

SULFUR VULCANIZABLE ETHYLENE-PROPYLENE RUBBERS*

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INTRODUCTION

Our research directed to obtaining new rubbers based on the copolymerization of ethylene with propylene started some years ago¹. We soon succeeded in establishing that it was possible to prepare copolymers of these two monomers showing interesting elastomeric properties². From the beginning, the problem arose of how to vulcanize these copolymers: while certain interesting methods for direct vulcanization³ were investigated and identified, we also investigated the possibility of terpolymers containing unsaturation and therefore vulcanizable with the ingredients normally employed in the rubber industry, particularly for the low unsaturated rubbers⁴.

The problem involved some difficulties, due to the following three reasons. (1) In order to maintain the peculiar characteristics of resistance to aging and chemicals, typical of ethylene-propylene copolymers, it was necessary to obtain terpolymers in which the unsaturation was present in a very small amount. (2) To obtain valuable properties in the vulcanizates, the unsaturation had to be well distributed in all the macromolecules. (3) In order to avoid branching or crosslinks, the residual double bond of the diene entering the polymer chain must not be able to react further during polymerization.

Our research led to a number of monomers which may copolymerize with ethylene and propylene and which, under suitable conditions, gave terpolymers having a sufficiently homogeneous composition. Investigation of the behavior, in anionic coordinated polymerization of hydrocarbons containing internal double bonds led to an interesting solution to the problem of producing terpolymers.

Olefins having internal unsaturation were believed not to polymerize in the presence of catalysts acting through an anionic coordinated mechanism. Our investigations enabled us, however, to establish that monomers of this type may copolymerize with other monomers free of steric hindrance. Thus, for instance, butene-2 or cyclopentene do not yield homopolymers in the presence of such catalysts. The opening of the double bond fails mainly because of steric hindrance. It is however possible to obtain copolymers of these monomers with ethylene, and in particular, we succeeded in preparing crystalline, alternating copolymers⁵ of ethylene with *cis*-butene-2 and, respectively, of ethylene with cyclopentene⁶.

By investigating the reactivity of the various cycloolefins in the copolymerization, we were able to ascertain that such reactivity is greatly influenced by steric factors connected with the more stable configuration of the ring after entering into the growing chains⁷.

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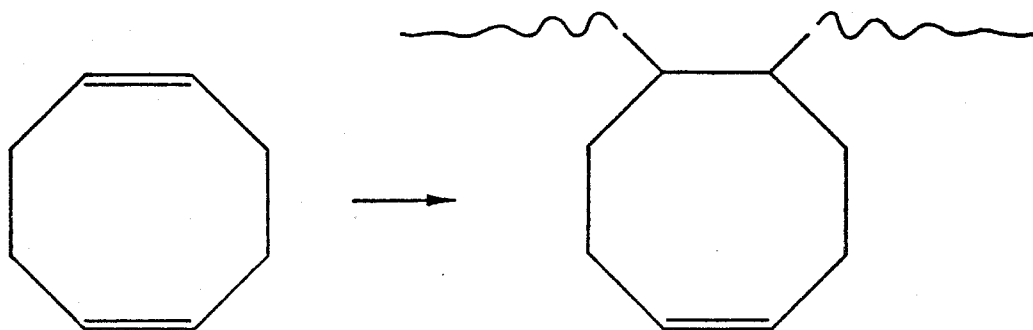


FIG. 1.—Monomeric unit in the terpolymer chain deriving from COD.

The results obtained prompted us to consider the possibility of using monomers of this type for preparing vulcanizable terpolymers based on ethylene and propylene. We have thus examined the behavior of a large number of cyclic polyenes in copolymerization with ethylene and with propylene; among the various monomers which proved to be copolymerizable, *cis,cis* cyclo-octadiene 1,5 (COD) was found of particular interest. This interest is chiefly due to the following reasons:

1. COD terpolymers show excellent properties;
2. COD terpolymers do not possess any branches or gel. The residual double bond present in the COD monomer unit (see Figure 1) can be considered as completely inert with respect to anionic coordinated polymerization, although it shows a high reactivity in the vulcanization with sulfur and accelerators.
3. COD can be easily produced starting from butadiene, a raw material which is easily available at a low price⁸.

On the basis of all these considerations and of broad experimental work (carried out for almost eight years), with many monomers of various type (aliphatic diolefins, acetylenic hydrocarbons, cyclic polyolefins of different types) we reached the conclusion that COD terpolymers possess a remarkable interest and, therefore, in this communication we will illustrate their properties.

ETHYLENE-PROPYLENE-CYCLO-OCTADIENE-1,5 TERPOLYMERIZATION

Ethylene-propylene-COD terpolymers were obtained by us in presence of certain particular catalysts acting through an anionic coordinated mechanism and prepared from organometallic compounds and transition metal compounds. Similarly to what we have already observed in binary copolymerization of ethylene with propylene, the best catalytic systems are those prepared starting from hydrocarbon-soluble vanadium compounds and from aluminium organometallic compounds^{1,9,10}. The catalysts are found to be homogeneous or colloiddally dispersed in the polymerization medium. In the presence of these catalytic systems (such as, for instance, $VCl_4-Al(C_6H_{13})_3$, $VCl_4-Al(C_2H_5)_2Cl$, $VCl_4-Al_2(C_2H_5)_3Cl_3$, $VOCl_3-Al(C_2H_5)_2Cl$, $VOCl_3-Al(C_4H_9)_2Cl$, etc.), copolymers and terpolymers are obtained that show a narrow distribution of both composition and molecular weight.

