JOURNAL OF APPLIED POLYMER SCIENCE VOL. 15, PP. 949–954 (1971)

# The Effects of Varying the Polymer Composition on the Cut Growth Characteristics of E/P/1,4 HD Tire Treads

C. W. STEWART, SR., and J. J. VERBANC, *E. I. du Pont de Nemours and Company, Inc., Elastomer Chemicals Department, Experimental Station, Wilmington, Delaware 19898*

## Synopsis

Experimental ethylene–propylene–1,4-hexadiene polymers covering a range of compositions which possess satisfactory processing characteristics and economics have been evaluated in passenger car tires with emphasis on groove cracking. The tearing energy criterion was used in a laboratory test to correctly predict the groove cracking behavior of the tires made from these polymers. Road tests indicate that ethylene–propylene–1,4-hexadiene tripolymers containing 36%–42% propylene and 1.8%–2.2% diene exhibit resistance to cut growth and abrasion which is superior to standard SBR–BR bias tires. Polymers containing more than 42% propylene or 2.2% diene were inferior in wear and resistance to groove cracking, but sufficient data are not available to pinpoint the reason.

## INTRODUCTION

Automobile and small truck tire treads are made principally from styrene–butadiene rubber (SBR) with varying amounts of *cis*-1,4-polybutadiene (BR) added to improve wear and reduce groove cracking. Natural rubber is commonly used for truck tires designed for severe service, since this polymer is resilient and has a low rate of heat buildup. Recently ethylene–propylene–diene monomer (EPDM) rubbers have received a great deal of attention for use in tires either alone or as a blend with other polymers, because of their excellent weather resistance, heat aging resistance, low temperature properties, and their capacity for high loadings of oil and carbon black.

In a series of articles, Satake and co-workers[1,2,3] have compared polymer processing, tire building, abrasion resistance, wet skid resistance, and flex cracking in EPDM rubbers having as termonomers 1,4-hexadiene, dicyclopentadiene, methyltetrahydroindene, and 5-ethylidene-2-norbornene. They concluded from various laboratory and field tests that EPDMs with 1,4-hexadiene as the termonomer exceeded the other EPDMs in processability, abrasion resistance, and flex crack resistance, although they did point out that other factors such as molecular weight distribution, sequence length, and ethylene content are very important also. For example, they found that as polymer viscosity and ethylene content increase, abrasion resistance increases while the plasticity at room temperature decreases and, consequently, processability during tire building becomes poorer. Furthermore, in order to avoid a slow curing rate and to make EPDMs suitable for blending with other rubbers, the diene level must be high. However, a high diene level has been found to decrease resistance to abrasion and flex cracking.[4]

It appears that those factors which improve the mixing, extrusion, building, and curing operations also tend to reduce the performance of the tire tread in some way. It is only after much trial and error that suitable compounds can be obtained and reasonable limits set for the selection of the final tread candidate, keeping in mind at all times the economics involved in producing the polymer and manufacturing the tires.

The purpose of this study was to determine the effects of changing the polymer composition on the performance of an EPDM-based tread compound. A series of experimental ethylene–propylene–1,4-hexadiene polymers were prepared covering a range of compositions known to give compounds which possess satisfactory processing characteristics and economics for the production of passenger car tires. In this series, the propylene content was varied between the limits of 36 to 47 weight per cent, the effective 1,4-hexadiene content was varied from 1.8 to 3.0 weight percent, while the Mooney viscosity [$ML_{1+4}$ (100°C)] was held constant at 57. These polymers are related but not identical to commercially available "Nordel" hydrocarbon rubbers (Du Pont).

The major emphasis in this study was on cut growth characteristics, since early tire tests indicated that EPDM tread compounds had a tendency to groove crack to a serious extent.[4] Furthermore, there were no laboratory tests available when previous tests were made that could be used to quantitatively predict groove cracking behavior. Recently, however, a method was described which enables one to estimate the elastic energy available for fracture from the amount by which a small crack opens.[5] Thus, a convenient laboratory test is now possible based on the concept of the tearing energy. Unfortunately, there are no data available in the literature which compare the cut growth rate of various EPDM compositions as a function of the tearing energy.

## TEARING ENERGY CRITERION

The elastically stored energy which is expended when the length of a cut is increased by a given small amount at constant overall deformation of the test piece is found to be independent of the shape of the test piece and of the manner in which the deforming forces are applied to it.[6] This energy is, therefore, directly related to tearing of the material and is an appropriate parameter for the determination of the basic growth properties of flaws in a rubber sample in a quantitative and generally applicable way.

As a bias tire rotates, the deformation at the base of each groove is approximately one of pure shear, with the thick ribs of the tread acting as long clamps.[5] A small section of each groove near the area of contact with the road undergoes an increase in tensile strain, whereas in the contact region itself the strain is relaxed to zero. When the cut length is equal to about half the unstrained width of the groove, the maximum crack opening is sufficient to completely relax the strain.[5] Thus, for longer cuts, the tearing energy becomes independent of the cut length.

