

Ethylene-Propylene Copolymers Containing Un saturations

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ABSTRACT

Previous communications have described the synthesis and properties of amorphous linear high-molecular-weight ethylene-olefin copolymers. These show interesting mechanical and dynamic properties and can be considered as general purpose rubbers, with the advantage that they can be obtained from cheap monomers available in quantity. Moreover their resistance to degradation is remarkable, because they are essentially free from double bonds.

The vulcanisation of ethylene-propylene copolymers has been achieved using particular methods, which were studied and developed, and which gave satisfactory results.

In order to obtain the vulcanisation of these elastomers, employing conventional recipes based on sulphur and accelerating agents, without markedly reducing resistance to degradation there has been carried out a series of researches resulting in the preparation of copolymers which contain small amounts of unsaturation homogeneously distributed.

In this communication there are described the fundamental mechanical and dynamic properties of ethylene-propylene copolymers containing unsaturation random distributed, cured with the aid of recipes usually employed for known elastomers having a low degree of unsaturation. The properties of vulcanisates are discussed on the basis of the raw polymer properties, and in particular on the basis of their Mooney viscosity and of their content of unsaturation; these parameters may be easily varied over a wide range according to the conditions of synthesis of the copolymer.

Tests performed on these elastomers indicate that they constitute a new class of general purpose rubbers having good processability, excellent mechanical and dynamic properties, and outstanding resistance to ageing.

INTRODUCTION

In this communication we wish to refer to some vulcanisation characteristics and to the main properties of the vulcanisates, obtained from elastomers of low unsaturation content, whose macromolecules prevailingly consist of ethylene and propylene. As already described in previous papers¹, the new methods of polymerisation acting through an anionic coordinated mechanism permit the synthesis of new saturated (or prevailingly saturated) rubbers, which exhibit excellent mechanical and dynamic properties as well as excellent resistance to degradation agents.

¹ G. Natta, *Rubb. Plastics Age*, 1957, **38**, 495; G. Natta, G. Mazzanti, A. Valvassori, and G. Pajaro, *Chimica e Industria*, 1957, **39**, 733; G. Natta and G. Crespi, *Chimica e Industria*, 1959, **41**, 123; *Rubb. Age*, N.Y., 1960, **87**, 459.

The properties of linear, amorphous, high-molecular-weight ethylene-alpha-olefin copolymers, having a statistical distribution of the two monomeric units, and cured by different crosslinking methods have been described in previous papers². These copolymers represent a new type of general purpose rubber; they can be used for the production of many articles which require good mechanical and dynamic properties, as well as good resistance to ageing and to chemical reagents.

Vulcanisation of ethylene-propylene copolymers (Dutral) can be easily effected with the aid of organic peroxides, and of small amounts of sulphur; compounding and vulcanisation can be performed by the standard equipment of the rubber industry; but special considerations are necessary in the choice of the compounding ingredients.

The synthesis of copolymers prevailingly consisting of ethylene and propylene and containing a low proportion of double bonds suitably distributed along the chains, yields a rubber-like material which maintains practically unaltered the physical and chemical properties of the parent materials and can be cured by recipes (based on sulphur and accelerating agents) already used with low unsaturation-content rubbers.

The production of copolymers containing unsaturations can be effected by different methods: in particular, by copolymerisation with monomers containing more than one unsaturation per molecule³. Only when operating with certain monomers and under particular conditions is it possible to obtain copolymers with a homogeneous composition, corresponding to a statistical distribution of the double bonds, which is necessary for obtaining products yielding vulcanisates with low initial elastic modulus and high mechanical properties.

In a subsequent paper we will refer to the synthesis and to the chemical composition of these copolymers. In this communication we deal only with the properties of the copolymers containing unsaturations; in fact their properties depend only on the number, on the regularity of distribution of the unsaturations, and on their reactivity, and to a first approximation are independent of the composition of the monomer used in the preparation of these rubbers.

PROPERTIES OF THE RAW MATERIALS

By analogy with ethylene-propylene copolymers these new elastomers containing small amounts of unsaturations, can be prepared within a wide range of composition and of molecular weight by suitable control of polymerisation conditions. For the sake of simplicity, only the copolymers which appear amorphous by X-ray analysis and which contain the same ethylene/propylene molar ratio will be examined in this communication.

Even though the number of double bonds present in the polymeric chains can be regulated over a wide range we preferred, for practical purposes, to limit our study to elastomers containing less than 4 double bonds per one hundred monomeric units. The total unsaturation content was determined by infra-red spectrography and radiochemical analyses.

The molecular weight of these elastomers can be regulated directly in synthesis; in

² G. Natta, G. Crespi, and M. Bruzzone, *Kaut.u. Gummi.*, 1961, **14**, 54 WT; E. Di Giulio and G. Ballini, Deutsche Kautschuk Gesellschaft, Berlin, 4-8 October, 1960; G. Natta, G. Crespi, E. Di Giulio, G. Ballini, and M. Bruzzone. *Rubb. Plastics Age*, 1961, **42**, 53.