In agreement with what has already been observed in ethylene-propylene copolymerization^{10,11}, the catalysts capable of promoting ethylene-propylene-COD terpolymerization should preferably contain at least one halogen atom, either on the aluminium alkyl compound or on the transition metal compound.

In Table 1 the most important factors influencing the over-all rate of the terpolymerization process are given.

TABLE 1

MAIN FACTORS INFLUENCING THE OVER-ALL RATE OF ETHYLENE-PROPYLENE-CYCLO-OCTADIENE 1,5-TERPOLYMERIZATION

The over-all rate increases with increase of the following parameters:

- a. $\frac{\text{moles aluminum compound}}{\text{moles vanadium compound}}$ (at least within certain limits)
- b. catalyst concentration
- c. monomer concentration in the reacting phase
- d. $\frac{\text{moles } C_2H_4}{\text{molec } C_3H_6}$ in the reacting phase
- e. Reciprocal of the polymerization temperature (within certain limits)

As to the influence exerted by the molar ratio of aluminum compound to vanadium compound on the rate of terpolymerization, we have observed for instance that operating with a catalyst prepared from $Al(C_2H_5)_2Cl$ and VCl_4 such influence is particularly marked if this ratio is increased from 2:1 to 3:1, while it is rather limited if this ratio is increased from 3:1 to 10:1 (see Figure 2).

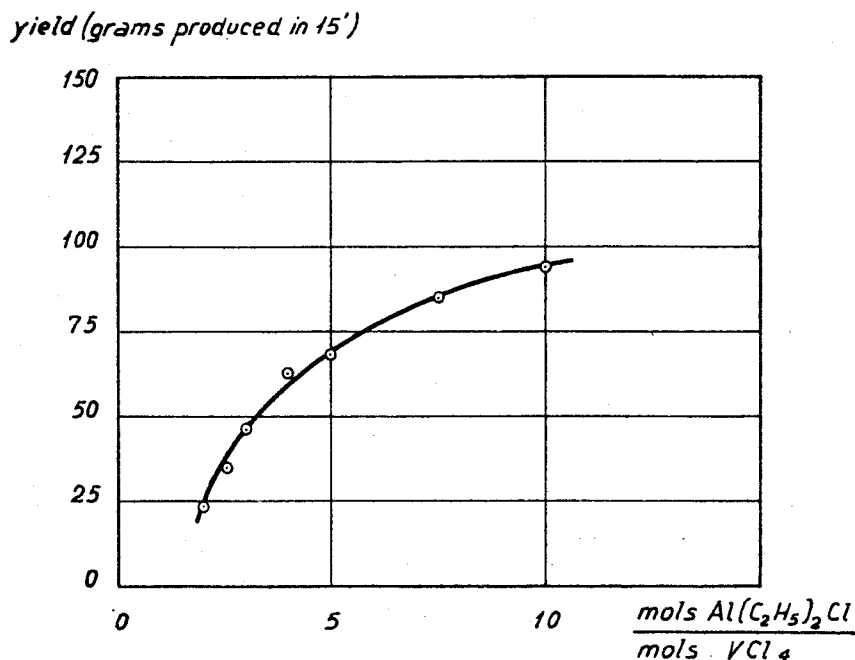


FIG. 2.—Dependence of the terpolymer yield (in grams of terpolymer obtained in 15 minutes) on the molar ratio $Al(C_2H_5)_2Cl/VCl_4$. Experimental conditions: polymerization temperature, $-20^\circ C$; abs. pressure, 1 atm; solvent, *n*-heptane, weight% C_3H_6 unit in the terpolymer, 53; weight % COD unit in the terpolymer, 1.8; molar ratio $C_2H_4:C_3H_6:COD$ and the concentration of VCl_4 are the same in each run.

By equal concentrations of the monomers present in the dissolved phase when both catalyst preparation and polymerization are carried out at low temperature (e.g., below $0^\circ C$), higher over-all terpolymerization rates are reached than those observed operating at higher temperatures, e.g., $25^\circ-30^\circ C$. This behavior is attributable to a decreased aging rate of the catalyst at the lower temperatures¹⁰.

The influence exerted by the various factors on the intrinsic viscosity of the terpolymers was studied. It was found that the intrinsic viscosity of the terpolymers decreases with increase of the following parameters: (a) moles aluminum compound/moles vanadium compound; (b) catalyst concentration; (c) moles

C_3H_6 /moles C_2H_4 in reacting phase; and (d) polymerization temperature. The influence exerted by Al/V ratio on the degree of polymerization may be attributed to the existence of a transfer process between the growing chains and the aluminum alkyl compound. The decrease in intrinsic viscosity of the terpolymer with increasing catalyst concentration may be interpreted in a similar way, analogously to what was already observed in the case of C_2-C_3 copolymerization¹⁰.

The terpolymer composition varies with the principal polymerization conditions and depends on type of V compound and the ratio between the concentrations of the monomers. It is independent of the moles Al compound/moles V compound (at least between 2/1 and 20/1), the catalyst concentration and the time of polymerization. Unlike what was previously observed in ethylene-propylene-higher alpha olefin (e.g., butene-1) terpolymerization¹², we have noticed that in ethylene-propylene-COD terpolymerization, all other factors being equal (thus by equal ethylene-propylene molar ratio in the reacting phase) on increasing the concentration of the diolefin in the reacting phase, an increase in the ethylene to propylene molar ratio is observed in the terpolymer (see Figure 3).

