Anisotropy of Ultimate Properties in Vulcanizates of EPDM/High-Diene Rubber Blends

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Introduction

Ethylene-propylene-diene monomer (EPDM) rubber has been blended with high-diene rubbers (e.g. NR, BR, SBR, etc.) to give compositions of extremely good resistance to the effects of ozone [1]. If enough EPDM rubber is used (35 to 45 %), essentially ozone-proof compositions can be obtained. However, in such cases two major types of problems can occur :

(a) The domains of EPDM rubber can be greatly under-cured because of cure-rate incompatibility [2-6] ; EPDM rubber, the slow-curing rubber almost becomes the no-curing rubber in the presence of the aggressively reactive high-diene rubber ;

(b) At the high concentrations of EPDM necessary for the ozone protection (in the range of concentrations wherein co-continuous phase-morphology generally occurs), large, highly shaped, sheet-like or fiber-like EPDM rubber domains can form.

One might expect that the highly shaped domains would be predominantly oriented in the direction of the flow of the unvulcanized rubber during the processing of the rubber. In the case of a tire sidewall *(figure 1)*, the rubber is extruded circumferentially with respect to the finished tire.

Weaknesses then can result from the formation of rather large circumferentially oriented domains which can act as failure-initiating flaws. Thus the sidewall is weakest in the direction of greatest stress during its use. Also sheet-like domains would tend to be parallel to the sidewall-carcass interface. This would give rise to a tendency towards delamination-type failures or even poor apparent adhesion between the EPDM-containing sidewall and the carcass.

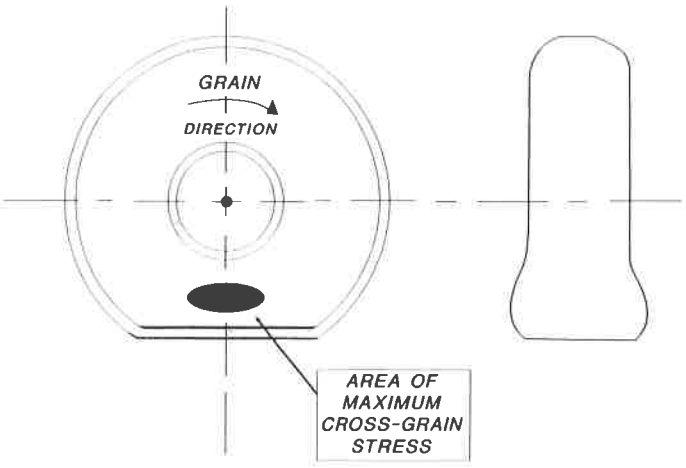

FIGURE 1. - *Flexing of a tire sidewall during its use.*

We have now found that both of these problems can be alleviated if two techniques are used :

(a) The EPDM is modified by a treatment with maleic anhydride to give EPDM whose molecules have succinic anhydride groups appended thereto, and :

(b) The EPDM is thoroughly mixed with the high-diene rubber before the addition of zinc oxide, the zinc oxide being added later, but while the mixing of the polymers is continued.

The result of this is that the EPDM becomes dynamically vulcanized and is forced to be in the form of small particles of low shape factor and thus of low flaw-forming tendency. Although the EPDM rubber is crosslinked by the action of the zinc oxide (which gives ion-cluster crosslinks), the composition is still millable and otherwise processable since the high-diene rubber is still unvulcanized. The pendent succinic anhydride groups on the EPDM molecules provide a vulcanization chemistry for the EPDM which is independent of the accelerated-sulfur vulcanization used later in the cure of the high-diene rubber (in the hot mold). The dynamic vulcanization process provides a means for controlling microphase domain morphology to prevent the potential disasters which can result from anisotropy in ultimate properties (tearing, interply delamination, circumferential fatigue cracking, etc.). In this report we present techniques and new test results which support the above.

Experimental

The EPDM used in this work was Epsyn (reg. TM) 70 A.

