TECHNICAL

Intrinsic defect effects on NR permeability

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Fracture of rubber occurs when the tearing energy (strain energy release rate) reaches a catastrophic level.

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Executive summary

Recent evidence of the ability of viral-size particles to pass through ostensibly intact latex rubber films calls into question the ability of latex rubber gloves and condoms to function effectively as prophylactics. The origin of this permeability is presently unknown. Herein we report the size of the intrinsic flaws in natural rubber of varying grades and in guayule rubber. We also describe experiments measuring the permeation of micron- and submicron-size particles through latex rubber films.

Usually rubber is subjected to strain energies too low to cause immediate failure; cracks and the stress concentration they engender, grow over time, eventually giving rise to fracture. However, the mechanical lifetime of rubber is not governed solely by the propagation rate of cracks. It also depends on their initial size.

The nature of the flaws in rubber is of great interest. Under some circumstances, defects can be introduced during processing (for example, at the wire ends in the trimmed belt of a radial tire). However, flaw initiation per se is unnecessary because all materials can be considered to possess pre-existing "intrinsic" flaws.[1] Their origin is speculative, since intrinsic flaws never are observed literally. Indirect evidence for their existence includes the broad distribution of fatigue lifetimes and other failure properties of rubber, and the fact that "material properties" such as tensile strength can depend on the size of the test specimen used for measurement. Intrinsic flaws can be directly probed by small-angle X-ray scattering. The scattering contrast is due to the density difference between the material, and the void comprising is a flaw. This method has been applied to elastomers,[2] although the scattering angles are too small to obtain much information. Small angle neutron scattering may have more potential because longer wave lengths (and thus smaller scattering vectors) are available.

The sizes reported for the intrinsic flaws in rubber are on the order of 10-5 meters.[1] These values are inferred from failure properties and, hence, rely on some assumption about the shape of the flaw. They only represent effective sizes, reflecting a given degree of stress concentration. Recently, interest in the intrinsic flaws in rubber has intensified because of concerns about the barrier performance of rubber film used for prophylaxis (for example, surgical gloves and condoms).[3] These concerns are exacerbated by Food and Drug Administration studies revealing their own mandated tests of condom integrity to be insensitive to holes smaller than about 10 microns.[4-6] The causative agents for AIDS and hepatitis B are two orders of magnitude smaller. In fact, both in vivo[7,8] and in vitro[9-11] studies suggest the facile passage of submicron-size particles through intact latex rubber.

It is unknown whether any connection exists between the intrinsic flaws in rubber and the failure of latex film to prevent contagion. We are investigating the relationship between the morphology of latex film and its permeability. Herein, we describe the effect of natural rubber's purity on the size of its intrinsic flaws and, without implying any relationship to these flaws, we report on the barrier effectiveness of NR latex film.

Inherent flaws in natural rubber

The cis-1,4-polyisoprenes, listed in **Table I**, included three grades of Hevea brasiliensis natural rubber and a guayule rubber (Perthenium argentatum Gray). The latter was an ASTM 2227 "grade 5," obtained from S.F. Thames of the University of Southern Mississippi. The deproteinized NR is a commercial product from the H. A. Astlett Co. The rubbers differed in their purity, as reflected in the quantity of

