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The Elastomeric Properties of Certain Unsaturated Copolymers

Containing

Ethylene and Propylene

As previously reported (1), linear, high molecular weight amorphous ethylene-propylene random copolymers with very interesting elastomeric properties were prepared by us several years ago.

The vulcanization of these copolymers can be carried out by using several different methods (2), which though yielding good results are based on compounds and techniques that are not normally employed in the rubber industry. Therefore our research work in the field of amorphous ethylene- α -olefins copolymers was accompanied from the very beginning by systematic investigations with the express purpose of obtaining copolymers containing unsaturations in the macromolecules.

These unsaturations should be present in limited number in order not to reduce to any great extent the very desirable properties of resistance to aging and to oxidation which are characteristic of rubbers based on ethylene-propylene copolymers. On the other hand, in order to obtain vulcanized products having good mechanical properties by vulcanization with the aid of compounds normally used for synthetic rubbers of low unsaturation, it is necessary that unsaturations

TABLE I—FORMULATIONS OF THE DIFFERENT COMPOUNDS USED

	Gum Type Compound Recipe A	Tread Type Compound Recipe B	Tread Type Compound Recipe C
Copolymer	100	100	100
Zinc Oxide	5	5	5
Stearic Acid	2	2	2
Antioxidant (F β NA)	1	1	1
Sulfur	2	2.5	2.5
TMTD	1	1.25	1.25
MBT	0.5	0.75	0.75
HAF Black	—	50	50
Necton 60 (oil)	—	—	10

be present in all the macromolecules. Furthermore, they must be distributed in a suitable way in each macromolecule.

Using particular catalytic systems and particular types of monomers, we succeeded in preparing unsaturated, sulfur-vulcanizable copolymers of

TABLE II—PROPERTIES OF THE COPOLYMERS VULCANIZED IN THE ABSENCE OF REINFORCING FILLERS, USING RECIPE A—VULCANIZATION 150°C. x 30 MINUTES

Sample No.	Properties of Raw Polymers			Properties of Vulcanizates						Q _m
	Double bonds, Content, %	Intrinsic Viscosity, dl./g.	Mooney Viscosity, ML 1-4	Tensile strength, kg/cm ²	Elongation at break, %	Modulus at 300%, kg/cm ²	Hardness, Shore A	Resilience at 20°C., at 90°C., %		
1	0.65	2.06	70	60	750	10.5	65	76	76	3.68
2	1.15	1.92	—	27	620	9.8	58	75	70	3.55
3	1.25	1.96	66	21	550	10.0	62	75	74	3.46
4	1.45	1.63	—	24	510	11.8	56	66	72	3.43
5	1.8	1.74	51	33	465	14.5	64	76	78	3.01
6	2.2	1.55	22	22	460	12.0	58	69	71	3.57
7	2.2	1.62	35	34	460	15.2	65	80	82	3.00
8	2.8	1.80	54	25	325	21.5	68	80	86	2.78

mm. (i.e. rubber thickness up to 3 mm.) but below this, the abrasion loss appears to change in different ways for different compounds. The assumption is that this is due to the inter-relation between modulus, friability and abrasion already mentioned, and therefore reflects the mechanism of abrasion of a tire. Ultimately, to obtain maximum correlation with road-wear, the dimensions of the boss may have to be adjusted so that the compound bending and torsional resistance of the disk (measured under the conditions of "crab walk") is similar to that of a tire when account is taken of its size.

Conclusions

The above descriptions show that while much work still remains to be done on the subject, especially in connection with correlations with fleet-testing of tires, a simple and practical laboratory method of studying abrasion of tread and similar compounds, and of studying the relation between compounding and processing on the one hand and abrasion resistance on the other has been proposed which is within the reach of the most modest laboratory.

In proposing the wider use of this modification, I wish to make it quite clear that I do not consider that a laboratory test of any complexity will take the place of fleet testing. However, the use of such a device is likely to be able to provide information on particular aspects of abrasion which, because of the complex picture offered by fleet testing, would not be capable of identification or study.

Communications received relating to the work in the above stage pointed out that the abrasion losses recorded were up to 40 times as large as would be obtained in road fleet-testing, and that it might not be permissible to extrapolate the graphs by more than one cycle. It was suggested that abrasion against wire gauze might reduce the losses to more reasonable rates. Following the work reported above, we have used 40 mesh steel wire gauze and obtained the result plotted in Figure 4. Under these conditions, one hour abrasion at each angle setting is required for reliable readings to be obtained.