Modified EPDM was Epsyn 70A rubber which had been treated at an elevated temperature (*ca.* 230 °C) with 2 phr of maleic anhydride in the presence of 0.2 phr bisbenzothiazole disulfide (MBTS) [1]. Masterbatches of EPDM, maleic anhydride-modified EPDM and natural rubber (NR) were prepared by mixing each of the rubbers with 50 phr of N-326 carbon black, 10 phr of oil

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(Circosol 4240), and 1 phr of stearic acid. Two EPDM/NR masterbatches, one from the unmodified EPDM and one from the maleic-modified EPDM were prepared. In the case of each composition to be evaluated, the appropriate EPDM masterbatch was mixed in the Banbury mixer with the NR masterbatch. The proportions of the masterbatches were such that the EPDM comprised 40 % of the rubber in the final blend. Also in each case, only after the blended masterbatch was thoroughly mixed (after about 3 minutes) was 5.5 phr of zinc oxide added with continued mixing. Mixing was further continued for about 2 minutes and the batch was dumped at about 135-150 °C. Stocks for vulcanization and evaluation were prepared from each of the EPDM/NR masterbatch blends by the addition of 2 phr sulfur, 0.5 phr of Santocure (reg. TM) NS accelerator (t-butyl-2-benzothiazole-sulfenamide), and 2 phr of Santoflex (reg. TM) 13 antidegradant on a roll mill. Similarly, an all natural rubber stock was prepared on the mill. In addition, a 50/50 natural rubber (SM-5)/butadiene rubber (BR) (cis-1203) masterbatch with 50 phr N-330 carbon black, 12.5 phr oil (10 of Sundex 790 and 2.5 of Sunolite 240), 5.5 phr of zinc oxide and 1 phr of stearic acid was prepared as a model sidewall masterbatch for comparisons. In this case, 2 phr of sulfur, and 1 phr of Santocure NS, and 3 phr of Santoflex 13 were added on the roll mill. For the study of adhesion of the experimental EPDM/NR stocks to a carcass ply, a model carcass stock was prepared from a masterbatch containing 50 phr SMR-5, 36 phr SBR 1778 (of which 10 phr is oil), 24 phr SBR 1502, 70 phr N-660 carbon black, 10 phr Piccopale 100 and 1 phr stearic acid. The carcass stock was prepared from this masterbatch by the addition of 2 phr Santoflex DD, 2.5 phr insoluble sulfur 60, 0.8 phr MBTS and 0.5 of Santocure NS on the roll mill.

In order to measure the effects of flow-induced anisotropy, we have devised tests to be done in addition to the usual tests. In the case of stress-strain, we label the three directions : x for the direction of milling in preparation for the molding of test slabs, y for the direction perpendicular to x, and z for the thickness direction. The maximum tensile strength anisotropy is obtained by comparing the tensile strength measured in the x direction to the tensile strength measured in the z direction. The tensile strength in the z direction was measured by testing a specimen which was cut from a tensile test slab which was prepared by lamination of the milled sheet *(figure 2)*. Four or five strips were cut from the central area of an unvulcanized test slab in the direction perpendicular to the milling direction. The strips were about 2.5 mm wide. These strips were rotated 90 degrees about their length-wise axes and the unvulcanized test slab was spliced back together (by using the "solvent-freshening" technique). Thus, if the specimen is horizontally laid, the grain of the centrally modified area of the slab is in the vertical orientation. Tensile test specimens were cut perpendicular to the length-wise axes of the rotated strips of the modified test slab.

