Note

Anisotropy Induced during Compression Molding of Rubber

Many physical tests of elastomeric vulcanizates are carried out using specimens cut from flat sheets that were prepared by compression molding. Generally, an excess quantity of rubber is placed into the mold to assure that the mold cavity will be completely filled after pressing. During molding, the elastomer composition undergoes viscous flow as the mold cavity fills. Shear strains result in alignment of the elastomer molecules in the direction of flow. After mold filling, if there is not sufficient time for the molecules to relax back to their random coil configuration before crosslinking commences, the resulting vulcanizate may exhibit anisotropy in its mechanical properties. Experiments have been performed in which rubber sheets were molded under conditions which led to anisotropy, as illustrated in their stress–strain response. In this note, results of these experiments are presented.

The elastomer composition (by weight) used in this investigation consisted of natural rubber, 100; N-330 carbon black, 50; stearic acid, 0.5; zinc oxide, 5.0; sulfur, 6.0; and *N*-oxydiethylenebenzothiazole-2-sulfenamide, 1.0. The mold cavity was a plate containing a rectangular hole whose dimensions are shown in Figure 1. A strip of rubber cut from a milled sheet was placed in the mold, as also shown in Figure 1. Flat steel plates were then placed on both sides of the mold cavity and the sample cured under high pressure in a hydraulic press for 30 min at 150°C. During molding, the rubber flowed to fill the mold cavity and was simultaneously vulcanized. From cured sheets, strip samples (13 mm × 50 mm) were cut both perpendicular and parallel to the apparent flow direction. Additionally, half of the strips were given an edge flaw of depth 4 mm with a razor blade. Various specimens are shown in Figure 2. Sample types I and III were cut parallel to the apparent flow direction, whereas types II and IV were cut perpendicular to this direction. As shown, samples III and IV contained a precut. Samples were tested in uniaxial tension in an Instron test machine using a strain rate of 10 min^{-1}.

Table I gives tensile results for specimens that contained no intentional precut. Given here are the stress and strain at break obtained for six different molded sheets. There is no significant difference between type I and type II samples. This will now be contrasted to the results obtained when

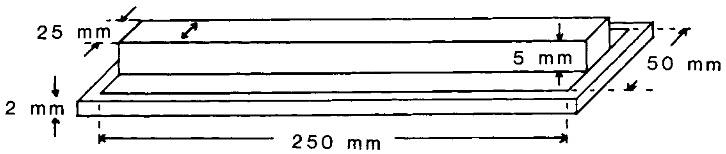

Fig. 1. Mold and sample dimensions before compression molding (25% excess sample).

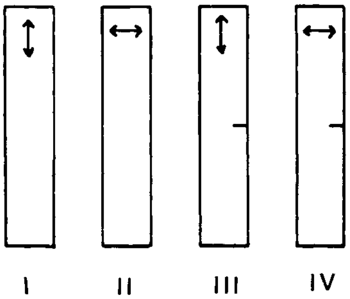

Fig. 2. Various strip test specimens used in tensile testing. Arrow indicates apparent flow direction during molding.

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TABLE I
Stress–Strain Results for Nonprecut Samples

Sample type	Stress at break, MPa	Stress, MPa, at strain = 1.0	Strain at break
I	19.7	4.34	3.63
	19.0	4.21	3.61
	19.5	4.46	3.59
	19.7	4.79	3.45
	21.7	4.75	3.82
	19.3	4.55	3.53
II	19.2	4.55	3.93
	21.1	4.47	3.75
	21.9	4.27	3.58
	20.5	4.23	3.66
	20.9	4.22	3.95
	19.3	4.30	3.52

TABLE II
Stress–Strain Results for Precut Samples

Sample type	Stress at break, MPa	Stress, MPa, at strain = 1	Strain at break
III	3.95	3.95	1.00
	4.10	3.37	1.21
	3.47	—	0.94
	4.25	4.05	1.04
	3.67	—	0.95
	4.09	4.08	1.03
IV	6.90	3.84	2.51
	7.93	3.98	2.67
	9.10	3.88	2.80
	7.15	3.85	2.31
	6.58	3.74	2.18
	6.36	3.84	2.36

testing samples of types III and IV (Table II). When an intentional precut is present in the specimens, there is a clear anisotropy in the tensile results. Unexpectedly, stress and strain at break are greater when the precut was oriented parallel to the apparent flow direction than if in a direction perpendicular to flow. Furthermore, in all cases, secondary cracking at the cut tip was observed before catastrophic propagation of the razor cut, and crack growth did not proceed perpendicular to the test direction.