It was also found advisable to standardize on a reference compound which would not be as sensitive

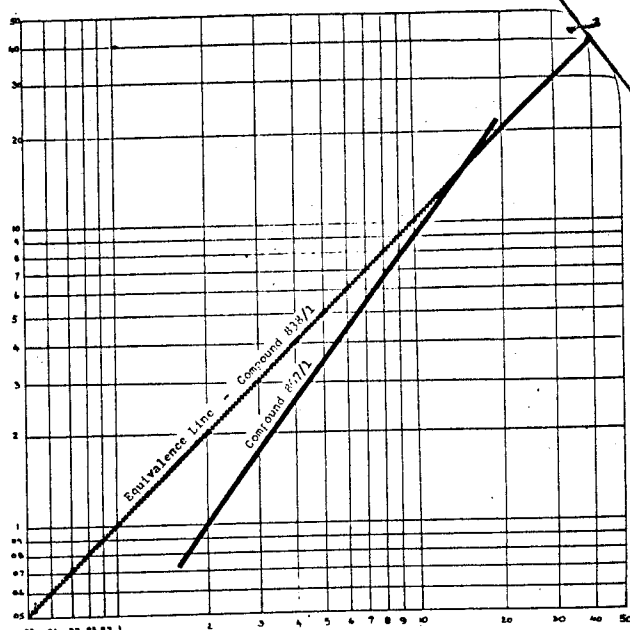


FIG. 4.—Abrasion losses against 40 mesh steel wire gauze. Compound 838/1 has been adopted as standard in subsequent work.

to variations of mixing techniques as are natural rubber/carbon black dry mixed compounds. Accordingly, we have standardized on Compound 838/1 detailed in Table III and Figure 4.

ACKNOWLEDGMENTS

The work on which this note is based forms part of a larger study, made possible by a grant from the Ministry of Commerce and Industry, and the U.S.-Israel Joint Fund, on the properties and applications of reclaimed rubber.

The assistance of Mr. Stephan Fass in carrying out much of the technical work involved is gratefully acknowledged.

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TABLE III—FORMULATIONS OF TWO TEST COMPOUNDS

	838/1	867/1
Smoked sheets	—	100
SBR 4650	165	—
Stearic acid	1.5	2
Zinc oxide	5	4
BLE	1	—
Bayer 4010	1	—
PBN	—	1
Flectol H	—	1
HAF	—	45
Vulcatard A	—	0.5
Santocure	1.25	0.5
Sulfur	1.75	2.5
Cure Temperature (°C.)	145	138
Cure Time (minutes)	40	30

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homogeneous composition which were free of gel products.

More precisely, the copolymerization products prepared are made up of macromolecules essentially consisting of ethylene and propylene monomeric units and containing small amounts of double bonds. These double bonds are distributed in such a homogenous way as to render the crude copolymers easily vulcanizable when using the ingredients and conditions normally employed in the rubber industry.

In this paper we wish to discuss in a preliminary way the behavior of these new copolymers with respect to vulcanization, and to report some properties of the vulcanized products thus obtained.

Characteristics of the Copolymers

The copolymers described in this paper are completely amorphous upon X-ray examination and contain almost equal molar proportions of ethylene and propylene. In addition they contain various amounts of double bonds, up to a maximum of 3 double bonds per 100 total monomeric units. The

composition of these ethylene-propylene copolymers has been evaluated by infrared and radiochemical analyses.

Adopting particular polymerization conditions, we have prepared by direct synthesis crude copolymers having a controlled molecular weight (intrinsic viscosity in toluene at 30°C. is between 1.5 and 2.1), which possess very good processability.

We can produce copolymers with a desired molecular weight and Mooney viscosity within a wide range. The copolymers reported in this paper, as shown in the Tables below, possess Mooney viscosity values ranging between 20 and 70 (determined at 100°C., ML 1-4).