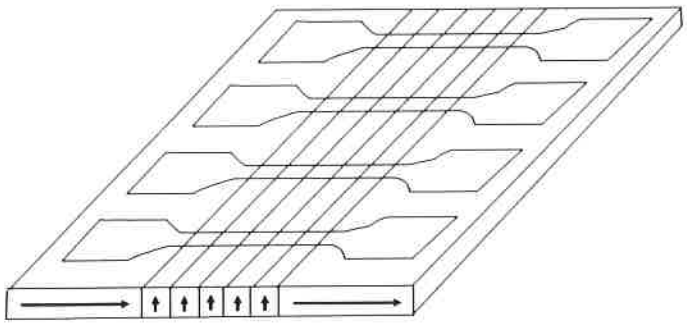

FIGURE 2. - *Lay-up of laminated specimens for the determination of ultimate tensile strength in the "thichness" direction.*

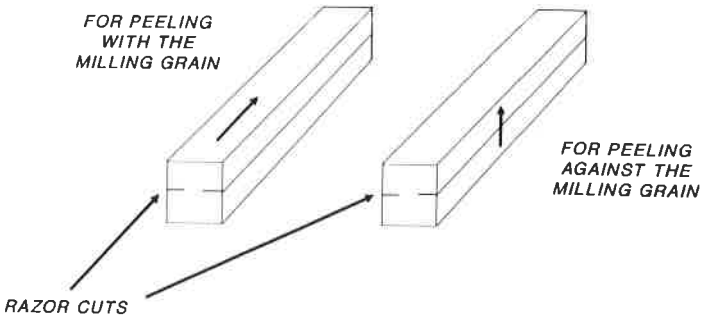

FIGURE 3. - *Specimen for peel strength measurements. Milling-grain direction is given by arrow on specimen.*

In the case of peel strength anisotropy, strips were cut from Ross flex test specimens which were 6.25 mm wide and 6.25 mm thick *(figure 3)*. Some of the Ross flex specimens were molded with the milling directions running parallel to their lengths and others were molded with the milling directions running parallel to the widths of the Ross specimens (which measured 2.5 cm wide by 6.25 mm thick by 15 cm long). Razor cuts, approximately 2.5 mm deep, were centrally cut along the lengths of the 15 cm-long strips. Some were cut with the grain and some against the grain. Peeling was initiated by 25 cm-long razor cuts and completed by pulling the specimens apart in an Instron tester. Peel strength was obtained by dividing the average peak force for peeling by the average distance between longitudinal razor-cut grooves. Peel-strength anisotropy was measured by dividing the peel strength measured across the grain by the peel strength measured with the grain. In addition to these peel strength measurements, peel forces to separate the traditional 2.5 cm-wide peel pad were measured.

Results and discussion

Results of testing are summarized by *figures 4-10*. The properties of the compositions are indeed anisotropic ; they differ with respect to the direction of measurement. However, the tendency towards anisotropy (and, thus the tendency towards weakness in certain directions, e.g. a tendency towards tearing in the direction of the milling grain) is greatly reduced by dynamic vulcanization.

The EPDM/NR composition in which the EPDM is not modified or dynamically vulcanized is very much more anisotropic than is the dynamically vulcanized composition. This can be seen with respect to ultimate tensile properties in *figure 4*.

Dynamic vulcanization also greatly improves peel strength, especially in the with-the-grain direction. This can be concluded from the data illustrated by *figure 5*. In addition, the interply adhesion to the model carcass stock is greatly improved by using the dynamic vulcanization technique in the preparation of the EPDM/NR blend *(figure 6)*. Fatigue life as measured by the Ross flex test *(figure 7)* is also greatly improved with respect to cuts growing in the with-the-grain direction.

