

Curing Ethylene-Propylene Rubber Terpolymers with Dimethacrylate Monomers. II. Effect of Unsaturation

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Synopsis

In a previous paper it was shown that the vulcanization obtained with ethylene-propylene-diene terpolymer is equivalent or superior to that obtained with ethylene-propylene copolymer when a peroxide-dimethacrylate coagent cure system was used. In order to determine the effect of the unsaturation on the physical properties in the terpolymer, the terpolymer had been hydrogenated to remove the double bonds. Infrared spectra and bromination were used to check the extent of hydrogenation. Tensile strength, Shore A hardness, per cent elongation, and modulus indicated no decrease in vulcanization efficiency after hydrogenation. The data show that the unsaturation in the terpolymer does not contribute to the vulcanization cure with the peroxide-dimethacrylate coagent curing system.

INTRODUCTION

In a previous paper¹ we have shown that vulcanization can be obtained with an ethylene-propylene-diene terpolymer (duPont Nordel 1070) which is equivalent or superior to that obtained with an ethylene-propylene copolymer (Enjay 404) when a peroxide-dimethacrylate coagent cure system is used. The degree of vulcanization which can be obtained is not limited by the amount of unsaturation in the terpolymer and is essentially of the same character as that obtained with the copolymer.

Two postulates for explaining the improved physical properties obtained with the vulcanizate from the terpolymer are: (a) the vulcanizing ability of the ethylenic double bonds; (b) the branched structure of the terpolymer.

In this paper, in order to evaluate the effect of the ethylenic double bonds, the vulcanizing properties of an ethylene-propylene terpolymer were evaluated by physical property measurements before and after hydrogenation to remove residual double bonds.

EXPERIMENTAL

Materials

Nordel 1040 (lot 502502, du Pont), an ethylene-propylene terpolymer, was used in this work. It is of lower molecular weight than the Nordel 1070

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used in the previous paper and is easier to handle in solution. It is believed to be a terpolymer of ethylene, propylene, and 1,5-hexadiene. Since the Nordel 1040 is a commercial product, other additives or impurities may be present. However, no nonterminal unsaturation is indicated by the infrared spectrum of the polymer. The cyclohexane was spectro grade. The carbon tetrachloride was reagent grade. Acetone was reagent grade. The activated carbon was KB grade Darco (Atlas Powder Co.). The catalyst was Girdler G-49B (Chemetron Corp.), reduced and stabilized nickel on kieselguhr catalyst.

Hydrogenation Procedure

Hydrogenation 46-37. About 150 g. of terpolymer sample was used to make a 10% solution in cyclohexane. The catalyst (1%) was added to the viscous solution which was stirred thoroughly to disperse the powdered catalyst. This solution was added to the autoclave which had been flushed with nitrogen and hydrogen. The hydrogenation was run at temperatures of 70–130°C. and pressures up to 295 psi for 24 hr. The catalyst was removed by adding activated carbon and filtering. The terpolymer product was purified by putting it into solution in carbon tetrachloride, adding activated carbon, and filtering. A clear solution was obtained. The product was precipitated with acetone and vacuum-dried. The product obtained (120 g.) was used for the compounding as shown in Table I.

TABLE I
Formulation Data on Nordel 1040 and Hydrogenated Nordel 1040

	Parts by weight	
	Compound A (hydrogenated)	Compound B (nonhydrogenated)
Nordel 1040 (hydrogenated)	100	—
Nordel 1040 (lot 502502)	—	100
Whitex clay	125	125
EPC black	10	10
Petrolatum	5	5
Luperco 130XL	3	3
SR-206 (ethylene dimethacrylate)	5	5
Cure 30 min. at 350°F.		

Hydrogenation 46-39, 46-57. About 150 g. of terpolymer was hydrogenated for 12 hr. as above, 5% catalyst being used. Temperatures were 40–100°C. and pressure was maintained at 200–400 psi. Benzene was used as solvent. The product was purified by dissolving in benzene and was then precipitated with acetone and vacuum-dried. The products were used in the compounding in Table I.

After the first hydrogenation there was some doubt as to whether residual carbon tetrachloride could have acted as a chain transfer agent. Testing

results of the vulcanizates from the two sets of hydrogenations, the second one with benzene, do not indicate any such effect.