## EXPERIMENTAL

To develop an EPDM tread candidate suitable for use in passenger car tires, a series of experimental ethylene–propylene–1,4-hexadiene polymers were prepared covering the range of compositions described above. Tread compounds of these polymers were prepared using the recipe given in the appendix. For road tests, four tires were built from each stock employing the Firestone "Deluxe Champion" design of size 7.75 in. × 14 in. with two-ply nylon (four-ply rating) cords. For laboratory tests, sheets approximately 1 mm thick were vulcanized between polished steel plates, and tensile strips 6 in. × 1 in. were cut from these. For comparison, tensile strips were also cut from various sections of the treads at the completion of the road tests. As a control, commercial SBR–BR Firestone "Deluxe Champion" tires of the same size and design as the EPDM tires were also road tested, and tensile strips were cut from various sections of their treads.

### Laboratory Tests

To determine the cut growth characteristics of the tread compounds using tensile strips, the experimental procedure described by Lake and Lindley was followed.[7] The testing machine was set up in an air oven at 50°C to simulate conditions under which fatigue occurs on the road. The deformations in simple extension were confined to strains less than 20%, and the frequency of the cyclic process was chosen to be 200 cpm. To allow for permanent set due to structural breakdown in these black-filled vulcanizates, the samples were precycled for 24 hr. The strain energy density was then determined from the load deflection curve for the sample, and a small cut was made in one edge of the test strip to begin the test. It was found that when cut growth measurements were made in this way, the results using tensile strips cut from vulcanized sheets closely agreed with those for strips cut from the treads of tires which had been road tested.

The rate of cut growth is plotted as a function of tearing energy for the EPDM tread compounds and SBR–BR control in Figure 1. It is seen that the EPDMs become more resistant to cut growth as the percentages of propylene and 1,4-hexadiene are lowered. A decrease in the propylene content causes an increase in the crystallinity of these polymers and gives them a tendency to crystallize further on stretching.[8] As with natural rubber and *cis*-1,4-polybutadiene, crystallinity would tend to increase the resistance to cut growth. A high level of diene monomer appears to produce an overcured state and seems to make the compound somewhat brittle.

## Road Tests

The tires were mounted on 5.5 K × 14 in. rims with 24 psig cold air pressure and 1280 lb load per tire. They were run over a selected highway route in Texas, during the summer, at an average speed of 60 mph and were examined and rotated every 500 miles. A few small cuts, less than 0.1 in. long, appeared in all tires at random throughout the test, and these were probably due to running over stones or sharp objects on the road. Also, several cuts were deliberately made in the grooves of the tires at various stages, and the growth rate of each cut was closely followed throughout the test.

The maximum tearing energy $T_m$ in the grooves of a tire at it rotates was determined from the amount by which a small crack opened, as described by Lake.[5] The width of the grooves in the tires used for this study was 0.2 in. Since the deformation is approximately one of pure shear, the maximum crack opening is independent of its length for cuts larger than 0.1 in., and the tearing energy becomes a constant. For the tires and conditions used in this test, the value of this constant tearing energy was found to be $T_m$ = 0.6 lb/in.

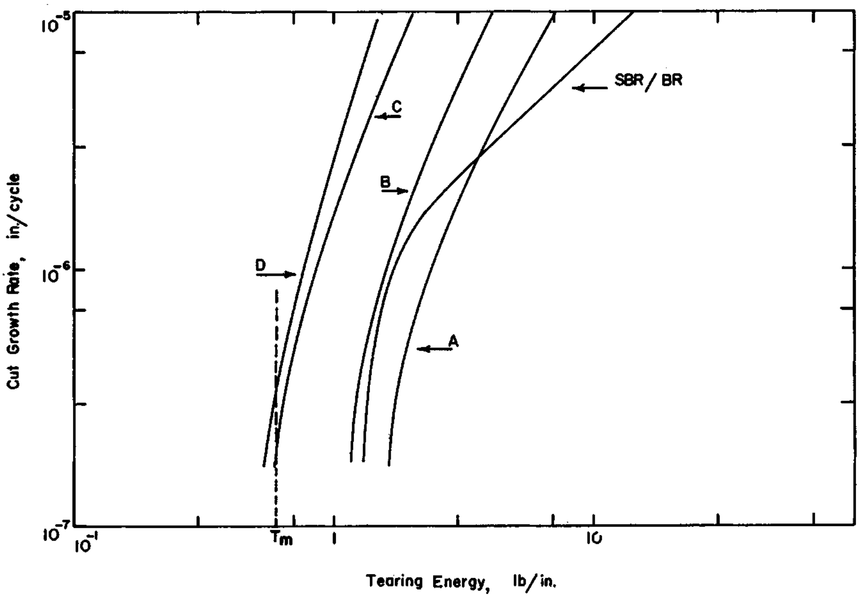

Fig. 1. Cut growth characteristics of EPDM and SBR–BR tread compounds: (A) 42% propylene, 1.8% diene; (B) 36% propylene, 2.2% diene; (C) 47% propylene, 2.2% diene; (D) 41% propylene, 3% diene.