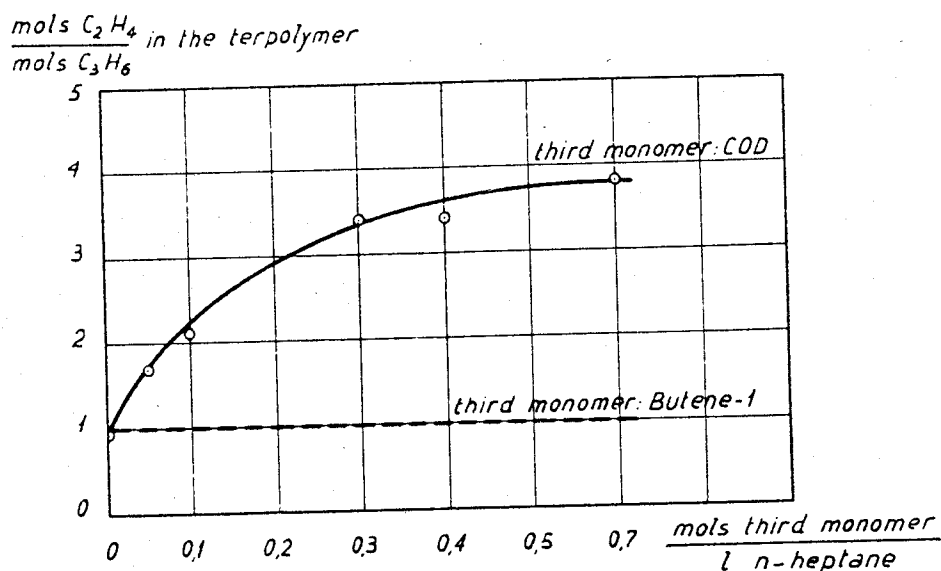


FIG. 3.—Terpolymerization of ethylene and propylene with a third monomer. Dependence of C_2H_4/C_3H_6 molar ratio in the terpolymer on the concentration of the third monomer in the reacting phase.

(—) Ethylene-propylene-COD terpolymerization. Experimental conditions: polymerization temperature $-10^\circ C$; abs. pressure, 1 atm; solvent, *n*-heptane; moles C_2H_6 /moles C_2H_4 in the gaseous feed 2; VCl_4 0.5 mmole/1 *n*-heptane; moles $Al(C_2H_5)_2Cl$ /moles $VCl_4 = 5$.

(---) Ethylene-propylene-butene-1 terpolymerization. Experimental conditions: polymerization temperature $25^\circ C$; abs. pressure, 1 atm; solvent, *n*-heptane; moles C_3H_6 /moles C_2H_4 in the gaseous feed, 2; VCl_4 1 mmole/1 *n*-heptane; moles $Al(C_2H_5)_2$ /moles $VCl_4 = 2.5$.

Such a marked influence cannot be justified only by the hypothesis that, owing to steric hindrances, no addition processes leading to direct enchainment between two COD units or between one COD unit and one propylene unit may occur. It should rather be assumed that the observed influence is due to an interaction (e.g., complexing) of cyclo-octadiene with the catalyst.

PROPERTIES OF ETHYLENE-PROPYLENE-CYCLO-OCTADIENE TERPOLYMERS

Vulcanization conditions.—By suitably selecting catalytic systems and conditions under which the catalyst is prepared and the polymerization is carried out, we succeeded in obtaining completely amorphous terpolymers, having variable unsaturation contents and showing a homogeneous distribution of the unsaturation

TABLE 2
DISTRIBUTION OF UNSATURATIONS IN THE DIFFERENT FRACTIONS (OBTAINED BY FRACTIONAL PRECIPITATION) OF AN ETHYLENE-PROPYLENE-1,5-CYCLO-OCTADIENE TERPOLYMER*

Fraction No.	% of total terpolymer	Weight % of COD
1	4.2	2.4
2	3.3	2.8
3	2.5	2.8
4	6.2	2.9
5	4.6	2.8
6	5.8	2.9
7	7.8	2.9
8	8.1	2.7
9	5.5	2.8
10	10.0	2.8
11	5.5	2.6
12	9.1	2.6
13	9.6	2.6
14	7.2	2.4
15	8.7	nd
	98.1	

* Weight % of COD in the total terpolymer = 2.7.

TABLE 3
ACCELERATORS EMPLOYED IN CURING ETHYLENE-PROPYLENE-CYCLO-OCTADIENE TERPOLYMERS

Primary	Secondary
Tetramethylthiuramdisulfide (TMTD)	2-Mercaptobenzothiazole (MBT)
Tetramethylthiurammonosulfide (MS) Zinc diethyldithiocarbamate (ZnDMDC)	2-Benzothiazyl disulfide (MBTS)
Dipentamethylene thiurametrasulfide Selenium diethyldithiocarbamate Tellurium diethyldithiocarbamate	Diphenylguanidine

in all the macromolecules (see Table 2). Vulcanization of these elastomers may be conveniently carried out by taking advantage of the reactivity of the double bonds present along the chains. Crosslinking is generally effected by means of mixes based on sulfur and accelerators, in the presence of zinc oxide as activator. The accelerators usually used are the ones of the "ultrarapid" type, alone or, possibly, in combination with secondary accelerators (see Table 3).

Also, with the aid of accelerators commonly used with highly unsaturated rubbers such as, e.g., N-cyclohexyl-2-benzothiazolesulfenamide (Vulcafor HBS, Santocure) or N-oxydiethylene-2-benzothiazolesulfenamide (NOBS special) it is possible to vulcanize these terpolymers, but in most cases with poorer results.