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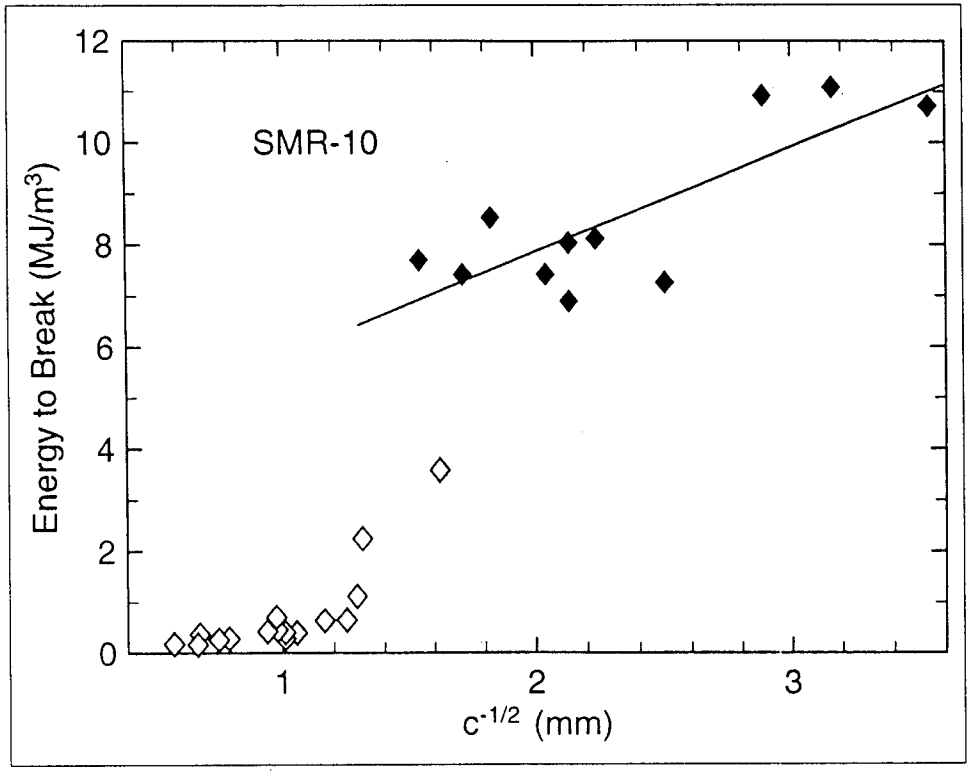
Table I. Elastomers.

				intrinsic	flaw size
rubber	**symbol**	**dirt (%)**	**ash (%)**	**fatigue life**	**strength**
deproteinized NR	DPNR	0.003	0.09	10 μm	16 μm
high quality NR	SMR-L	< 0.03	< 0.50	17 μm	26 μm
ribbed smoked sheet	SMR-10	< 0.05	< 0.60	21 μm	29 μm
guayule	GR	< 0.10	< 0.75	26 μm	29 μm

Fig. 1. The energy to break measured for "ribbed smoked sheet" natural rubber after introduction of edge cracks of varying size. The solid line is the least-squares fit to the data (solid symbols) from samples having small initial cracks. For large initial cracks (hollow symbols), there is no strain-induced crystallization in the bulk of the test piece, and thus failure occurs at low stresses (σb < 4 Mpa).



particulate contamination. In order to focus on the material in its "as received" condition, the only formulating of the rubbers was the addition of 1.0 parts per hundred of rubber Varox Agerite-D antioxidant (R.T. Vanderbilt Co.) and 2.5-2.9 phr of dicumyl peroxide (Vanderbilt's Varox DCP-R). The exact quantity of the peroxide was adjusted so that the elastomers all had the same relaxed modulus, 1.1 MegaPascals at 30 percent elongation.

There are two methods available to deduce intrinsic flaw sizes. The first takes advantage of the fact that the rate of mechanical cut growth in rubber can be described over many decades by a power law[1]:

Equation 1

$$\frac{dc}{dn} = aG^b$$

where the cut growth parameters a and b are material constants. For uniaxial extension, the proportionality between the tearing energy, G, and the strain energy, W, is:

Equation 2

$$G = 2\pi\lambda^{-1/2} c W$$

where λ is the stretch ratio and c the flaw size. Combining **equations 1 and 2** and integrating gives an expression for the fatigue life:

Equation 3

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

This fatigue life is just the number of cycles required for a flaw to grow from its initial size, c_0, to the value at which catastrophic failure transpires. By measuring cut growth rates and fatigue life-

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times over a range of strain energies, we used **equations 1 through 3** to deduce the value of c_0 for the four rubbers. As seen in **Table I,** the rubbers less contaminated with debris have smaller intrinsic flaws. Another measure of c_0 can be obtained from an elastomer's strength. The tensile strength corresponds to the stress at which N in **equation 3** is unity. When the tip radius of a crack is much smaller than its length, the tensile strength of an elastic material is inversely proportional to the square root of the flaw size[1]:

Equation 4

$$\sigma_B \propto c^{-1/2}$$

If flaws are intentionally introduced into test specimens, a plot of the measured tensile strength versus the inverse of the square root of the flaw size is expected to be a straight line. Extrapolation of this line to the value of σ_B corresponding to the tensile strength of uncut specimens provides a measure of the intrinsic flaw size.