Product Analysis

Bromination Analysis. Residual double bond measurement can be readily made by bromination procedures. The method used in this paper² involves the use of a solution of pyridine sulfate dibromide in glacial acetic acid as the bromine addition reagent with mercuric acetate as catalyst. The excess reagent is measured by adding potassium iodide and titrating the resultant iodine with sodium thiosulfate. Error on bromination is likely to be due to substitution giving a high reading. Three separate hydrogenations were run. Bromination results are shown in Table II. There was a definite decrease in per cent residual double bonds after hydrogenation, indicating that hydrogenation has removed essentially all of the double bonds.

TABLE II
Bromination Results

	Double bonds calculated as propylene groups, %
Original terpolymer (Nordel 1040, lot 502502)	
Initial testing	4.6, 4.0
Tested 6 months later	3.7
Tested 1 year later	5.5
Hydrogenated terpolymer (Nordel 1040, lot 502502)	
Hydrogenation (46-37)	0.9, 1.25
Hydrogenation (46-39)	1.45
Hydrogenation (46-57)	0.7, 1.1

Infrared Analysis. Infrared analysis is also a good method for determining the change in the number of terminal double bonds resulting from hydrogenations. Samples were run as a film between NaCl plates with a NaCl prism and at 927 resolution. An absorption band at 885 cm^{-1} characteristic of asymmetrically disubstituted ethylenes $\text{R}_1\text{R}_2\text{C}=\text{CH}_2$ was observed for any change after hydrogenation (Fig. 1). The infrared spectra of hydrogenated terpolymer and original terpolymer are identical, with the exception that the 885 cm^{-1} absorption band is absent from the spectra of hydrogenated terpolymers. The absence of this absorption band indicates the hydrogenation was successful for this type of linkage. An absorption band at 965 cm^{-1} may occur with *trans*-substituted double bonds, but in this case the band at this frequency represents a CH_3 rocking (mixed with CH_2 and CH rocking) and does not appear to be significantly altered. There is observed a slightly increased absorption in this peak after hydrogenation. Data from infrared analysis of ethylene-propylene copolymers where no unsaturation is expected show this same absorption band with es-

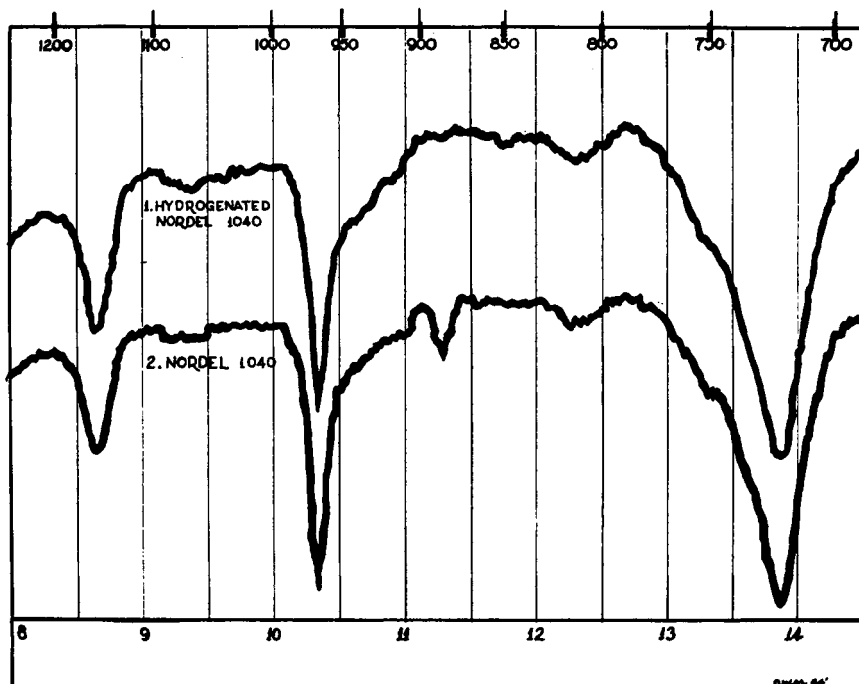


Fig. 1. Infrared spectra.

essentially the same intensity of absorption,³ confirming that this band is not due to unsaturation. No new substituents were introduced by the hydrogenation process. The infrared data also show that hydrogenation appears to have removed essentially all of the terminal double bonds. No nonterminal double bonds are indicated on the infrared spectra, indicating that the terpolymer was an ethylene-propylene-1,5-hexadiene type rather than a 1,4-hexadiene terpolymer, since the 1,4-hexadiene terpolymer would have internal residual double bonds.