## RESULTS

From Figure 1, one would expect that tires A and B and the SBR–BR would not groove crack under the test conditions since the rate of cut growth at a tearing energy of 0.6 lb/in. is extremely small. It was in fact observed that cuts in these tires, whether made deliberately or due to unknown road hazards, did not grow at all during the tests. On the other hand, one would expect cuts to grow at the rate of 1.7 in. per 10,000 miles ($8.5 \times 10^6$ cycles) in polymer C and at the rate of 2.8 in. per 10,000 miles in polymer D. As is usual for a crack growth process, there was some variability of the results; however, after averaging it was found that cuts in tires C grew at the rate of 2.0 in. per 10,000 miles and cuts in D grew at the rate of 3.2 in. per 10,000 miles. For example, after 12,000 miles the four tires of polymer C contained a total of eight cracks with length between 1.5 and 2.5 in., all due to small accidental cuts which occurred during the first 4,000 miles. Likewise, the four tires of polymer D contained a total of 12 cracks with lengths between 2.5 and 3.5 in. after the first 12,000 miles. The tires made from these two polymers also had many smaller cracks which were initiated later in the test and then grew at a constant rate closely approximated by the value predicted in laboratory tests on tensile strips.

The crack growth rates observed during road tests were slightly higher than those observed in the laboratory. The reason for this is that the tearing energy in the groove of a tire increases with cornering. It was found, through the use of high-speed photography, that the tearing energy depends as expected on the traveling velocity, the slip velocity, wheel stiffness, and the location of the groove. This complicates the situation for road tests that contain a large number of sharp curves; however, the tearing energy criterion can still be used to select the polymer composition and tread compound which best resist groove cracking by determining the maximum strain energy which the polymer will be subjected to in use. For the polymer compositions in Figure 1, polymer A would be most suitable if the tearing energy remained less than 3 lb/in.

It should be noted that there seemed to be some correlation between cut growth resistance and abrasion resistance of the EPDM tires in the road tests. Although no quantitative relationship is possible at this time, it was observed that polymers A and B exhibited about a 10% to 20% greater abrasion resistance than SBR–BR as measured by tread wear, while polymers C and D had 5% to 10% less abrasion resistance than SBR–BR.

The traction of EPDM tires on ice and snow is excellent[9]; however, the wet skid resistance has been reported as being slightly less than standard SBR–BR tires.[4] If the paraffinic or naphthenic oil previously used in EPDM tread stocks is replaced with a highly aromatic oil, as is the case with SBR–BR treads, it is found that the resilience of the compound decreases, the wet skid resistance becomes equal to the standard SBR–BR, and cut growth resistance is improved by approximately 10%.[10]

## Appendix

Experimental ethylene–propylene–1,4-hexadiene polymers were prepared having the following compositions: (A) 42 wt-% propylene, 1.8 wt-% effective hexadiene; (B) 36 wt-% propylene, 2.2 wt-% diene; (C) 47 wt-% propylene, 2.2 wt-% diene; (D) 41 wt-% propylene, 3 wt-% diene. The Mooney viscosity [$ML_{1+4}$(100°C)] was held constant at 57.

Tread compounds were prepared from each polymer by Banbury mixing the following formulation, based on 100 phr: 100 phr EPDM; 100 phr ISAF carbon black; 75 phr Sunpar (Trademark of Sun Oil Co.)–150 oil; 5.0 phr zinc oxide; 1.0 phr stearic acid; 1.5 phr sulfur; 1.5 phr tetramethyl thiuram monosulfide; 0.8 phr mercaptobenzothiazole. The tires were vulcanized for 25 min at 330°F.

The authors wish to express their gratitude to C. C. McCabe and H. Leibu for their assistance during this program and for supplying road test data.

## References

1. K. Satake, T. Sone, and M. Hamada, *J. IRI*, **4**, 21 (1970).
2. K. Satake, T. Sone, and M. Hamada, *J. IRI*, **4**, 71 (1970).
3. K. Satake, T. Wada, T. Sone, and M. Hamada, *J. IRI*, **4**, 102 (1970).
4. R. W. Kindle and S. van der Burg, *Rubber Age*, **98**, 65 (1966).
5. G. J. Lake, paper presented at the Yield, Deformation and Fracture of Polymers Conference, Cambridge, England, March-April 1970.
6. R. S. Rivlin and A. G. Thomas, *J. Polym. Sci.*, **10**, 219 (1953).
7. G. J. Lake and P. B. Lindley, *Rubber J.*, **146**, 24 (1964).
8. U. Flisi, G. Crespi, and A. Valvassori, *Rubber Chem. Technol.*, **43**, 778 (1970).
9. C. C. McCabe, R. G. Arnold, and J. J. Verbanc, paper presented at the Division of Rubber Chemistry, ACS, Spring Meeting, Cleveland, April 24, 1968.
10. H. K. Frensdorff, private communication.

Received December 9, 1970