³ G. Natta, G. Crespi, G. Mazzanti, A. Valvassori, G. Sartori, and P. Scaglione, *Rubb. Age*, N.Y., 1961. **89**, 636; G. Natta, G. Mazzanti, and G. Boschi, Belgian P. 558728, 559111.

order to secure good processability the Mooney viscosity values (ML 1 + 4 at 100°C.) do not exceed 70. However, it is also possible to prepare copolymers containing unsaturations, with high viscosity values (Mooney values higher than 90); they can be extended with the aid of a high proportion of plasticising oil, and after vulcanisation they yield products with good mechanical and dynamic properties.

COMPOUNDING AND VULCANISATION

The recipes used for the vulcanisation of these materials were based on the use of sulphur and accelerating agents of the ultra-rapid type, by analogy with what is already known for low-unsaturation rubbers. Besides vulcanising ingredients, reinforcing fillers, plasticising oils, and the like can be present. Vulcanisation has usually been effected in a press at 150°C. using different periods to permit comparison between the various elastomers and the various compounding conditions. Obviously, the types and the amounts of the ingredients, and vulcanisation temperatures and times can be suitably varied, to suit copolymers of different degrees of unsaturation, so as to reach the desired degree of crosslinking.

INFLUENCE OF THE DEGREE OF UNSATURATION

By using the same recipe and keeping unaltered the vulcanisation conditions for copolymers with different content of double bonds, a degree of crosslinking has been obtained which regularly increases with increase of unsaturation. This variation can easily be observed both from the data of Table I (vulcanisates in the absence of reinforcing fillers)

TABLE I

PROPERTIES OF COPOLYMERS VULCANISED IN THE ABSENCE OF REINFORCING FILLERS
VULCANISATION 150°C FOR 60 MINUTES

Properties of Raw Polymers		Properties of Vulcanisates				Q_m^{\pm}
Double bond Content, %	Mooney Viscosity ML 1—4	Tensile strength kg/cm ²	Elongation at break, %	Modulus at 300% kg/cm ²	Resilience at 20°C, %	
0.65	70	58	700	11.4	77	3.45
1.15	—	15	350	11.7	75	3.27
1.25	66	31	510	13.4	75	3.22
1.45	—	22	400	14.4	70	3.20
1.8	51	26	365	17.8	79	2.87
2.2	22	20	360	15.7	71	3.27
2.2	35	28	370	19.0	81	2.77
2.8	54	24	285	—	80	2.69

Q_m^{\pm} = swelling ratio in benzene at 30°C

Recipe :—Copolymer 100; Zinc Oxide 5; Stearic Acid 2; Phenyl- β -naphthylamine 1; Sulphur 2; TMTD 1; MBT 0.5.

and of Table II (vulcanisates containing HAF carbon black). When comparing copolymers having almost the same average molecular weight, the value of the 300% elongation modulus of the vulcanisates indicated in Table II is directly proportional to the content of double bonds of the starting copolymer (Figure 1).

TABLE II
PROPERTIES OF THE COPOLYMERS VULCANISED IN THE PRESENCE OF REINFORCING FILLERS
VULCANISATION 150°C FOR 30 MINUTES

Properties of Raw Polymers		Properties of Vulcanisates				
Double bond Content, %	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, %
0.65	70	175	590	47	75	55
1.25	66	240	620	71	73	53
1.45	—	224	530	89	71	45
1.8	51	230	430	120	75	54
2.2	22	196	440	121	73	43
2.2	35	227	400	154	74	54
2.8	54	191	280	—	78	54

Recipe :—Copolymer 100; Zinc Oxide 5; Stearic Acid 2; Phenyl- β -naphthylamine 1; Sulphur 2.5; TMTD 1.25; MBT 0.75; HAF Black 50.

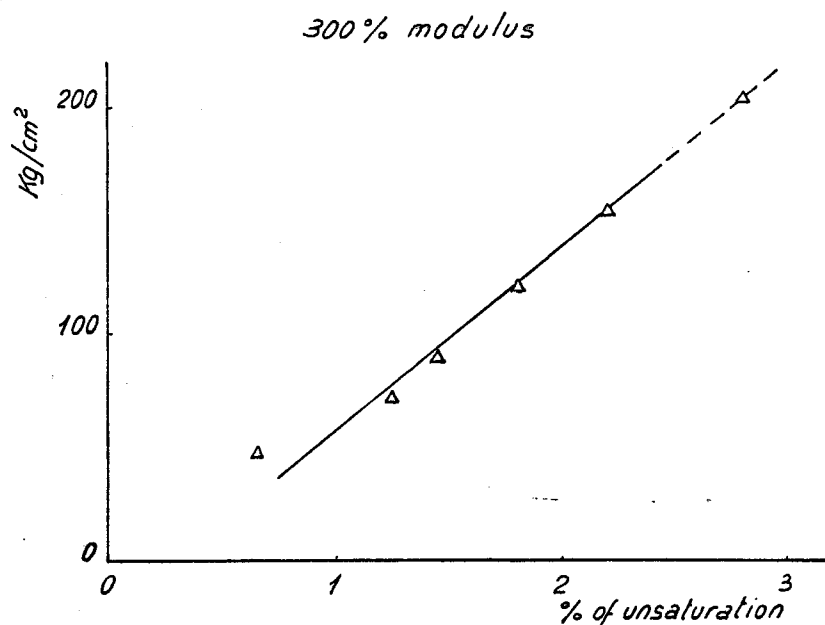


FIGURE 1. Modulus at 300% elongation vs. unsaturation content of copolymers.