Compounding and Vulcanization

In order to compare the vulcanization behavior of copolymers having a different degree of unsaturation, we have used rather simple mixes based on sulphur and accelerating agents. We have operated either in the absence of reinforcing fillers or in the presence of carbon black. The compositions of the different

TABLE III—PROPERTIES OF THE COPOLYMERS VULCANIZED IN THE ABSENCE OF REINFORCING FILLERS, USING RECIPE A—VULCANIZATION 150°C. x 60 MINUTES

Sample No.	Properties of Raw Polymers			Properties of Vulcanizates						
	Double bonds, Content, %	Intrinsic Viscosity, dl./g.	Mooney Viscosity, ML 1-4	Tensile strength, kg/cm ²	Elongation at break, %	Modulus at 300%, kg/cm ²	Hardness, Shore A	Resilience		Q _m
								at 20°C., %	at 90°C., %	
1	0.65	2.06	70	58	700	11.4	65	77	78	3.45
2	1.15	1.92	—	15	350	11.7	62	75	76	3.27
3	1.25	1.96	66	31	510	13.4	65	75	76	3.22
4	1.45	1.63	—	22	400	14.4	60	70	75	3.20
5	1.8	1.74	51	26	365	17.8	66	79	83	2.87
6	2.2	1.55	22	20	360	15.7	63	71	78	3.27
7	2.2	1.62	35	28	370	19.0	66	81	84	2.77
8	2.8	1.80	54	24	285	—	71	80	85	2.69

TABLE IV—PROPERTIES OF THE COPOLYMERS VULCANIZED IN THE PRESENCE OF REINFORCING FILLERS, USING RECIPE B—VULCANIZATION 150°C. x 30 MINUTES

Sample No.	Properties of Raw Polymers			Properties of Vulcanizates					
	Double bonds, Content, %	Intrinsic Viscosity, dl./g.	Mooney Viscosity, ML 1-4	Tensile strength kg/cm ²	Elongation at break, %	Modulus at 300%, kg/cm ²	Hardness, Shore A	Resilience	
								at 20°C., %	at 90°C., %
1	0.65	2.06	70	175	590	47	82	55	56
3	1.25	1.96	66	240	620	71	86	53	56
4	1.45	1.63	—	224	530	89	80	45	54
5	1.8	1.74	51	230	430	120	85	54	60
6	2.2	1.55	22	196	440	121	85	43	53
7	2.2	1.62	35	227	400	154	84	54	60
8	2.8	1.80	54	191	280	—	90	54	64

mixes are reported in Table I. Of course, for a certain degree of unsaturation in the copolymer, the use of more active recipes leads to more vulcanized products.

Mixing with the vulcanization ingredients and fillers is easy, because of the very good processability of the materials on the mill-mixer.

Vulcanization was carried out at 150°C. for different periods of time. Mechanical properties have been evaluated on specimens according to ASTM D-412 (specimens of C and D type) at a rate of separation of the grips of 500 mm./min. Resilience was determined with the aid of a Microrebound Pirelli apparatus (3). The volume swelling ratio at equilibrium (Q_m) was measured in benzene at 30°C.

Properties of the Vulcanizates

(1) Vulcanizates in the absence of reinforcing fillers. In Tables II and III, the most important properties of certain copolymers with different unsaturations after vulcanization at 150°C. (for 30 and 60 minutes respectively, using Compound A) are reported. From these tables one can see that:

(a) All other conditions being equal, the modulus at 300 percent and the degree of crosslinking increase

with an increase in double bond content. At the same time, the elongation at break decreases. Some apparent discrepancies (Samples No. 2, 3 and 6) depend on differences in molecular weight and Mooney viscosity.

(b) When protracting the time of vulcanization from 30 to 60 minutes, the degree of crosslinking increases, as is demonstrated by the increase of the modulus at 300 per cent and lowering of the swelling ratios. Reversion reactions were not detectable even when using vulcanization times up to 240 minutes.

(c) The degree of crosslinking is fairly high even in the case of copolymers having a Mooney viscosity as low as 22.

(d) The resilience of these copolymers is fairly high and is practically the same as the one of ethylene-propylene copolymers. The variation of resilience with temperature (between -50°C. and +150°C.), is illustrated in Figure 1. The temperature corresponding to a minimum of rebound is rather low (near to -35°C.). Resilience at room temperature is very high and remains between 85 and 90 per cent between 20° and 140°C.