Also with these terpolymers the presence of zinc oxide proves very convenient to obtain crosslinking when TMTD or MS are used as accelerators¹³; with mixes containing ZnDMDC as accelerator even in the absence of zinc oxide a certain degree of vulcanization of the terpolymer is obtained. The presence of stearic acid is not essential to a good vulcanization; however, addition to the mix of small amounts of this ingredient improves processability and dispersion of the fillers, especially when high loading of oil and carbon black is used.

TABLE 4
VARIOUS RECIPES EMPLOYED FOR EVALUATION OF TERPOLYMERS

	Recipe 1	Recipe 2	Recipe 3
Terpolymer	100	100	100
Stearic acid	1	1	1
Zinc oxide	5	5	5
HAF black (Vulcan 3)	50	50	50
Sulfur	2	1.5	1.5
TMTD	1	—	—
MS	—	1.5	—
ZnDMDC	—	—	1.5
MBT	0.5	0.5	—

Although all the above mentioned accelerators provide vulcanizates having good properties, we have preferred, in order to evaluate the different terpolymer samples and compare them with other elastomers having low unsaturation, to use mixes containing as accelerators TMTD or MS in combination with MBT, or ZnDMDC-based mixes (see Table 4).

Vulcanization conditions (temperatures and times) depend chiefly on the type of mix which is used. In Figure 4 the main mechanical characteristics in correspondence with the different curing times at 150° C for vulcanizates obtained from the first of the above mentioned mixes are given. The time required to reach maximum crosslinking (highest modulus at 300% and lowest elongation at break) is about 90 minutes, while beyond this time, practically no reversion phenomena occur, not even for vulcanization times of up to 4 hours. On comparing the rate of vulcanization of these terpolymers with the curing rates of butyl rubber, of dicyclopentadiene-containing terpolymers, of ethylene-propylene copolymers vulcanized with organic peroxides (dicumylperoxide) the rate of cure, with the aid of the abovementioned type of mixes is found, at least within certain ranges of temperature, satisfactory. In fact, the curing rate can, within the temperature range under consideration (150°–170° C), be considered somewhat higher than the rate of vulcanization of butyl rubber and much higher than the curing rate of dicyclopentadiene-containing terpolymers (Figure 5).

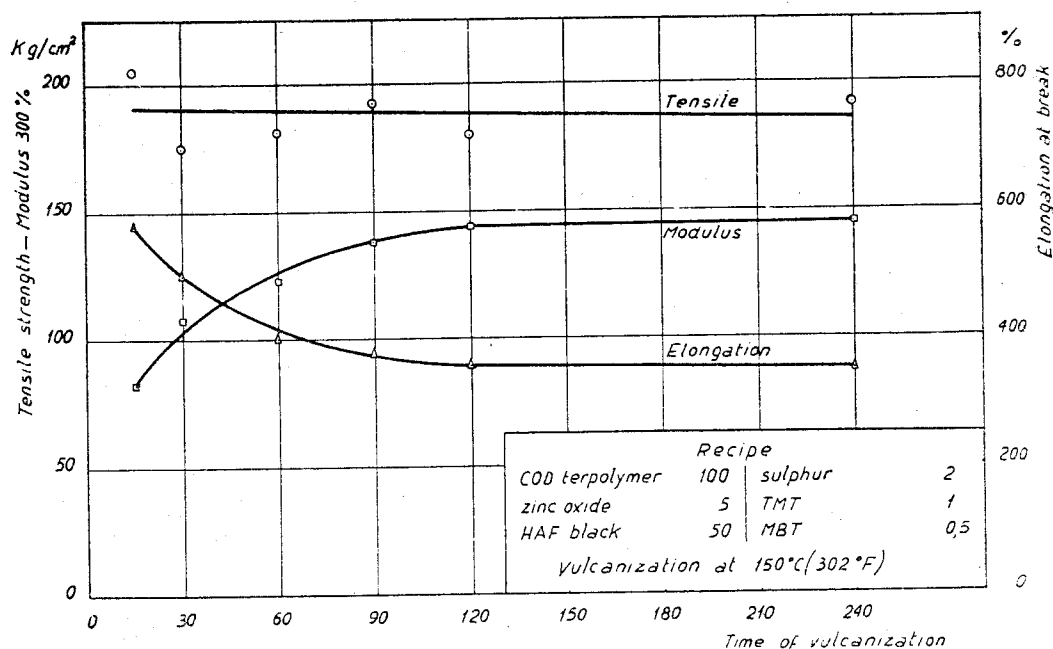


FIG. 4.—Main mechanical characteristics versus vulcanization time of vulcanizates obtained from COD terpolymer (weight % COD, 3.1; ML (1 + 4), 52).

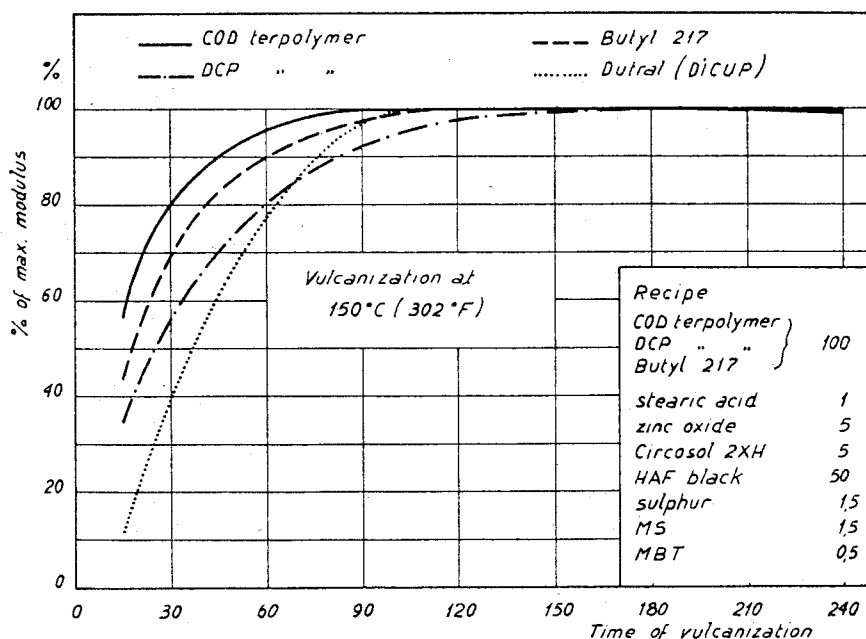


FIG. 5.—Rate of vulcanization of different rubbers at 150° C.