The mechanical properties of vulcanisates in the presence of reinforcing fillers are similar to those of the usual synthetic rubbers, when a suitable degree of crosslinking is

reached. Figure 2 shows the leading mechanical properties of three copolymers having almost the same average molecular weight (Mooney values $ML\ 1 + 4$ at 400°C ., ranging from 20 to 30) and different degrees of unsaturation, vs. the vulcanisation time. From this figure it can be deduced that: (a) vulcanisation degree regularly increases with the increase in unsaturation; (b) for vulcanisation times even longer than 3 h, apparent reversion is not observed; (c) even with copolymers having a low degree of unsaturation, vulcanisates with satisfactory mechanical properties can be obtained.

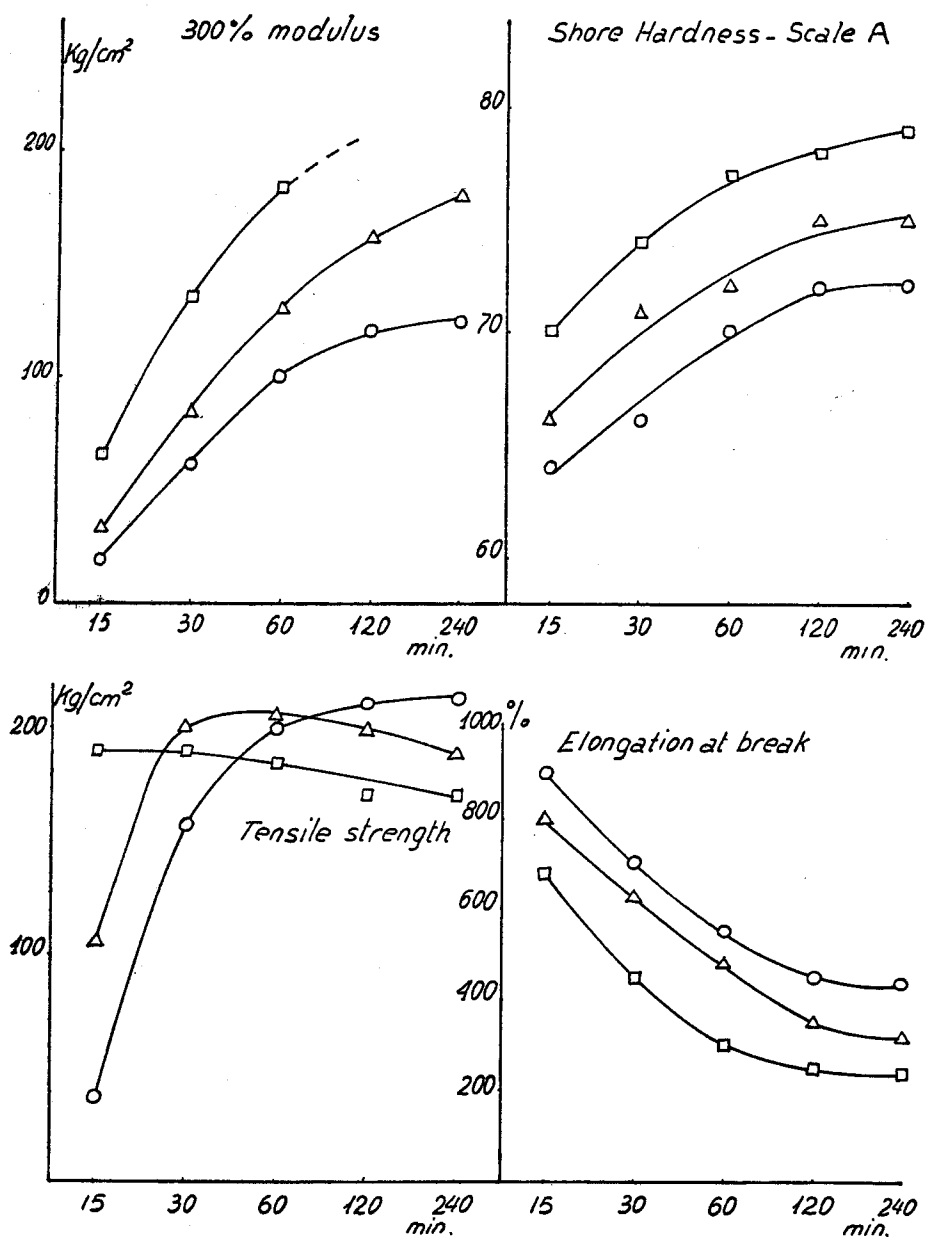


FIGURE 2. Characteristics of vulcanisates vs. vulcanisation time (at 150°C) for different copolymers.