It should be further noted that dynamic vulcanization gives rise to substantial improvements in tension set *(figure 8)*, torsional hysteresis and rebound *(figure 9)*. This, of course would indicate that the molecules of the modified EPDM are more densely crosslinked, because of the action of the zinc oxide to form ion-

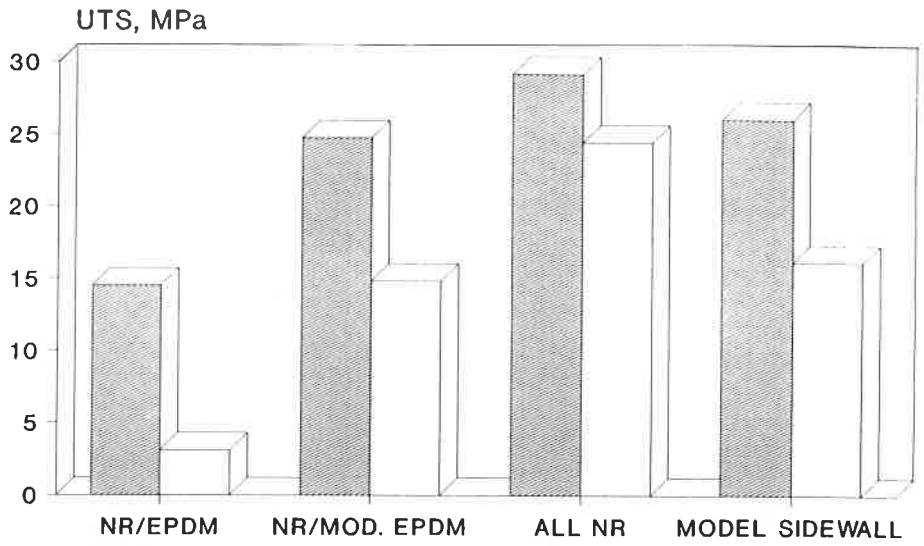

FIGURE 4. - *Ultimate tensile strength of vulcanizates measured in the strongest and weakest directions.*