TABLE III
Physical Property Data on Nordel 1040 and Hydrogenated Nordel 1040 (46-37) Compounded and Tested 8/6/63 and 7/8/64

	Compound A (hydrogenated)		Compound B (nonhydrogenated)	
	8/6	7/8	8/6	7/8
Tensile strength, psi	875	950	825	750
Elongation, %	300	250	400	400
100% Modulus	525	400	250	150
200% Modulus	785	800	500	375
300% Modulus	875	—	700	600
Hardness, Shore A	75	66	60	56

RESULTS

Material from the two hydrogenations was compounded and tested for physical properties as shown in Tables III and IV.

TABLE IV
Physical Property Data on Nordel 1040 and Hydrogenated Nordel 1040 (46-39, 46-57)
Compounded and Tested 12/9/63 and 12/13/62

	Compound A	Compound B	
	(hydrogenated)	(nonhydrogenated)	
	12/9	12/9	12/13
Tensile strength, psi	1200	1242	1170
Elongation, %	130	180	200
100% Modulus	1065	858	475
200% Modulus	—	—	1170
300% Modulus	—	—	—
Hardness, Shore A	80	76	63

Differences Between Table III and Table IV

It is to be noted that although the two sets of tests are very consistent in the relationship of all properties of the hydrogenated versus the unhydrogenated terpolymer, there is an appreciable difference in the testing results obtained six months apart. This difference has not been explained. It is possible that some room temperature or aging effect occurred which changed the properties. Aging has not been observed in the du Pont Laboratories.⁴ It is more likely that there is some systematic difference in the curing or compounding process between the rubber formulations prepared on the different dates.

DISCUSSION

The hydrogenated ethylene-propylene terpolymer in which the unsaturation was much reduced has higher tensile strength, lower per cent elongation, higher modulus, and greater hardness than the comparable unhydrogenated terpolymer in each case. There is certainly no indication that the unsaturated groups aided the vulcanization process. In fact, decreasing the residual unsaturation did not decrease the degree of vulcanization obtained. This suggests that these residual ethylenic unsaturated groups are not a factor in increasing the efficiency of peroxide-dimethacrylate coagent vulcanization. It is quite possible that the branched structure of the terpolymer is the factor giving physical properties which differ from those of the copolymer.

References

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Résumé

Dans une publication précédente, il a été démontré que la vulcanisation obtenue avec le terpolymère éthylène-propylène-diène est équivalente ou supérieure à celle obtenue avec le copolymère éthylène-propylène traité avec un coréactif peroxyde-diméthacrylate. Afin de déterminer l'influence de l'insaturation sur les propriétés physiques du terpolymère, celui-ci avait été hydrogéné pour éliminer les liaisons doubles. Des spectres infrarouges et la bromation ont été utilisés pour contrôler l'étendue de l'hydrogénation. La force de tension, la dureté shore A, le pourcentage d'élongation et le module ne montrent aucune diminution de l'efficacité de la vulcanisation après hydrogénation. Les résultats montrent que l'insaturation dans le terpolymère n'intervient pas dans le traitement de vulcanisation avec le système de traitement au moyen du coréactif peroxyde diméthacrylate.

Zusammenfassung

In einer früheren Mitteilung wurde gezeigt, dass die mit einem Athylen-Propylen-Dien-Terpolymeren erhaltene Vulkanisation bei Verwendung eines Peroxyd-Dimethacrylat-Vulkanisationssystems derjenigen mit einem Athylen-Propylen-Kopolymerem erhaltenen gleichwertig oder überlegen ist. Um den Einfluss des ungesättigten Charakters auf die physikalischen Eigenschaften des Terpolymeren zu bestimmen, wurde das Terpolymere zur Entfernung der Doppelbindungen hydriert. Zur Feststellung des Ausmasses der Hydrierung wurden Infrarotspektren sowie die Bromierung herangezogen. Zugfestigkeit, Shore-A-Härte, prozentuelle Dehnung und Modul liessen keine Abnahme der Vulkanisationsfähigkeit nach der Hydrierung erkennen. Die Ergebnisse zeigen, dass der ungesättigte Charakter des Terpolymeren nichts zur Vulkanisationsfähigkeit mit dem Peroxyd-Dimethacrylat-Vulkanisationssystem beiträgt.

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