- unsaturation 1.4%
- △ unsaturation 2.2%
- unsaturation 2.7%

Vulcanisation recipe as in Table II.

TABLE III

GRAECO-LATIN SQUARE

	0,75	1,0	1,25	1,5	TMT
MBT 0,5	Sulphur 2.5 Time min. 60	Sulphur 2.0 Time min. 90	Sulphur 1.5 Time min. 120	Sulphur 1.0 Time min. 30	
0,75	Sulphur 2.0 Time min. 30	Sulphur 2.5 Time min. 120	Sulphur 1.0 Time min. 90	Sulphur 1.5 Time min. 60	
1,0	Sulphur 1.0 Time min. 120	Sulphur 1.5 Time min. 30	Sulphur 2.0 Time min. 60	Sulphur 2.5 Time min. 90	
1,25	Sulphur 1.5 Time min. 90	Sulphur 1.0 Time min. 60	Sulphur 2.5 Time min. 30	Sulphur 2.0 Time min. 120	

(ML 1 + 4 (100°C) = 20 — % unsaturation = 3,4)

Recipe :—Copolymer 100; Stearic Acid 2; Zinc Oxide 5; Sulphur as indicated;
TMT as indicated; MBT as indicated; HAF Black 50; Cure at 150°C
× Times as indicated.

TABLE IV

PHYSICAL PROPERTIES OF VULCANISATES
OBTAINED AS INDICATED IN GRAECO-LATIN
SQUARE OF TABLE III

207	190	184	184
100	148	179	73
540	380	320	660
159	177	190	184
54	177	101	140
700	300	500	420
196	174	180	173
86	63	140	—
560	680	380	280
228	208	184	180
105	84	93	180
580	600	560	300

Tensile Strength	Kg/cm ²
Modulus 300%	Kg/cm ²
Elongation at break	%

INFLUENCE OF THE VULCANISATION INGREDIENTS

Not only the degree of unsaturation of the copolymers but obviously also the type and amount of the vulcanisation ingredients used, exert an influence on the amount of cross-linking which can be obtained with these copolymers. The choice of the various accelerating and vulcanisation agents has to be made in view of the vulcanisation conditions (temperature, time) and the final use of the vulcanisate.

When using mixtures based on tetramethylthiuram disulphide, 2-mercaptobenzthiazole, and sulphur an examination has been made of influence of the various parameters on the degree of crosslinking (300% modulus) and on the mechanical properties, by means