With COD terpolymers the vulcanization maximum at 150° C is attained in 90 minutes and 90% of final value is reached within 45 minutes, while with butyl rubber complete vulcanization is reached only in 120 minutes and 90% is reached in 60 minutes.

Terpolymers with dicyclopentadiene require, at 150° C, 240 minutes for complete vulcanization and 80 minutes to exceed 90% of final value.

At higher temperatures (160°–170° C), for long vulcanization times using the mixes above mentioned, a slight reversion is noticed, which however is contained within rather moderate limits (modulus at 300% goes down only 5–6%) (see Figures 6 and 7) and in any case is lower than the revision shown by butyl rubber.

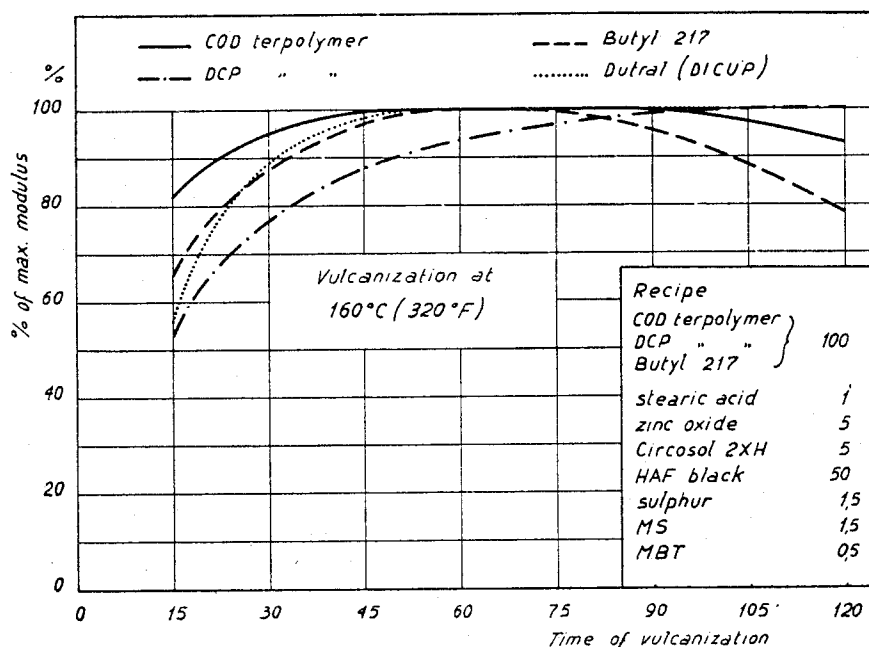


FIG. 6.—Rate of vulcanization of different rubbers at 160° C.

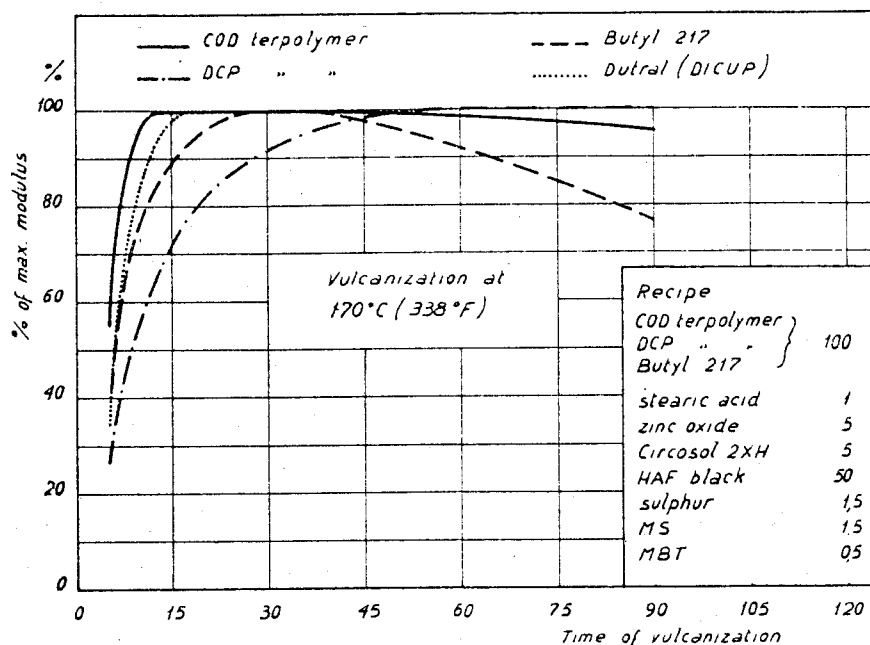


FIG. 7.—Rate of vulcanization of different rubbers at 170° C.