(2) Vulcanizates in the presence of reinforcing fillers. The properties of the copolymers vulcanized in the presence of reinforcing fillers (Recipe B) at

TABLE V—PROPERTIES OF THE COPOLYMERS, VULCANIZED IN THE PRESENCE OF REINFORCING FILLERS, USING RECIPE B—VULCANIZATION 150°C. x 60 MINUTES

Sample No.	Properties of Raw Polymers			Properties of Vulcanizates					
	Double bonds, Content, %	Intrinsic Viscosity, dl./g.	Mooney Viscosity, ML 1-4	Tensile strength kg/cm ²	Elongation at break, %	Modulus at 300%, kg/cm ²	Hardness, Shore A	Resilience	
								at 20°C., %	at 90°C., %
1	0.65	2.06	70	266	680	56	85	55	56
3	1.25	1.96	66	246	495	102	85	55	59
5	1.8	1.74	51	225	360	170	85	55	61
6	2.2	1.55	22	206	320	192	87	45	57
7	2.2	1.62	35	209	290	—	87	54	56
8	2.8	1.80	54	210	240	—	87	55	66

FILLERS, (E VI—PROPERTIES OF THE COPOLYMERS, VULCANIZED IN THE PRESENCE OF REINFORCING FILLERS, USING RECIPE C—VULCANIZATION 150°C. x 15 MINUTES

Sample No.	Properties of Raw Polymers			Properties of Vulcanizates				Resilience	
	Double bonds, Content, %	Intrinsic Viscosity, dl./g.	Mooney Viscosity, ML 1-4	Tensile strength kg/cm ²	Elongation at break, %	Modulus at 300%, kg/cm ²	Hardness, Shore A	at 20°C., %	at 90°C., %
1	0.65	2.06	70	265	780	36	80	55	57
3	1.25	1.96	66	255	640	64	79	55	58
4	1.45	1.63	—	210	520	86	79	48	57
5	1.8	1.74	51	228	450	104	82	55	62
6	2.2	1.55	22	196	430	121	80	44	55
7	2.2	1.62	35	207	390	135	85	53	55
8	2.8	1.80	54	218	330	185	84	56	67

150°C. are reported in Table IV (vulcanization time, 30 minutes) and in Table V (vulcanization time, 60 minutes).

The properties of the products vulcanized at 150°C. for 45 minutes using Recipe C are indicated in Table VI.

When examining these last tables, in addition to the considerations already stated for Tables II and III, one can observe that the carbon black-reinforced products generally possess good properties which are equal to or better than those of the most common synthetic rubbers.

Furthermore we have observed that different mechanical properties within a wide range can be obtained by varying the content in ethylene; or the molecular weight of the copolymer (similar to what was already observed for previously described ethylene-propylene copolymers), or the degree of unsaturation.

The copolymers also possess good resistance to aging due to the low content in double bonds. Aging tests, carried out on the copolymers vulcanized as

indicated in Table V, showed that no practical alteration of the properties occurred after the samples were maintained for eight days in an air-circulating oven at 100°C.

Conclusions

The random copolymers described in this paper essentially consist of ethylene and propylene and contain small amounts of double bonds. They are easily vulcanizable by the usual methods and represent a new type of general purpose rubber.

With respect to the previously known general purpose rubbers (e.g., SBR), these new rubbers possess similar mechanical properties, together with a much higher resistance to aging.

With respect to other low unsaturated rubbers (e.g., butyl rubber) the new copolymers possess remarkably better dynamic and mechanical properties.

The high content in ethylene and propylene indicates that the production of these copolymers will be fairly economical, making possible their use on a large scale commercial basis.

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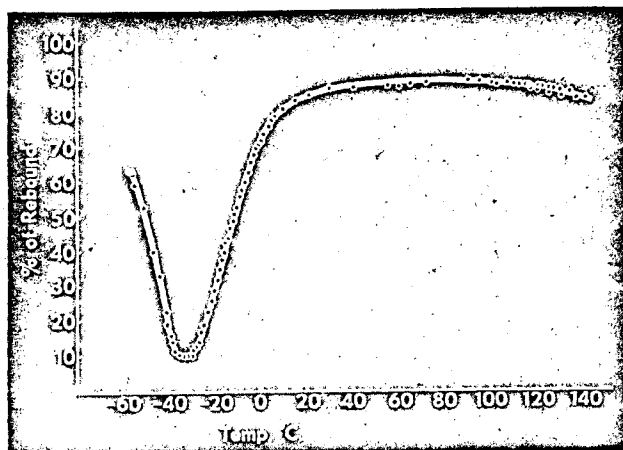


FIG. 1—Typical rebound curve vs. temperature of a vulcanized ethylene-propylene copolymer (Recipe A). Degree of unsaturation in starting copolymer: two double bonds per 100 monomeric units.