

# Effect of Water on the Strength of Filled Polychloroprene Vulcanizates

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## Synopsis

Three commercial rubber compounds used in marine applications were immersed in water or in 3.5% NaCl solution for up to 250 days. Tear strengths, measured with the "trousers" test piece, decreased in the order dry > salt water exposed > fresh water exposed, and changes of up to 50% were seen. Tensile strengths also decreased, but not always in the same proportion, suggesting a possible change in structure of the voids which initiate fracture. Results are discussed in terms of osmotic swelling and extraction of rubber components.

## INTRODUCTION

In marine applications, polychloroprene compounds are often exposed continuously to fresh or salt water, so that it becomes important to understand the effect of water on the strength of these compounds.

Simple tensile measurements are easy to perform and are a standard part of the specification and testing of rubber compounds. However, failure can also result from fatigue or slow crack growth at stresses an order of magnitude or more below the breaking stress.<sup>1</sup> Thus, tearing tests may provide a more fundamental measure of ultimate properties.

The present report describes the effect of water on three chloroprene rubber formulations as determined using swelling, tear, and tensile tests.

## EXPERIMENTAL

The three rubbers subjected to study are somewhat different in composition and properties. Each contains some 18 ingredients. Some of the principal differences among the rubbers are outlined in Table I. Compound 29 is designed specifically to prevent fouling by marine organisms, while 45 is a structural compound.

Samples were obtained from the manufacturer in the form of 1.91 mm thick ASTM test plaques.<sup>2</sup> Table I summarizes the material designations. One plaque of each composition was wrapped in aluminum foil and kept at room temperature. A second plaque was cut in half, and each half was placed in a zip-lock plastic bag containing either distilled water or aqueous 3.5% NaCl. The plastic bags were kept in a constant-temperature bath of 100°F (37.8°C); periodically the samples were removed, blotted dry, and weighed. Tensile strengths were measured after 120 days. After the tensile pieces had been cut

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TABLE I  
Differences in Major Compounding Ingredients

Ingredient	Compound no.		
	29	35	45
Tributyltin oxide	Yes	Yes	No
Sulfur	No	No	Yes
Hydrated silica	No	No	Yes

out, the remaining portions of the sheets were replaced in the bags with fresh liquid and stored for an additional 130 days at 100°F (37.8°C) until the tear measurements could be made. In this report, the suffixes D, F, and S denote samples stored dry at room temperature, in fresh water, or in salt water, respectively.

### Swelling

Linear swelling ratios were calculated from the weight gains, assuming additivity of volumes and an initial rubber density of 1.33 (determined by weighing a small piece in air and in water). Results after 120 days' immersion are given in Table II.

The samples apparently did not reach swelling equilibrium during the soaking period; Figure 1 shows representative water uptake curves.

### Tear Strength

Tearing energy was determined with the "trousers" test piece<sup>3</sup> [Fig. 2(a)]. It proved impossible to propagate a steady tear from a simple cut in the test piece. Whenever this was attempted, the tear front became extremely ragged and the tear usually diverged toward the edge of the sample. A manageable tear was obtained by cutting part way through from both sides of the sheet with a razor blade, leaving about 1.2 mm of rubber to tear through. These surface grooves or cuts served to guide the crack down the center of the specimen. After the halves of the specimen were separated, the torn thickness was visible on the fracture surface as a roughened region quite distinct from

TABLE II  
Swelling Properties (120-Day Immersion at 37.8°C)

Sample	Swelling ratio	300% modulus (MPa)
29D	—	4.11 ± .10
29S	1.047	4.09
29F	1.129	4.50
35D	—	6.48
35S	1.046	6.01
35F	1.109	6.44
45D	—	5.53
45S	1.051	6.30
45F	1.083	6.31