Of course, with COD terpolymers, as in the case of other rubbers at low unsaturation content, type and amount of ingredients in the recipe may be varied within wide limits so that vulcanizates meeting the different requirements desired in the finished product are obtained.

Suitable variations in type and amounts of the vulcanization ingredients may lead to vulcanization times lower than the one mentioned and also to improved aging properties of the vulcanizates.

Properties of the vulcanizates.—Mechanical and elastic properties of the vulcanizates are affected by the characteristics of the starting terpolymers, the principal parameters being ethylene to propylene ratio, unsaturation content (COD content) of the terpolymer and average molecular weight.

The ethylene content in the terpolymer does not appear to affect appreciably the mechanical properties of the vulcanizates, at least for ethylene molar percentages below 70. This is shown in Table 5, where the main mechanical characteristics are reported for vulcanized terpolymers containing different amounts of ethylene and about the same amount of COD. However by increasing the ethylene content in the terpolymer, the low temperature properties may be considerably improved as in the case of ethylene-propylene copolymers².

On the other hand, by increasing the ethylene molar content to above 75% a very high modulus at 300% may be reached; this may be attributed to the presence in the crude terpolymer, of small amounts of crystallinity; in these cases elastic recovery of the vulcanizates is poorer.

The percentage of unsaturation in the crude terpolymer has very marked influence on the properties of the vulcanizates; in Figure 8 the values relating to modulus at 300% and elongation at break are given as a function of the COD unit content. It can be seen that a 3% COD unit content by weight provides vulcanizates having a high value of the degree of crosslinking (values of the modulus at 300%), which in many cases may permit use of these elastomers with a lower curatives level or the possibility of adding to them considerable amounts of plasticizing oils.

TABLE 5
 PROPERTIES OF CYCLO-OCTADIENE-TERPOLYMERS WITH VARIOUS ETHYLENE UNIT CONTENT*

Analysis of terpolymers		Properties of vulcanizates			
COD unit content, % by wt	C ₂ H ₄ unit content, % in moles	Tensile strength kg/cm ²	Elongation at break %	Modulus at 200% kg/cm ²	Modulus at 300%
3.15	46	200	300	—	200
3.0	57	208	280	145	—
3.14	67	220	260	140	—
2.54	46	211	380	—	160
2.5	55	190	380	—	140
2.56	57	220	400	—	160
2.49	60	220	360	—	175

* Recipe: COD terpolymer 100
 Stearic acid 1
 Zinc oxide 5
 Sulfur 2
 TMTD 1
 MBT 0.5

Cured 150° C for 60 minutes.

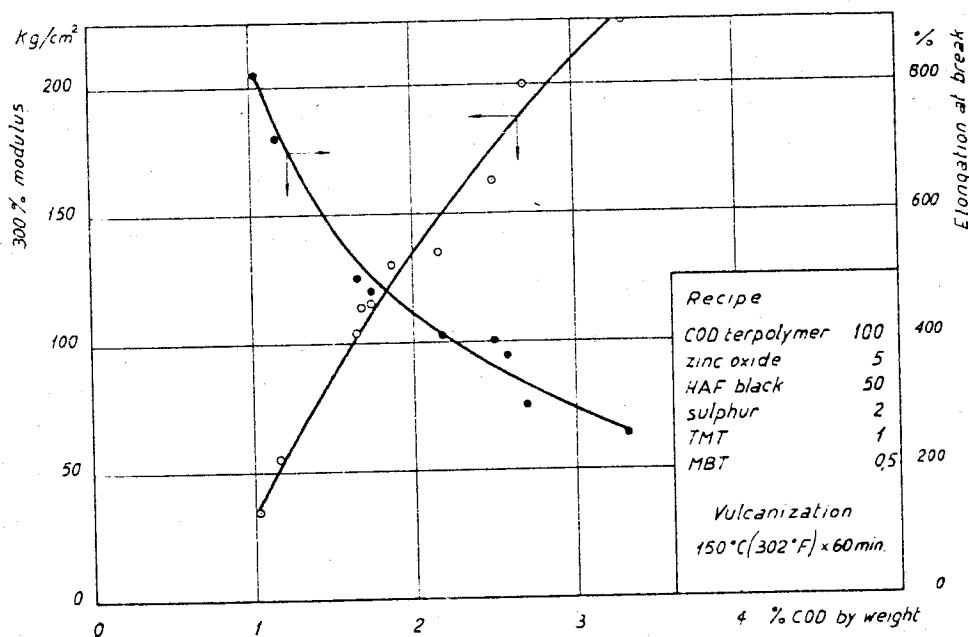


FIG. 8.—Influence of COD unit content in the terpolymer on vulcanizate properties.

The properties of the vulcanizates are also affected by the average molecular weight of the crude terpolymer; such parameter can be evaluated from the intrinsic viscosity measured in toluene at 30° C as well as from the Mooney viscosities (ML 1 + 4 at 100° C).

Generally Mooney viscosity can be easily varied from 10 to 130. As is apparent from Figure 9, an increase in the Mooney viscosity of the crude terpolymer exerts initially a strong influence on the properties of the vulcanizate, whereas above a certain value, the effect becomes weaker.

Influence of fillers and oils.—The vulcanizates obtained from these terpolymers in the absence of reinforcing fillers, show low tensile strength. Therefore, in order to be use them in practice, it is advantageous to add reinforcing fillers such as carbon black, finely dispersed silica, etc.

