displayed in Table II, the results suggest the relative failure performance to rank order as: **GR > SMR-10 > SMR-L > DPNR**. In agreement with the fatigue lifetimes, the GR and SMR-10 have superior fracture properties, notwithstanding their *larger* intrinsic defects.

These results imply that GR and SMR-10 will exhibit especially high performance in any failure mechanism that is not sensitive to intrinsic flaws. The tear strength, G_c, of rubber is defined as the value of the tearing energy associated catastrophic failure. Since tearing involves continuous fracture of the rubber, the tear strength does not depend on the defect size; it reflects only the material's fracture resistance. "Trouser" tear strengths were measured for the elastomers (Table II), indicating: **GR, SMR-10 ≫ SMR-L, DPNR**. The relative per-

TABLE III

INTRINSIC FLAW SIZES

	c_0 (μm)	
cis-1,4-polyisoprene	W_B [Equation(5)]	N [Equation(3)]
SMR-10	29	21
SMR-L	26	17
DPNR	16	10
GR	29	26

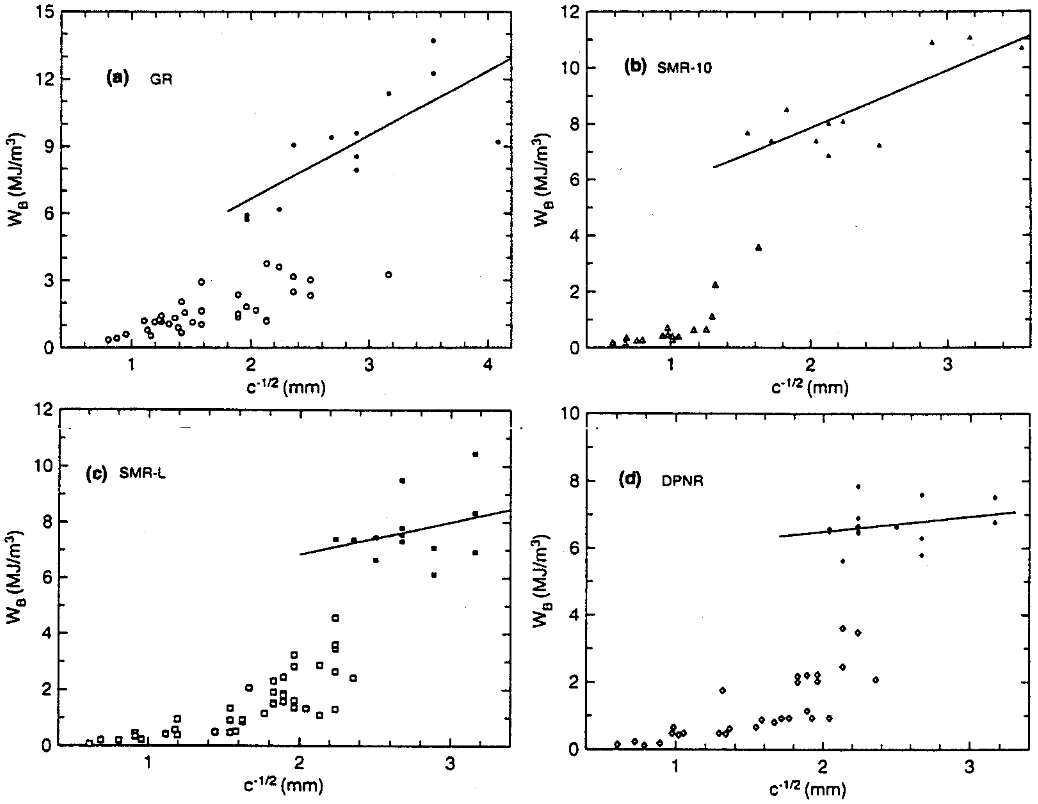

FIG. 2. — The energy to break measured after introduction of edge cracks of varying size for the four elastomers: **(a)** GR; **(b)** SMR-10; **(c)** SMR-L; **(d)** DPNR. The solid lines are the least-squares-fit to the data (solid symbols) from samples having small initial cracks. Failure for larger initial cracks (hollow symbols) occurs without strain-induced crystallization in the bulk of the test piece, and thus at low stresses ($\sigma_b < 4$ Mpa).

formance of the GR and SMR-10 substantially exceeds that of the two purer forms of natural rubbers.