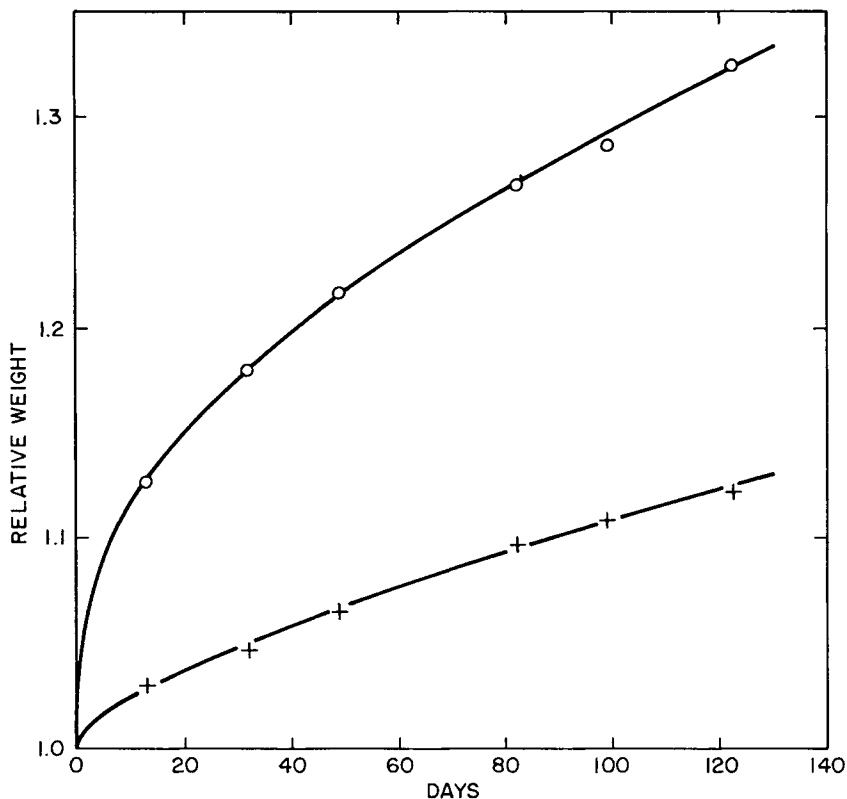


Fig. 1. Water uptake of sample 29: (○) fresh water; (+) salt water.

the smooth cuts [Fig. 2(b)]. The torn thickness  $t$  was measured on the fracture plane with a travelling microscope.

Compound 45 did not tear straight through the thickness, but rather the separated surfaces had a tongue-and-groove appearance. In this case, the tearing work was normalized by the "tongue" area, which could be measured on a photograph of the sample cross section.

With a wide rubber strip, the tearing energy  $T$  can be calculated from

$$T = 2F/t \quad (1)$$

where  $F$  is the tearing force and  $t$  is the thickness torn through. Because the amount of materials available was somewhat limited, some samples were too narrow to satisfy the assumptions implicit in eq. (1), so that a slightly modified analysis was used (see Appendix). With this analysis, data from identical samples of various widths could be superposed within the experimental scatter (typically 20%). The tearing force was averaged over a distance torn of 2 mm or more; rates were varied in random order to check repeatability.

### Tensile Measurements

Tensile dogbones were cut with a die similar to ASTM D412-D, but with a 0.5 in. (1.27 cm) gauge length. Gauge marks were made with a castor-oil-based

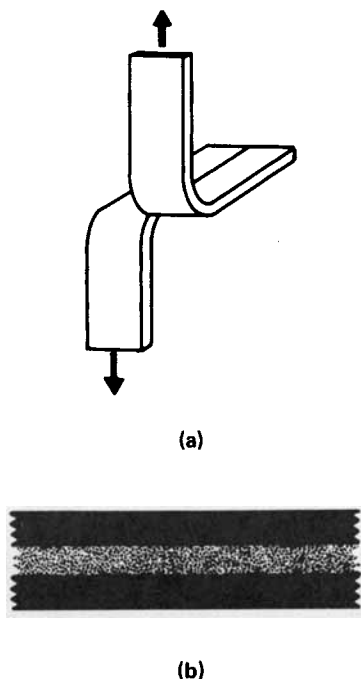


Fig. 2. (a) Trousers test piece; (b) appearance of fracture plane.

ink which had been shown not to affect rubber strength. Samples were pulled in a mechanical tester at 50.8 cm/min crosshead speed. Elongation at break was estimated from the separation of the gauge marks. Each reported value of modulus, elongation, or strength is an average of results from three to five specimens.