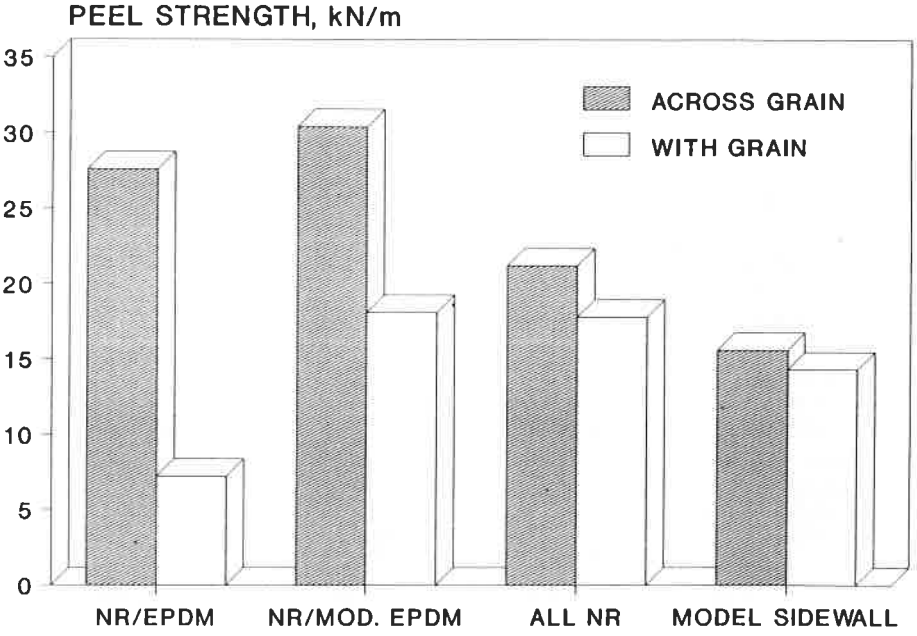

FIGURE 5. - *Peel strength.*

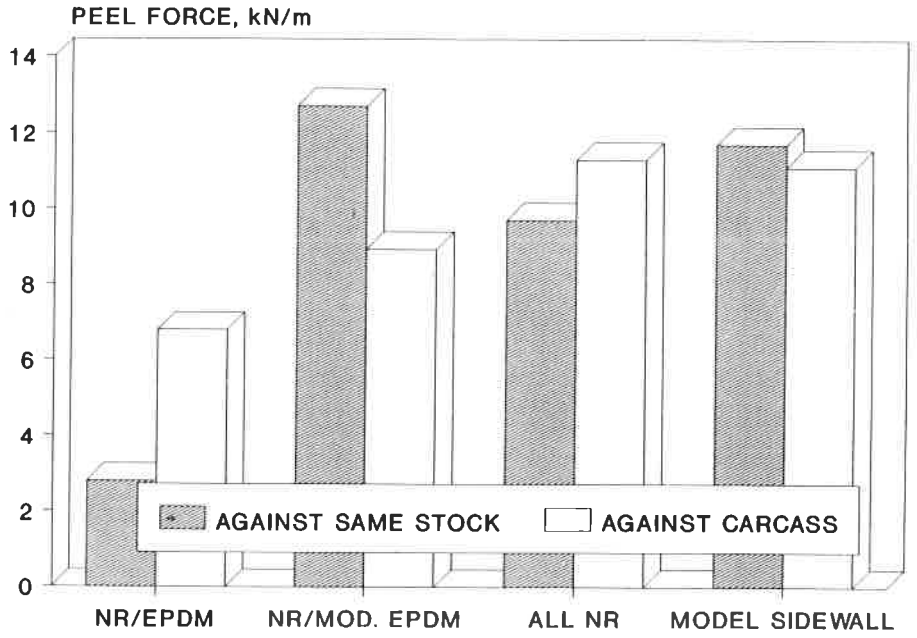

FIGURE 6. - *Inter-ply adhesion.*

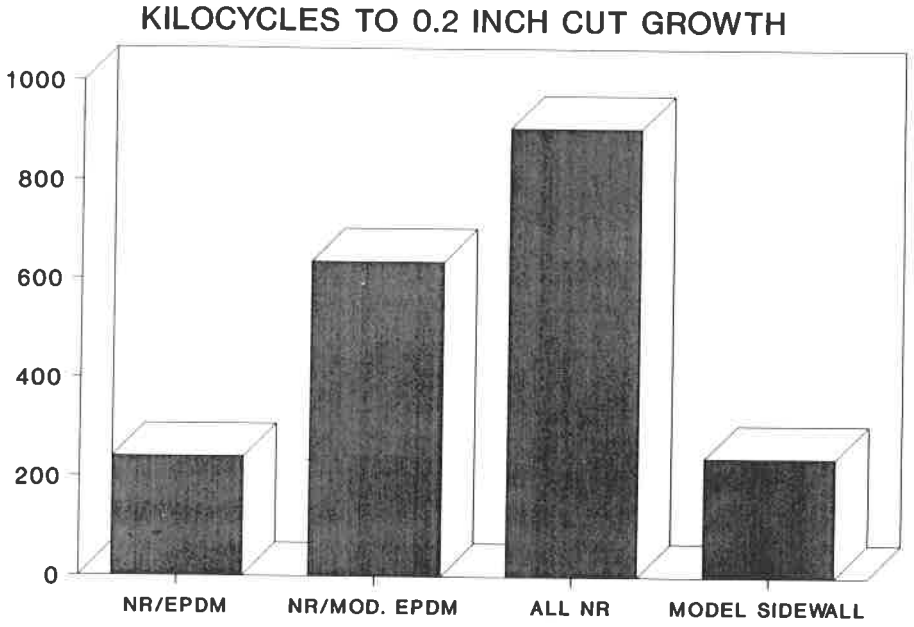

FIGURE 7. - *Ross flex test (bending fatigue).*

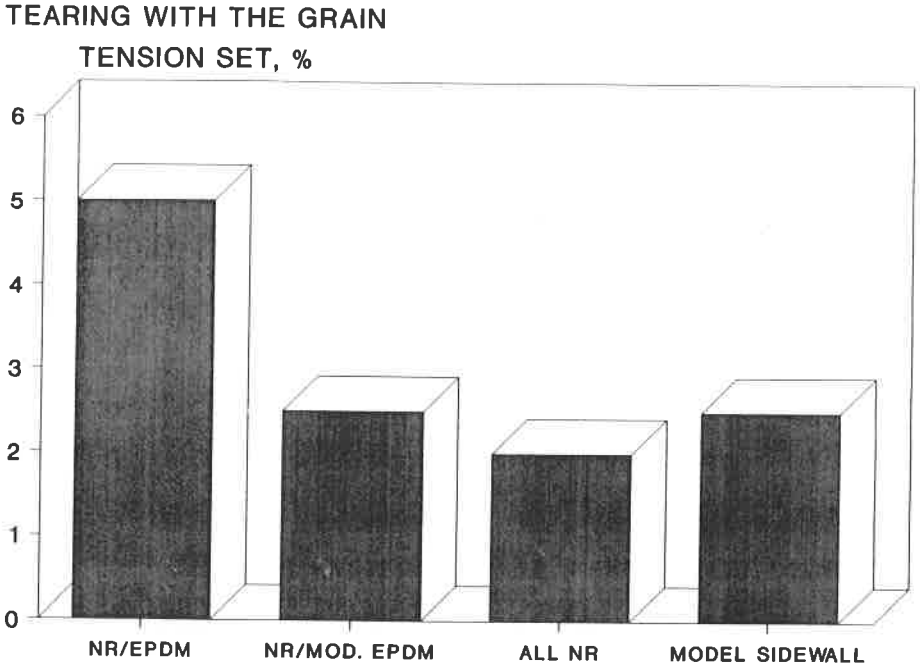

FIGURE 8. - *Tension set.*

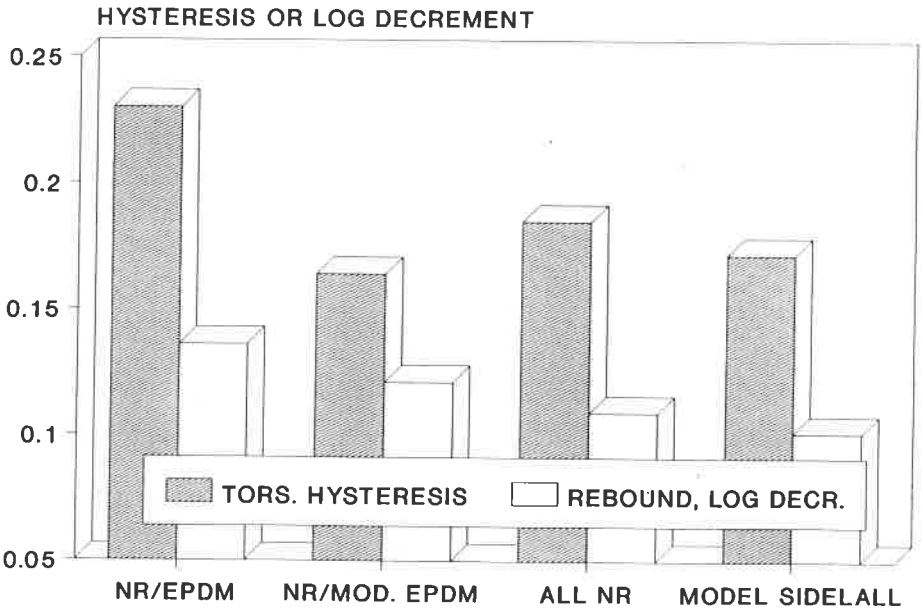

FIGURE 9. - *Torsional hysteresis and Lupke rebound.*

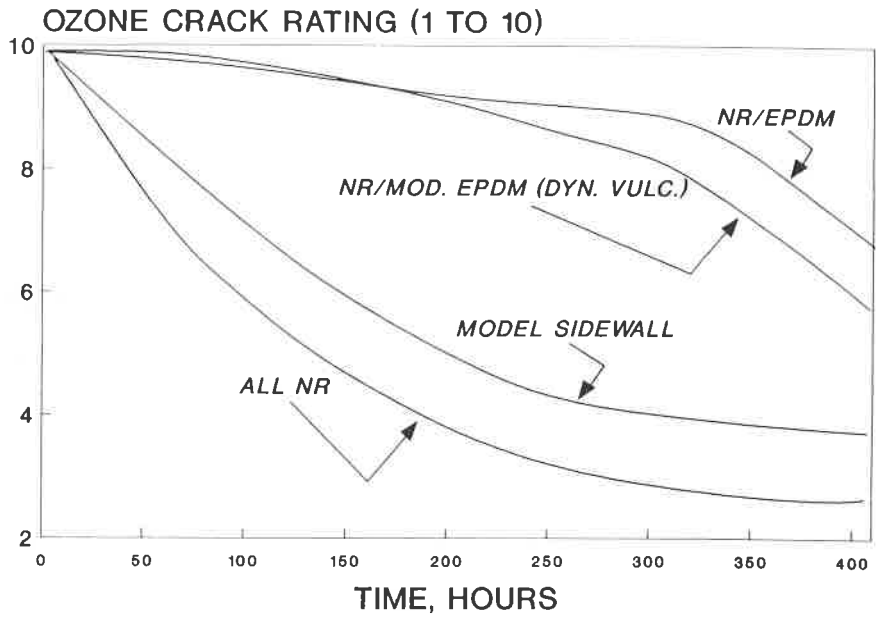

FIGURE 10. - *Belt-flex ozone resistance.*

cluster crosslinks, than they would be in the absence of the succinic anhydride pendent groups. This is similar to what has been earlier reported [2].

It is true that the dynamically vulcanized, maleic-modified EPDM-containing blend with NR is slightly less ozone resistant than the blend containing the unmodified EPDM *(figure 10)*. However the dynamically vulcanized blend performs best, overall, by a considerable margin.