An extension of this method[12,13] which takes into consideration the non-linear elasticity of rubber, gives the relation:

Equation 5

$$W_B \propto c^{-1/2}$$

where W_B is the strain energy at break. Note that the validity of extrapolating **equation 4 or 5** to determine c_0 is valid only for small precuts, so that the strains achieved are sufficient to cause bulk crystallization of the rubber; otherwise, the measured σ_B and W_B will be artificially low, whereby extrapolation underestimates the intrinsic flaw size.

Cuts (made with a heated wire) were introduced into the edge of tensile specimens of the four elastomers in **Table I.** The samples were then elongated to the breaking point. In **Fig. 1**, we show a representative plot of the measured energy to break vs. precut length. For small precuts, the strength is very low, because of the absence of strain crystallization of the bulk rubber. For small precuts, however, proportionality between W_B and $c^{-1/2}$ is observed. By extrapolating to the breaking energy of uncut specimens, we obtain a measure of the intrinsic flaw size (listed for all four rubbers in **Table I**). Again, the cleaner rubbers have smaller intrinsic flaws. Although exact correspondence between the two measures of c_0 was neither obtained nor expected, the results in **Table I** are in qualitative accord.

The data in **Table I** suggests the intrinsic flaws in naturally occurring cis-1,4- polyisoprenes can be identified with particulates and other insoluble contaminants. This is not surprising since previous studies have found the size of intrinsic flaws to show some dependence on carbon black type[14] and the dispersion of compounding ingredients.[15] The failure properties of rubber obviously depend upon the size of flaws; this dependence was used to measure c_0 herein. More interesting is the degree to which intrinsic flaws affect the barrier performance of rubber. In the next section we report some recent results concerning the permeation of viral-sized particles through ostensibly intact natural rubber films. The films are actually commercial latex rubber products (condoms). It is presently unknown what connection, if any, exists between the intrinsic flaws deduced from the failure properties of rubber and its permeability.

Barrier performance of natural rubber latex

The defining feature of viruses is their diminutive size. For example, the AIDS virus is only 0.15 microns, and the hepatitis B virus is even smaller. Given the presence in rubber of intrinsic defects two orders of magnitude larger in size, the ability of a condom or surgical glove to prevent transmission of viral particles is problematic. To determine the extent to which small particles can pass through latex rubber, we adapted the method of Carey, et.al.[9]

This technique makes use of an aqueous suspension of fluorescent-labeled polystyrene particles ("Fluoresbrite" from Polyscience Inc.). In our experiments, particles having diameters equal to 0.1 and 1.0 μm were used. A quantity (ca. 8.8 milliliters) of the Fluoresbrite suspension, containing roughly 10^{10} particles per ml, was placed in a cell, the top of which was covered with a sheet of rubber cut from commercial latex condoms. Two brands were tested "A," which was ca. 50 μm thick, and "B," about 90 μm in thickness.

The contact area between the rubber film and the liquid was typically 8 square centimeters. The rubber was sealed to the cell with a plastic ring, after which the entire assembly was immersed in 10 ml of pure water. After varying time periods, aliquots of this surrounding water were removed for fluorescence measurements. Using a calibration curve determined for the Fluoresbrite, the concentration of particles having diffused through the rubber film could be calculated from the fluorescent intensity.

Typical results are shown in **Fig. 2.** More than one million of the 0.1 μm par-

ticles pass through a square centimeter of rubber within 30 minutes. Fluoresbrite particles having a diameter of 0.1 μm pass through more readily than do the 10-times larger particles. The permeability of the two brands of condoms is comparable, with perhaps more passing through the thinner latex rubber.

The data in **Fig. 2** shows that small particles can pass through latex rubber films; it does not reveal the cause of this permeability. Latex processing per se, rather than the rubber itself, may give rise to the poor barrier performance. Latex rubber is formed from discrete particles, which are coated with naturally occurring proteins and surfactants, and dispersed in an aqueous medium. During commercial processing, drying and curing are almost simultaneous. This can cause the coalescence of the particles to be incomplete, resulting in a residual capillary structure[16-21] and concomitant permeability. These issues are currently being addressed in our laboratory.

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Fig. 2. The number of Fluoresbrite particles (having the indicated average diameters) passing through sections of film taken from two brands of latex condoms.