### Differential Scanning Calorimetry

DSC measurements were performed with a DuPont 990 thermal analyzer at 10°C/min heating rate after a liquid nitrogen quench to  $-120^{\circ}\text{C}$ .

### Electron Microscopy

Freshly torn rubber pieces were given an evaporated gold coating and viewed at 5000X.

## RESULTS AND DISCUSSION

### Tearing Energy

Typical tear energy data as a function of tearing rate are shown in Figure 3. In spite of some scatter, it is evident for all three of the materials studied that water had an adverse effect on the tear energy, with fresh water causing the larger change. Table III shows this for the 0.5 cm/min rate, chosen arbitrarily to facilitate comparisons.

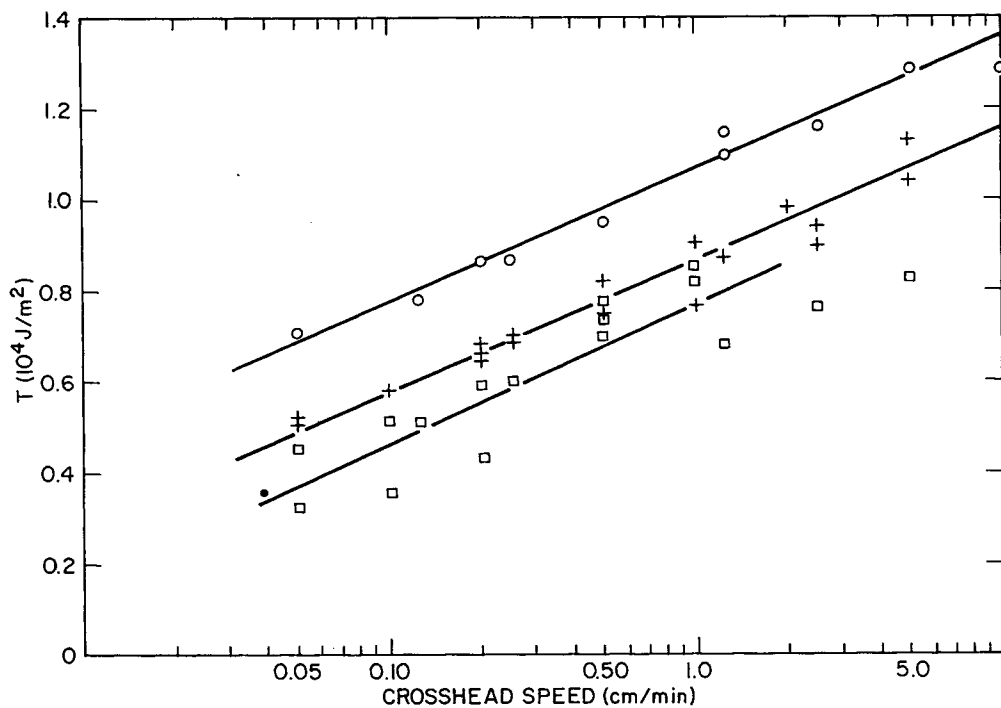


Fig. 3. Tear energy vs. crosshead speed for sample 29: (○) dry; (+) salt-water-treated; (□) fresh-water-treated

TABLE III  
Strength Properties

Sample	Tear energy <sup>a</sup> $10^{-4}T$ (J/m <sup>2</sup> )	Tensile strength <sup>b</sup> $\sigma_b$ (MPa)	Elongation-at-break <sup>b</sup> $\epsilon_b$	"Inherent flaw" size $T/\sigma_b\epsilon_b$ (mm)
29D	0.98	15.0	6.9	0.10
29S	0.76	12.5	6.1	0.10
29F	0.64	7.64	4.8	0.17
35D	0.52	13.1	4.8	0.08
35S	0.48	11.2	4.3	0.10
35F	0.44	7.96	3.7	0.15
45D	2.5	17.0	7.2	0.19
45S	1.37	13.4	5.2	0.20
45F	1.20	12.2	5.0	0.20

<sup>a</sup>From tear test at 0.5 cm/min crosshead speed.

<sup>b</sup>From tensile tests.