TS Tensile strength — M_{300} 300% Modulus — *EB* Elongation at break

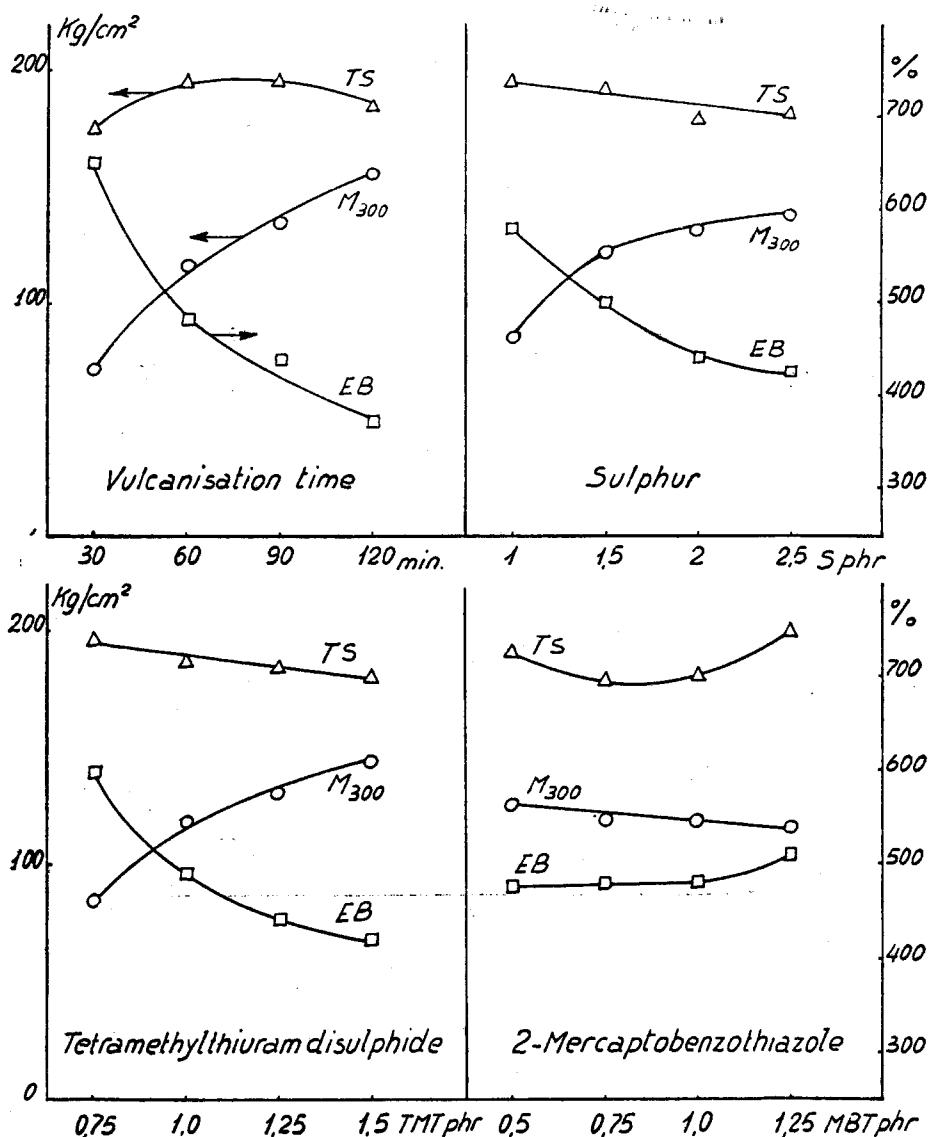


FIGURE 3. Influence of various ingredients and of vulcanisation time on the characteristics of vulcanisates, according to Graeco-Latin square of Table III.

of a set of runs in Graeco-Latin square, reported in Table III. In Table IV are reported the main characteristics of the various vulcanised products. The influences of the vulcanising agents and of vulcanisation times are set out in Figure 3, from which it is possible to observe that: (a) increase of sulphur causes a remarkable increase in degree of vulcanisation from 1 to 2 phr; a further increase does not exert a great influence on the 300% modulus; (b) an increase of TMT from 0.75 to 1.5 phr causes a continuous increase in the 300% modulus; (c) the influence of MBT, when it increases from 0.5 to 1.25 phr, is not very significant, and the 300% modulus progressively decreases; (d) the increase in vulcanisation time from 30 mins to 2 h causes a continuous and remarkable increase in degree of crosslinking.

INFLUENCE OF ZINC OXIDE AND OF STEARIC ACID

Tests have been performed on the action of the above ingredients on the vulcanisation, the other ingredients and the vulcanisation conditions being kept constant. Figure 4 shows the characteristics of vulcanisates obtained with various amounts of zinc oxide. As can be observed, vulcanisation does not occur in the absence of zinc oxide. A rather low degree of vulcanisation occurs with 1 phr but with an amount of zinc oxide higher than 3 phr, no noticeable variation of properties takes place.

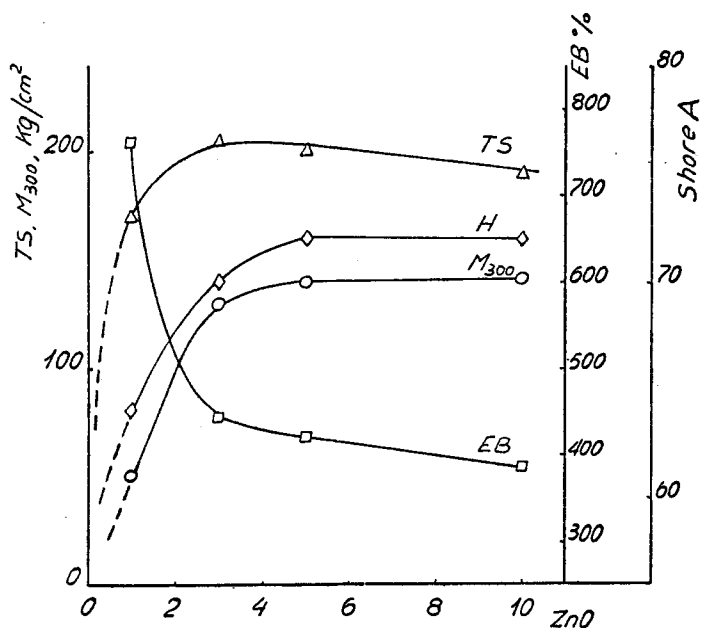


FIGURE 4. Influence of zinc oxide on the characteristics of vulcanisates (copolymer with Mooney viscosity of 20, unsaturation 1.5%).

Recipe :—Copolymer 100; Stearic Acid 2.5; Zinc Oxide as indicated; Sulphur 2.5; TMT 1.25; MBT 0.75; HAF Black 50; Cure: 150°C for 45 min.

The addition of stearic acid, on the contrary, acts in a substantially opposite way (Figure 5); best results are obtained in the absence of stearic acid. By increasing the proportion of stearic acid, the degree of crosslinking is progressively reduced.