CRYSTALLIZATION

The crack growth resistance of natural rubber at high energy release rates is governed primarily by strain-induced crystallization.[12,34] The better failure properties of GR and SMR-10, despite their larger c_0's, suggest a greater propensity for crystallization upon straining. Determination of the strain necessary for the onset of cystallization can be accomplished by various methods, including x-ray diffraction, optical and infrared birefringence, and the shape of the stress–strain curve.[36–38] The most sensitive measure is the strain-dependence of the time period required for equilibration of the stress after an increase in strain.

At low strains, this time is governed by viscoelastic relaxation, and is very similar for the four rubbers herein, since they have the same glass transition temperature and the same crosslink density. As seen in Figure 3, however, at larger extensions there is an increase in the time of stress decay, due to the onset of crystallization. Below *ca.* $\lambda = 3$, the relaxation time is independent of strain, equal to roughly 35 min. At higher strains there is a marked increase, signifying strain crystallization. The data in Figure 3 correlates with the failure properties of the rubbers (Table II), indicating that greater strain crystallization underlies the superior performance of GR and SMR-10.

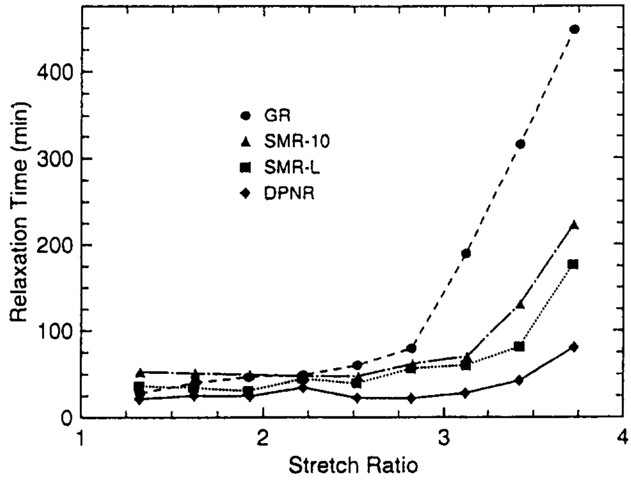

FIG. 3.—Stress relaxation times measured at various stretch ratios. Beyond about 200% elongation, the onset of crystallization causes a marked increase in the time scale of the stress decay. By this measure, GR has a greater propensity for strain-induced crystallization than the NR elastomers, in agreement with the high-strain hysteresis data in Table IV.

More direct evidence that the degree of strain-crystallization governs the rubbers' tear strength and other failure properties can be obtained from the mechanical hysteresis at high strains. Since crystallized chain segments are elastically inactive,[36] strain-induced crystallization causes a marked increase in hysteresis. At low strains and low strain rates, the four elastomers respond elastically, with minimal hysteresis (Table IV). The behavior is quite different, however, when this hysteresis is measured in a tensile retraction cycle to $\lambda = 5$, which is well beyond the strain necessary for crystallization (*cf.* Figure 3). As seen in Table IV, this high strain hysteresis is much larger than at low strains. Moreover, it is greatest for GR, and lowest for DPNR, consistent with the data in Figure 3, as well as their respective failure properties.

Finally, we compare the isotropic crystallizability of the rubbers. This was done on uncrosslinked samples, since crystallization of the networks in the absence of orientation is too slow to reliably measure.[39] For all four rubbers, crystallization at -25°C was found to be >90% complete after 8 hours, in agreement with an earlier study.[25] Figure 4 shows the DSC

TABLE IV

CRYSTALLIZATION

		W_{out}/W_{in}[b]	
cis-1,4-polyisoprene	Isotropic crystallinity[a]	$\lambda = 2$	$\lambda = 5$
SMR-10	35% ± 1%	>99%	74% ± 2%
SMR-L	36% ± 1%	>99%	75% ± 2%
DPNR	35% ± 1%	>99%	83% ± 2%
GR	36% ± 1%	>99%	59% ± 2%

[a] Uncrosslinked samples annealed 20 h at −25°C; values are the average of two measurements, and assume a perfect heat of fusion equal to 64 J/g.[39]

[b] Mechanical elasticity at indicated extension (5 mm/min cross-head speed; nominal extension rate ≈ 10^{-3} s^{-1}).