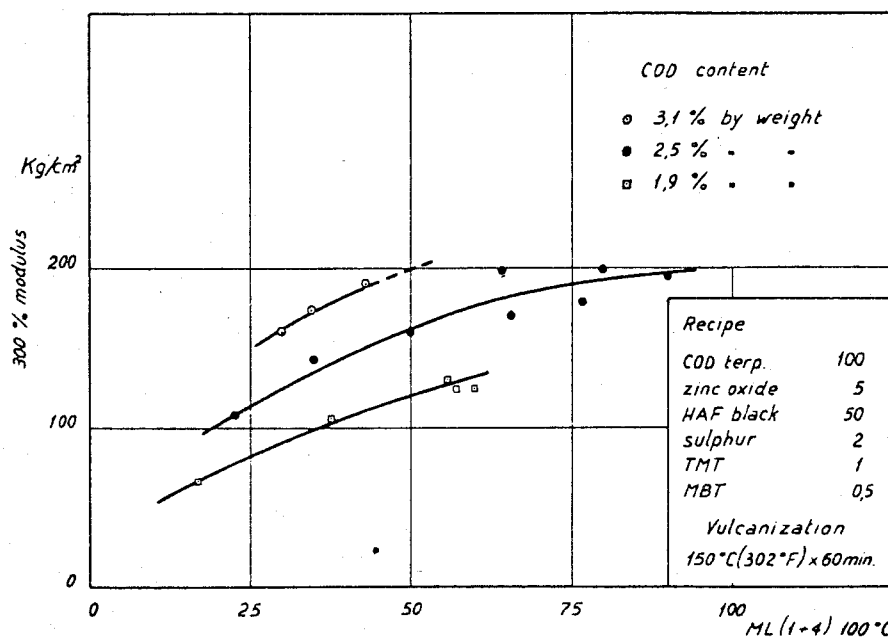


Fig. 9.—Influence of Mooney viscosity of the terpolymer on vulcanizate properties.

TABLE 6
INFLUENCE OF VARIOUS TYPES OF CARBON BLACK*

Carbon black		Tensile strength kg/cm ²	Elongation at break, %	Modulus at 300% kg/cm ²	Hardness I.H.R.D.	Resilience
Type	Quantity					
HAF	50	197	440	132	75	54
ISAF	50	236	460	136	75	52
MPC	50	240	640	80	73	53
SRF	80	117	320	112	78	57
FEF	70	180	300	180	82	48
MT	100	69	360	62	75	63

* Recipe: Terpolymer 100 (ML 1 + 4 at 100° C = 52, COD 3.1% by wt)
 Black as shown
 Circosol 2XH 5
 Sulfur 2
 MBT 0.5
 TMTD 1

Table 6 shows the most important mechanical characteristics of vulcanizates reinforced with various types of carbon black. From these data it may be observed how, with the aid of various types of carbon black, properties similar to the ones of the most common synthetic rubbers are obtained, in particular, high values for the tensile strength and modulus at 300% are reached together with good elastic (resilience) characteristics.

Very interesting from the commercial viewpoint is the possibility of extending these terpolymers with oils. These terpolymers prove in general to be compatible with oils of different types; oils can be added in large amounts, without damaging to any considerable extent their end-use properties.

Oil extension is conveniently carried out on terpolymers with high Mooney viscosity (above 80), though also products with lower Mooney viscosity easily bear considerable amounts of oil.

In Figure 10 the influence exerted on tensile strength, on modulus at 300% and elongation at break by various amounts of oil added to a terpolymer having relatively low Mooney viscosity (ML 1 + 4 at 100° C = 52) is shown with a recipe where the amount of carbon black is maintained unaltered with respect to the raw terpolymer. The curves refer to three types of oil and precisely to a pre-

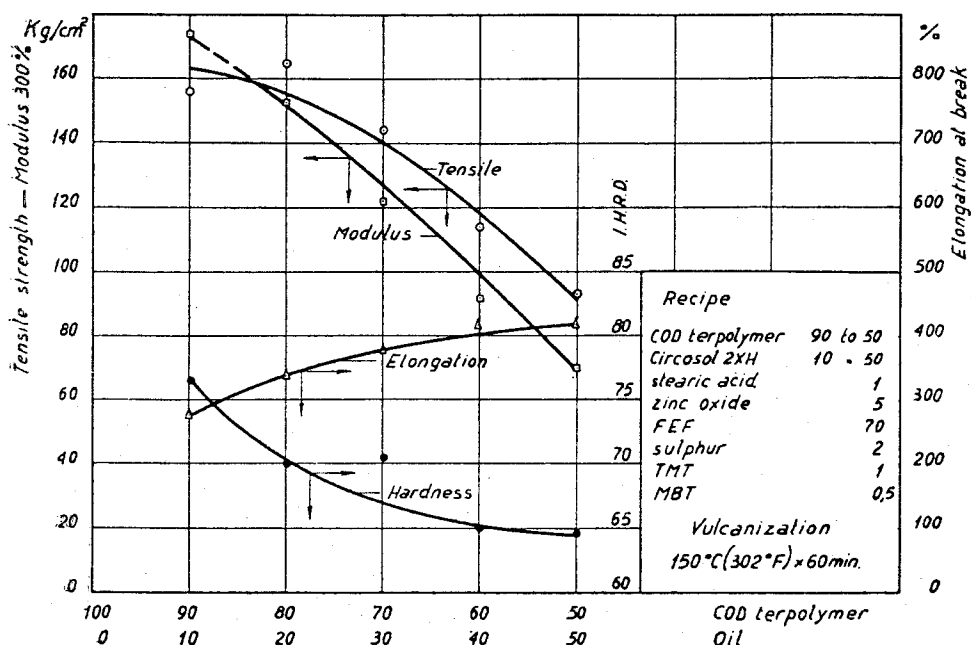


FIG. 10.—Influence of different types of oil on mechanical characteristics of vulcanizates.

vailingly paraffinic oil (Sun 551) to a prevailingly aromatic oil (Sundex 53) and to a prevailingly naphthenic oil (Circosol 2XH). From these data it may be observed that rather high tensile strengths may be reached even with 70–80 parts of oil; the characteristics are slightly more satisfactory with paraffinic and naphthenic oils. Moreover, an oil of aromatic type diminishes the values of hardness, resilience and elastic behavior at low temperature.