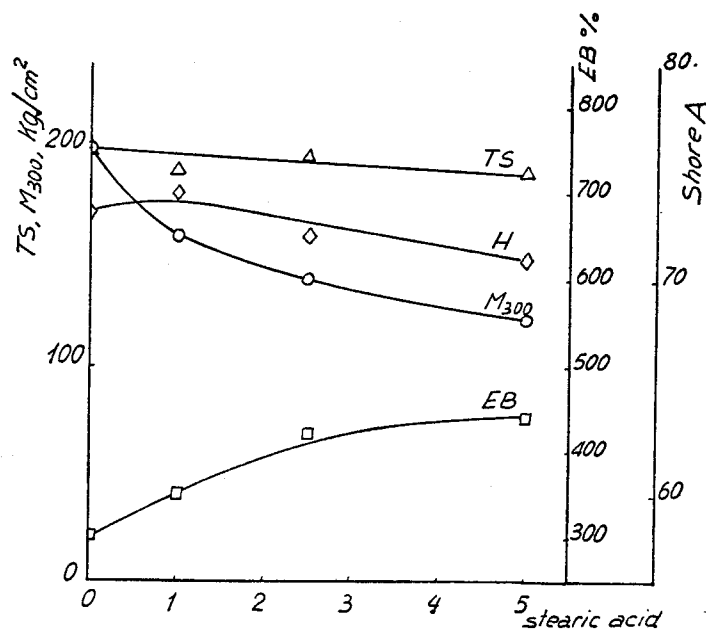


FIGURE 5. Influence of stearic acid on the characteristics of vulcanisates (same copolymer as in Figure 4).

Recipe :—Copolymer 100; Stearic Acid as indicated; Zinc Oxide 5; TMT 1.25; MBT 0.75; Sulphur 2.5; HAF Black 50; Cure 150°C for 45 min.

Therefore, by suitably varying the ratio of stearic acid to zinc oxide, it is possible to control the rate of vulcanisation and the final properties of the vulcanisate. Figures 6 and 7 show progressive vulcanisation runs carried out with different ratios of stearic acid to zinc oxide. It can be observed that when operating with a small amount of zinc oxide (Figure 6) reversion can occur, which, however, ceases when zinc oxide is present in considerable excess with respect to the stearic acid.

INFLUENCE OF OTHER INGREDIENTS

The type of carbon black added exerts an influence on the properties of the vulcanisate similar to that exerted in most synthetic rubbers. Channel-type blacks tend to retard vulcanisation, owing to their acid reaction. Plasticising oils are generally compatible with these elastomers; an addition of 10 phr of oil improves processability and does not influence remarkably the mechanical properties of the vulcanisate.

It is possible to add other types of fillers (such as silica, clay, and the like) to the compound, to obtain effects comparable with those occurring on ethylene-propylene copolymers.

AGEING

These elastomers being substantially saturated oppose a very good resistance to degradation agents. Vulcanisates subjected to accelerated ageing gave excellent results, as appears from Figures 8, 9, and 10, which relate to air circulating oven ageing at 100°C,

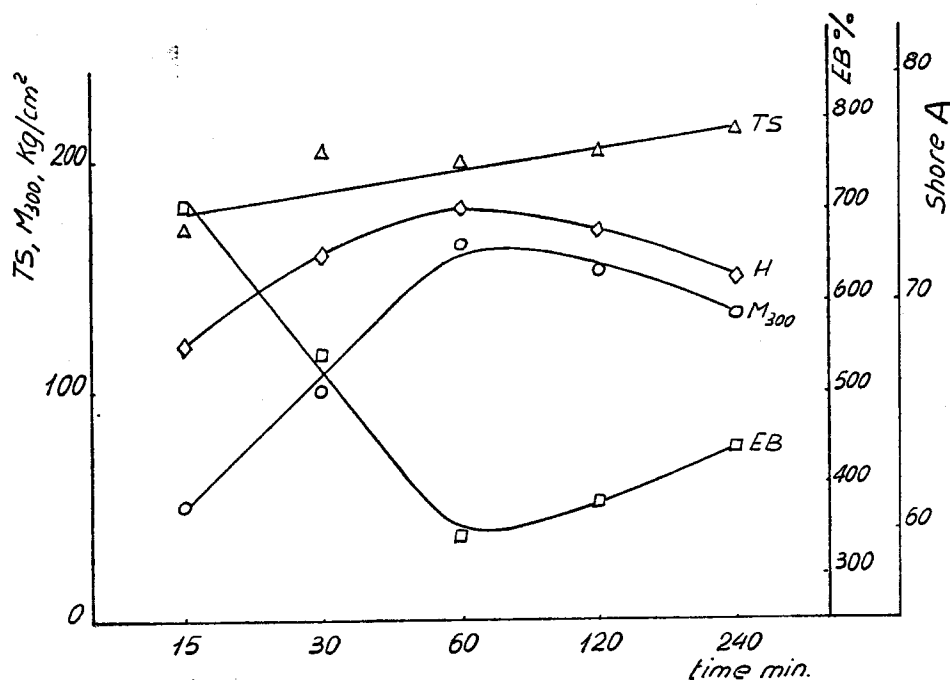


FIGURE 6. Influence of vulcanisation time on the characteristics of vulcanisates, with low ratio zinc oxide per stearic acid (same copolymer as in Figure 4).
 Recipe :—Copolymer 100; Stearic Acid 2.5; Zinc Oxide 3; Sulphur 2.5; TMT 1.25; MBT 0.75; HAF Black 50; Cure, 150°C for times as indicated.