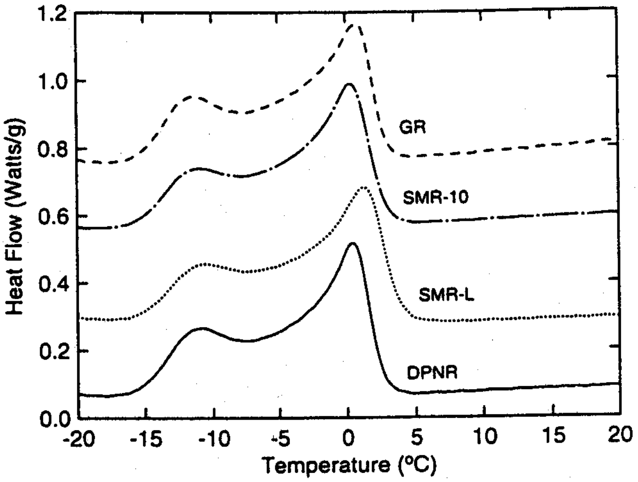

FIG. 4. — Differential scanning calorimetry (10 °/min) after crystallization for 20 hours at -25°C. The higher temperature endotherm is due to the α-lamella; the less stable β-lamellar crystals develop later during the crystallization process. The integrated intensity of the two peaks was equivalent: = 21.6 ± 0.4 J/g for the four elastomers (based on their polymer content).

heating curves after 20 hours crystallization at -25°C, whereby an invariant degree of crystallinity has been attained. The bimodal endotherms reflect melting of the two, morphologically differing, crystalline forms of *cis*-1,4-polyisoprene, a more stable α-lamella and a slower forming β-lamella.[40,41]. Both structures have the same crystal unit cell, but differ with respect to lamellar thickness and morphology.

Without orientation, the elastomers achieve equivalent degrees of crystallinity (Table IV), notwithstanding the variations in their orientational crystallization behavior (Figure 3 and Table IV). Such differences between isotropic and strain-induced crystallization are known. In the absence of orientation, *cis*-1,4-polyisoprene crystallizes through lamellar growth into radial spherulites, whereas strain-induced crystallization initiates by row nucleation, followed by lamellar growth perpendicular to the strain direction.[41-43] Early work[35] also showed that there is no correlation between low temperature, isotropic crystallization of natural rubber and the thermal stability of strain-induced crystallites.

SUMMARY

Fracture mechanics analysis enables the determination of intrinsic flaw sizes in rubber. While such results can not be taken too seriously in a quantitative sense, the data obtained herein from two different methods provides clear evidence that SMR-L and deproteinized *Hevea Brasiliensis* are both associated with smaller intrinsic defects than less purified natural rubber or guayule rubber. However, these flaw sizes are not manifested in the failure performance of the rubbers. GR and SMR-10 are superior in all measured properties — tensile strength, tear strength, energy to break, and fatigue life — despite having larger intrinsic flaws. This superiority is due to the fact that orientational crystallization occurs at lower strains and to a higher degree than for DPNR and SMR-L.

The origin of the enhanced strain-crystallizability requires further investigation, but is presumed to be related to the nucleating effect of nonpolymeric ingredients in the rubbers.[44] This is speculative, and must be reconciled with their very similar low temperature crystallization behavior in the isotropic, uncrosslinked condition.

Reincorporation of extracted material improves the tear strength of natural rubber.[45] It has been suggested[45] that this is due in part to the reinforcing effect of the nonpolymeric ingredients, such as the proteins. Of course, it is well known that small particulates reinforce rubber, the obvious example being carbon black. However, it is not obvious how such small quantities (*ca.* 5%) of "filler" could have so substantial an effect.

While the failure properties of these rubbers do not parallel the magnitude of their intrinsic defects, other properties, in particular the barrier performance, may be quite sensitive to these flaws. Moreover, in carbon black-reinforced compounds, the effect of the nonpolymeric ingredients on strain-crystallization might be minified, perhaps causing the intrinsic flaws to become more significant. Certainly the significance of the intrinsic defects in rubber remains to be broadly investigated.

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ERRATA

Intrinsic Defects and the Failure Properties of cis-1,4-Polyisoprene, I. S. Choi and C. M. Roland, **69**(4), 591 (1996). The commercial name for the antioxidant used in the formulation on page 592, polymerized 2,2,4-trimethyl-1,2-dihydroquinoline, was incorrect; it is Agerite® Resin D.