TABLE IV  
Glass Transition Temperatures

Sample	$T_g$ (°C)
29D	-38
29S	-33
29F	-34
35D	-45
35S	-42
35F	-40
45D	-36
45S	-33
45F	—

Bhowmick and Gent, on the other hand, found "barely significant" differences among chloroprene rubber gum formulations treated with water, air, or NaCl solution.<sup>4</sup> The different behavior may be related to the longer immersion times used in the present work, as well as to the difference in formulation.

In the simplest case, that of threshold fracture,<sup>5</sup> where breaking of molecular chains dominates the fracture energy,  $T$  should be proportional to the number of chains crossing unit area, i.e., to  $\lambda_s^{-2}$ , where  $\lambda_s$  is the swelling ratio. So, for example, with compound 29, where the linear swelling was about 5% in salt water and 13% in fresh water, one would expect decreases in  $T$  of 10 and 26%, respectively. The actual decreases (Table III) are much larger, amounting to 22 and 35% at 0.5 cm/min, and more at lower rates. Threshold conditions were thus not attained, and viscoelastic energy dissipation obviously contributes to the measured tear strengths.

Since it seemed unlikely that much water was molecularly dissolved in the exposed samples,<sup>6</sup> glass transition temperatures were determined using DSC in an effort to see whether plasticization was occurring. In every case, the samples which had been soaked showed glass transition temperatures 3–5°C *higher* than the corresponding dry material (Table IV). It is hypothesized that the water or salt solution extracted certain compounding ingredients or byproducts. The soaking solutions were not analyzed, although it had been noted that they became colored during the soaking period.

These facts are consistent with the slight trend toward higher modulus after water exposure seen in Table II.

### Tensile Strength

A Griffith approach to fracture asserts that the sample will fail when the stored strain energy overcomes the energy necessary to produce new surface adjacent to small inherent flaws in the material. These flaws might be cracks, voids, or nicks.

For a linearly elastic material, the tensile strength or breaking stress  $\sigma_b$  is given by

$$\sigma_b^2 = GE/\pi c$$

where  $E$  is Young's modulus,  $G$  is the fracture surface energy, and  $c$  is the depth of an edge notch. The corresponding more general relationship

$$W_b = T/(2kc)$$

applies to a rubber where now  $T$  is the tearing energy,  $W_b$  is the stored energy density at break, and  $k$  is a numerical factor close to unity.<sup>7</sup>

Therefore,

$$kc = T/2W_b$$

is an estimate of the hypothetical inherent flaw size. Calculated values of this quantity are shown in the last column of Table III. For this purpose,  $W_b$  was approximated as

$$W_b = \sigma_b \epsilon_b / 2$$

where  $\sigma_b$  and  $\epsilon_b$  are the nominal stress and strain at break. Actually, this equation overestimates  $W_b$  by about 25% for these materials compared to the actual area under the stress-strain curve, but the error is a systematic one and will be ignored.

The "inherent flaws" are thus seen to be about 0.1 mm in extent, very similar to what was obtained by Dreyfuss et al.<sup>8</sup> on polybutadiene, and larger by about a factor of 3 than Thomas' figure for natural rubber.<sup>1</sup> Perhaps more interesting is the suggestion that, in samples 29 and 35, fresh water increases the apparent flaw size.

The postulated flaws may be edge nicks or cuts introduced during die-cutting of the samples, or they may be interior voids or holes caused, for example, by dewetting of filler aggregates or impurity particles. Electron microscopy provides some slight evidence for this latter possibility. Particles in the fracture surface of sample 29F seem to be sitting in holes. On the fracture surface of sample 29D, which appears otherwise quite identical, one can find particles which seem to be adhering to the rubber (Fig. 4).

It is interesting to note that the large decreases in tensile strength seen in samples 29F and 35F are not proportional to the changes in inherent strength (measured in tear tests). Rather, they seem to result from changes in the structure (e.g., void content) of the samples. The apparent flaw size in compound 45, on the other hand, is not changed by soaking.