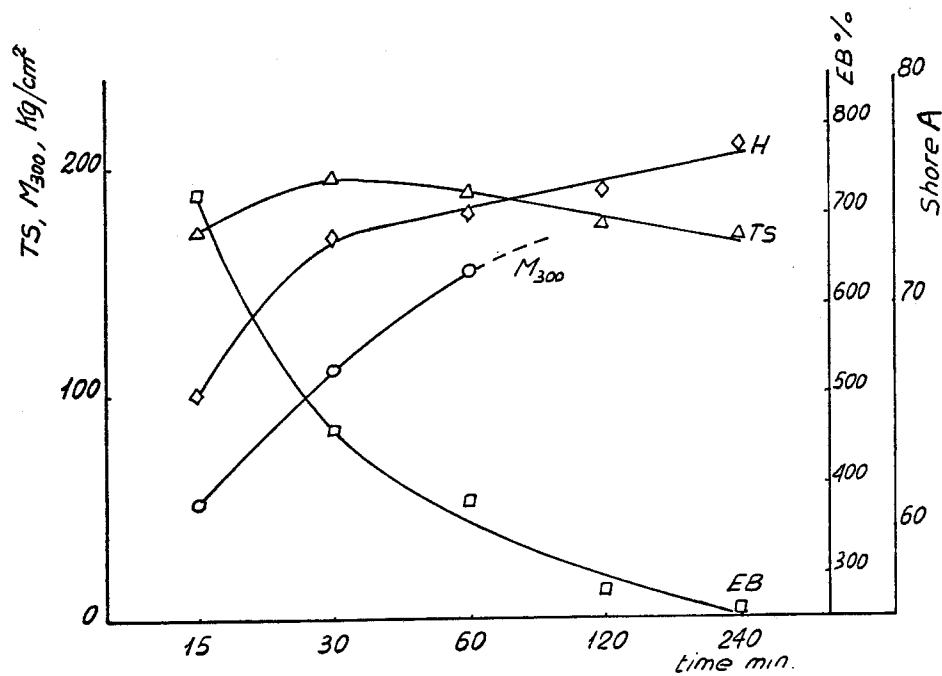


FIGURE 7. Influence of vulcanisation time on the characteristics of vulcanisates, with high ratio zinc oxide per stearic acid (same copolymer as in Figure 4).
 Recipe :—Copolymer 100; Stearic Acid 2.5; Zinc Oxide 10; Sulphur 2.5; TMT 1.25; MBT 0.75; HAF Black 50; Cure, 150°C for times as indicated.

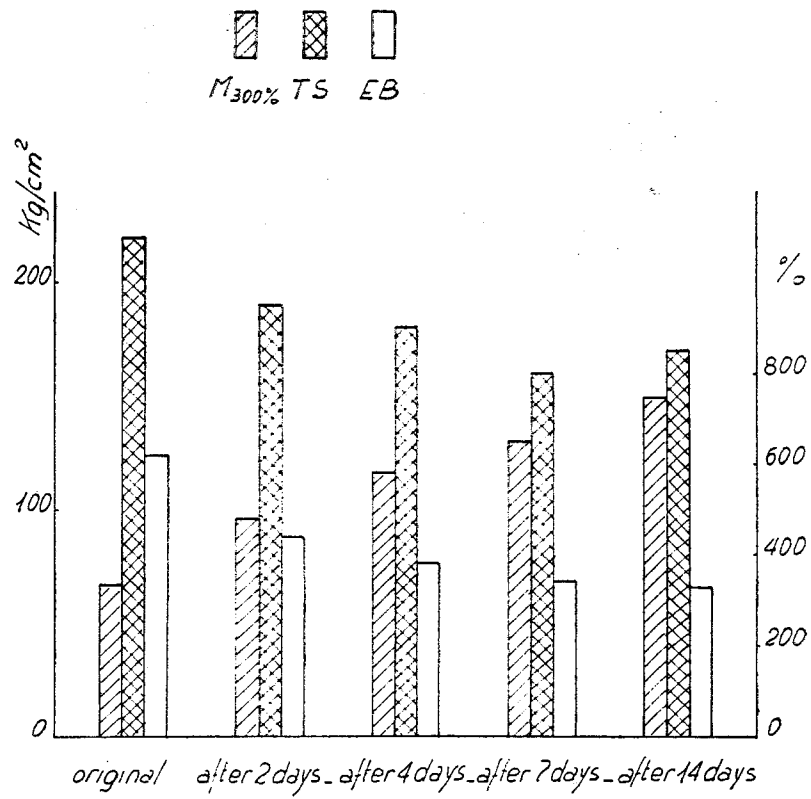


FIGURE 8. Ageing characteristics of vulcanised copolymers at 100°C (Mooney viscosity of the raw copolymer 30, unsaturation 1.85%).