In Figure 11 values of the mechanical characteristics obtained from the same terpolymer extended with an oil of naphthenic type, wherein the ingredients, calculated on the basis of terpolymer + oil = 100, are given. Also with a terpolymer to oil ratio of 1:1, tensile strengths of the order of 100 kg/cm² can be obtained together with sufficiently high modulus and hardness and with good values for elongation at break. These examples show how these terpolymers can be used

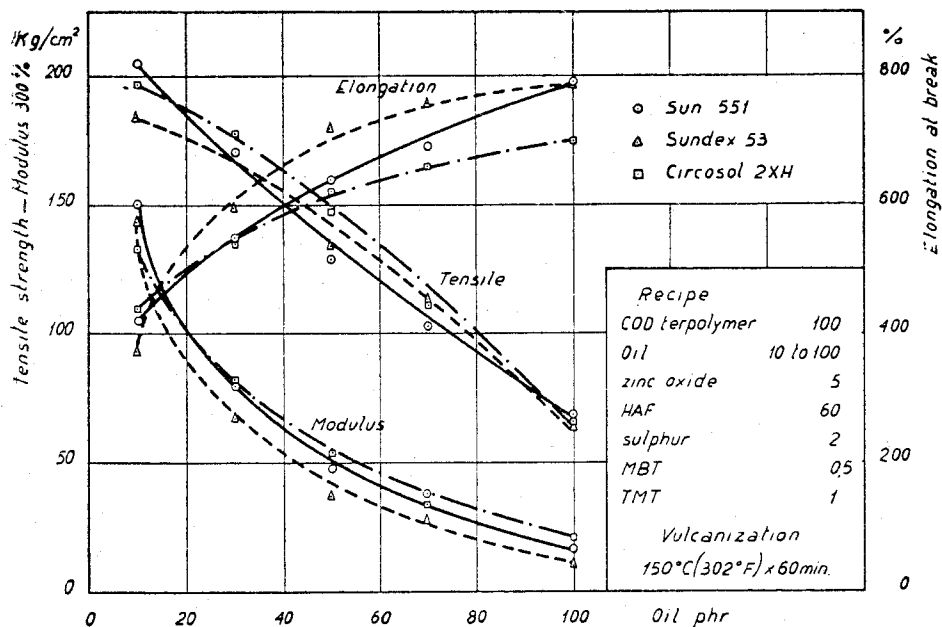


FIG. 11.—Influence of different amounts of naphthenic oil on mechanical characteristics of vulcanizates

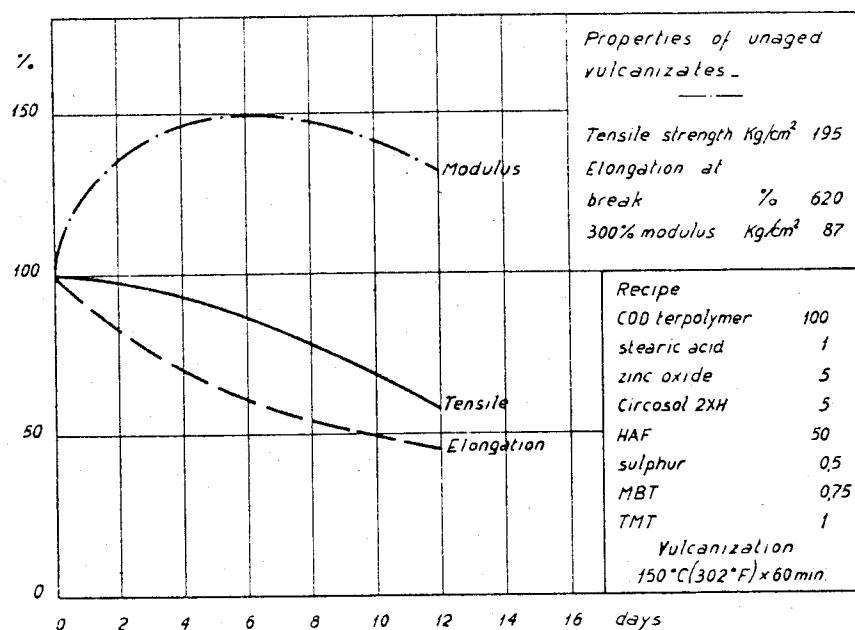


Fig. 12.—Resistance to aging of vulcanized COD terpolymers (oven air aging at 150° C).

with economical advantages in the form of heavily loaded products, which are easily processable and they show after vulcanization satisfactory mechanical properties together with good age resistance.

Age resistance.—The main chains of ethylene-propylene-COD terpolymers can be considered as essentially saturated chains. Actually the double bonds employed for vulcanization are not contained in the main chain. Therefore, their resistance to degradation agents is practically the same as that of ethylene-propylene copolymers.

Figure 12 shows the per cent variation of the main mechanical characteristics of vulcanizates versus the time of aging carried out in an air oven at 150° C. After 12 days the vulcanizates show still satisfactory properties. Also the resistance to other degradation agents (ozone, chemicals, etc.) is quite similar to that of ethylene-propylene copolymers.

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