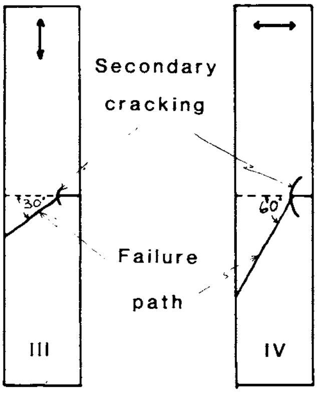

Fig. 3. Diagram of type III and type IV specimens showing secondary cracking and the average failure path.

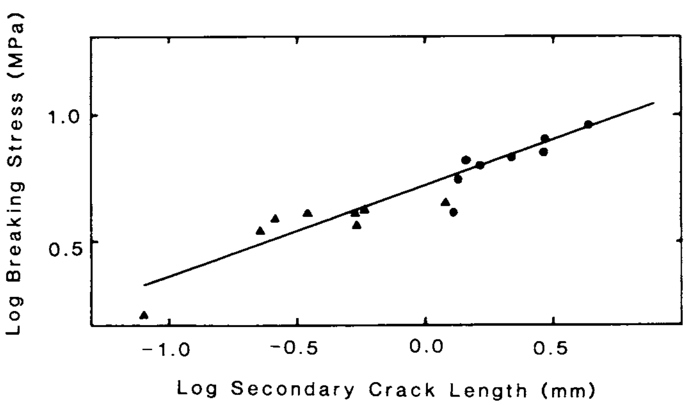

Fig. 4. Effect of secondary crack length on breaking stress for type III (▲) and type IV (●) specimens.

These facts are illustrated in Figure 3 for sample types III and IV. On average, specimens of type IV have a locus of failure that is at an angle of about 60° to the precut direction, whereas the cuts in type III samples propagate at about 30° to this direction. In contrast to this, failure proceeds straight across the test direction for all nonprecut samples. Close examination of specimens during and after testing shows that before catastrophic failure occurs, a secondary crack initiates at the tip of the razor cut. It grows in two directions (from the primary cut tip) back toward the edge of the specimen (see Fig. 3).

Postfracture analysis of the length of the secondary cracks was carried out using a low-power microscope. Figure 4 shows that there is an excellent correlation between the engineering stress at break and the total length of each sample's secondary crack. In fact, *both* type III and type IV specimens can be correlated continuously on the same plot. Apparently, the ability of type IV samples to form longer secondary cracks is responsible for the enhanced strength of these specimens relative to type III samples. Secondary cracking enhances the fracture strength because it provides a mechanism for releasing strain energy in the vicinity of the primary crack tip. That is, strain energy that would otherwise be available as a driving force for primary crack growth is released by secondary cracking. Clearly, the greater the extent of secondary cracking, the greater the amount of strain energy that will be relieved.

Still unanswered, however, is the reason that nonprecut specimens do not exhibit anisotropy in tensile properties whereas precut specimens clearly do. Further experimentation is needed to determine the cause of this behavior; however, one feasible explanation will be proposed. The elastomer used in this investigation was natural rubber, which is known to strain crystallize at sufficiently high deformations. Perhaps in the case of the nonprecut samples, any anisotropy in strength is "masked" by crystallization of the elastomer chains which reinforces the composition. On the other hand, precut samples may fail at sufficiently low stress levels that crystallization does not occur and hence does not interfere with differences due to chain alignment. In any event, from a practical standpoint, the difference in response between precut and nonprecut samples is quite important. Hence, even if standard tensile properties of a vulcanized sheet do not show anisotropic behavior, this does not mean that anisotropy will not be exhibited in another means of failure. Indeed, for example, a property of the rubber sheet such as cyclic cut growth may still exhibit substantial anisotropy. Presently, experiments are being performed to further examine the importance of scorch time and specimen size and shape (as placed in the mold cavity) on the anisotropy induced by compression molding. These will be the subject of a future publication.

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