In light of the differences in Table I, two possible mechanisms for void formation suggest themselves: (1) leaching of tributyltin oxide from the two compounds which contain it, and (2) formation of microscopic osmotic cells as water permeates to dilute the  $ZnCl_2$  and  $MgCl_2$  byproducts of the crosslinking reaction.<sup>9,10</sup> The roles of sulfur vulcanization and of silica<sup>10</sup> in preventing loss of strength are possible areas for further research. It must be mentioned, however, that these compositions also differ in a number of minor respects not considered in Table I.

## CONCLUSIONS

1. Water immersion can cause losses of up to 50% in the tensile strength of chloroprene rubber vulcanizates, even though the 300% modulus is only slightly affected.

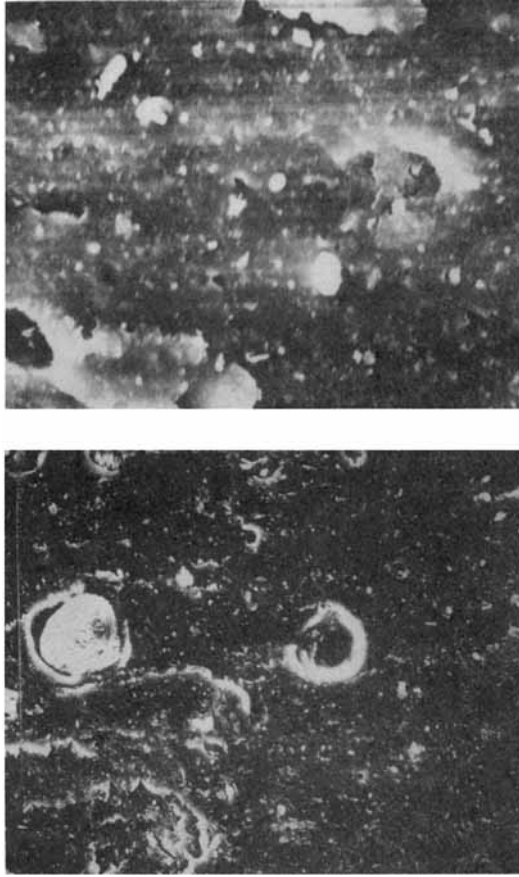


Fig. 4. Scanning electron micrographs of tear surfaces: (a) Sample 29D, 2000X; (b) Sample 29F, 500X.

2. Tear energies at the slower tearing rates measured (0.025 cm/min) are 10–50% lower in water-swollen compounds than in the corresponding dry materials. The change is probably related to extraction of low-molecular-weight constituents.

3. Fresh water exposure results in more swelling and greater strength deterioration than does salt water exposure.

4. In these samples, the change in ultimate properties of an unnotched tensile strip does not always exactly parallel the change in inherent (tear) strength. This has been interpreted to mean that water may affect flaws or voids in some compounds. In particular, fresh water increases the apparent flaw size in the nonstructural compounds studied.

## APPENDIX

The criterion for tearing is

$$\left[ \frac{\delta W}{\delta c} \right]_l = Tl,$$



which simply states that the decrease in energy  $W$  stored in the sample is equal in magnitude to the energy to create new surface when a cut grows. The derivative is taken at constant overall sample length to indicate that external forces do no work. In terms of the applied force  $F$ ,

$$\left[ \frac{\delta W}{\delta c} \right]_l = W_0 A_0 - 2F\lambda$$

where  $W_0$  is the stored elastic energy per unit volume,  $A_0$  is the initial cross-sectional area of the test piece, and  $\lambda$  is the extension ratio in the "legs" of the test piece. This is equation 6.8 of Ref. 3.

For small enough deformations, the load-deflection curve is linear with slope  $m$ ; i.e.,

$$(\lambda - 1) = mF$$

and

$$W_0 A_0 = \int_1^\lambda F \cdot d\lambda = m \int_0^F F' \cdot dF'$$

Combining all the previous relationships, we get finally

$$Tt = 2F + \frac{3}{2}mF^2$$

The second term is negligible for wide samples; for narrow samples stretching of the "legs" cannot be ignored. The slope  $m$  of the load-deflection curve was measured directly on one of the "legs" after the sample had been torn in two and used to correct the measured tearing forces. Typically, the correction was only 2% of the total, but for a very narrow sample (1.2 cm width) it approached 25%.

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