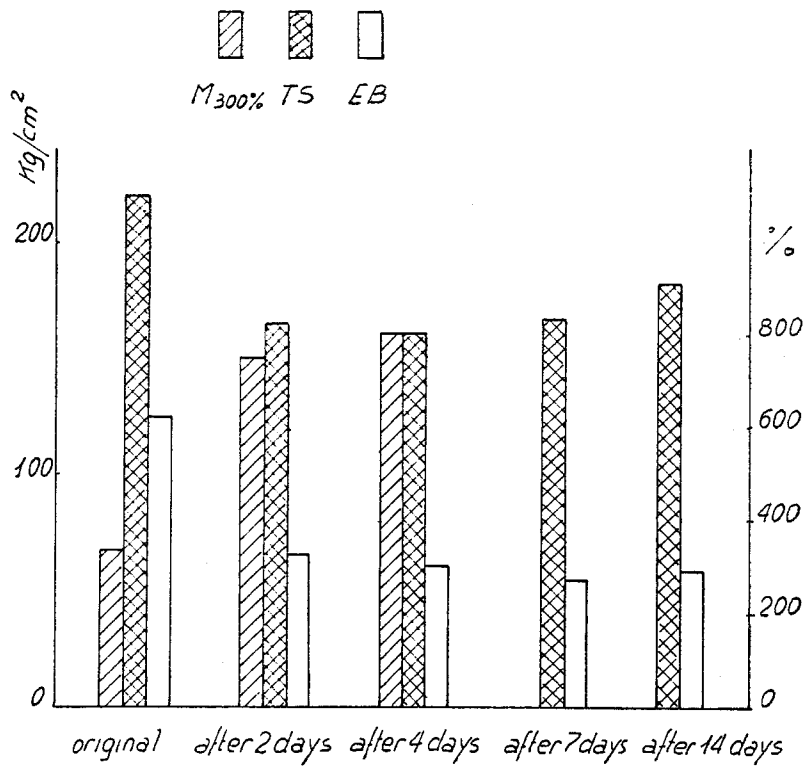


FIGURE 9. Ageing characteristics of vulcanised copolymers at 125°C (same copolymer as in Figure 8).

125°C, and 150°C respectively. As can be observed from the figures, the effect of ageing consists in a further progress of vulcanisation; a phenomenon which is the more marked the higher the ageing temperature. From these data it appears that the presence of a small number of double bonds, which in part are involved in the vulcanisation, does not markedly lower the excellent ageing characteristics, typical of saturated rubbers consisting of ethylene- α -olefin copolymers. Even better results can be obtained by using greater amounts of antioxidant, and by suitably varying the vulcanisation recipe.

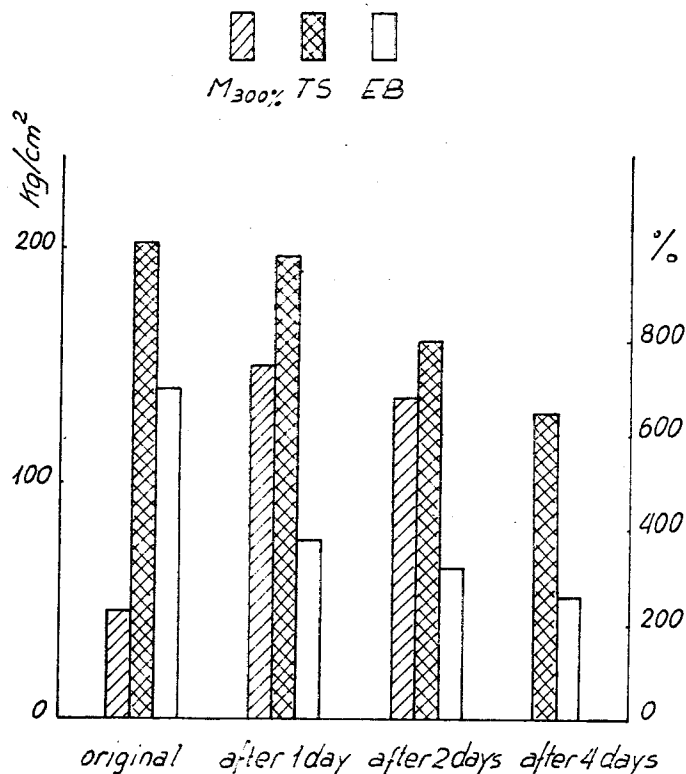


FIGURE 10. Ageing characteristics of vulcanised copolymers at 150°C (Mooney viscosity of the raw copolymer 20, unsaturation 1.7%).

CONCLUSIONS

On the basis of the foregoing statements it is possible to consider ethylene-propylene copolymers containing a small amount of unsaturation as a new type of rubber having properties which permit wide possibilities of development.

As compared with the low-unsaturation rubbers known up to now, they show the advantage of good hysteresis properties of the same order as those of the ethylene-propylene copolymers and of SBR. In comparison with the latter, however, they exhibit the added advantage of a considerable resistance to degradation agents. It is also possible to suppose that the price of these elastomers, which consist substantially of ethylene and propylene, will be low enough to compete with the other synthetic rubbers and to ensure their wide application in the most different types of manufactured articles.