All of the above relates to anisotropy in mechanical properties. In addition however, preliminary work with the electron microscope indicates that, indeed there is considerable anisotropy in blends of EPDM with high-diene rubbers. In a blends of unmodified EPDM with NR or with a mixture of NR and BR, the rod-like or sheet-like structures appear to form. However, when the EPDM was maleic-modified and the composition was dynamically vulcanized by the action of zinc oxide during the mixing process, no such sheet-like structures could be found.

Conclusions

It can be concluded from this work that the ultimate mechanical properties of NR/EPDM blends are indeed anisotropic, but that the tendency towards anisotropy (and, thus, the tendency towards weakness in certain directions, e.g. a tendency to tear with the processing-flow direction or grain) is greatly reduced by the dynamic vulcanization technique. This technique improves cut growth resistance, peel strength and inter-ply adhesion. Also, because of the modification of the EPDM to give reactive sites (pendent succinic anhydride groups) for vulcanization to occur by a means other than sulfur, the cure-rate incompatibility problem is greatly ameliorated. Thus, improvements in permanent set, hysteresis and rebound are obtained by using the techniques of this report.

References

[1] E.H. Andrews, *Rubber Chem. Technol.*, **1967,** *40*, 635.
[2] A. Coran, *Rubber Chem. Technol.*, **1987,** *61*, 281.
[3] G. Kerutt, H. Blumel, H. Weber, *Kautsch. Gummi, kunstst.*, **1969,** *22*, 413.
[4] M.E. Woods, J.A. Davidson, *Rubber Chem. Technol.*, **1976,** *49*, 112.
[5] W.H. Whittington, *Rubber Ind.*, **1976,** *9*, 151.
[6] V.A. Shershnev, *Rubber Chem. Technol.*, **1982,** *55*, 537.