

VULCANISATION AND ELASTOMERIC PROPERTIES OF ETHYLENE PROPYLENE COPOLYMERS

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Introduction: At the First International Synthetic Rubber Symposium in London⁽¹⁾ we illustrated the research work carried out in Italy on new types of synthetic elastomers. In particular, the following topics were discussed:

(1) Production of crystallisable butadiene polymers having regular steric structure and high steric purity;

(2) Production of linear, amorphous head-to-tail elastomers of α -olefins and of their copolymers with ethylene.

Research work in both fields has been carried out by us on a large scale in research laboratories and in pilot plants of the Montecatini company, and have led to results which justify the subsequent development, now in progress, of the commercial production of these elastomers.

In another communication⁽²⁾ presented at this Symposium, the properties of polybutadiene of high *cis*-1.4 content are described. In this communication we describe the properties of ethylene-propylene copolymers produced at the Montecatini plant in Ferrara.

The reasons which led us to expect interesting elastic properties of ethylene- α -olefin copolymers, and in particular of ethylene-propylene and ethylene-butene copolymers, have been described in previous communications of ours⁽³⁾.

The availability of large amounts of polymer, produced in the pilot plant, not only allowed us to confirm the results obtained on a laboratory scale, but also to evaluate the technological properties of the new rubbers.

Ethylene- α -olefin copolymers obtained by polymerisation processes which we call "anionic co-ordinated processes", constitute a new class of elastomers. Their practical interest derives not only from the low cost of the raw materials (ethylene and α -olefins) and from the high yields obtainable in the polymerisation, but also from such properties as the resistance to oxidation and to ageing which are higher than for unsaturated rubbers, and from their excellent elastic properties, which are better than those of the previously known saturated polymers⁽⁴⁾.

As has been discussed in previous communications, the elastic properties of hydrocarbon macromolecules depend on the potential barrier which hinders the free rotation of macromolecules around the carbon-carbon bonds of the main chain⁽³⁾. In saturated amorphous poly-

hydrocarbons, potential barriers are very low for the rotation of the $\text{CH}_2\text{-CH}_2$ bond. When one or more hydrogen atoms are substituted with groups larger in bulk than hydrogen the number of accessible configurations through rotations with low potential barriers is lower; that exerts an influence upon the dynamic properties of the polymer. Polymethylene (and linear polyethylene) does not behave as an elastomer, owing to its great tendency to crystallisation at room temperature, which stiffens the parallelised macromolecules and hinders the free rotation of the C-C bonds.

Crystallisation, however, is hindered by the introduction of statistically distributed substituents which destroy the steric regularity necessary for crystallisation.

This result was obtained with 'Hypalon' by introducing about 25-30 per cent of chlorine, which is enough to hinder crystallisation and to transform polyethylene in an elastomer; however, the dynamic properties of 'Hypalon' are poor, owing to the low mobility of the $\text{CH}_2\text{-CHCl}$ bonds and to the polar interactions among macromolecules. Our first investigations on the anionic co-ordinated polymerisation of α -olefins allowed us to obtain, back in 1954, linear atactic head-to-tail amorphous polymers⁽⁵⁾. Such high molecular weight polymers of α -olefins behave as elastomers and show good elastic properties: their dynamic properties (although better than those of polyisobutylene) are not very good, however, owing to the low mobility of the $\text{CH}_2\text{-CHR}$ bond which characterises the main chain⁽⁶⁾. We then recognised that the "amorphisation" of the polyethylene chain would be achieved by introducing a limited number of R groups, if these groups could be distributed at random along the chain, so as to leave sequences of $\text{CH}_2\text{-CH}_2$ groups numerous enough to permit a good mobility of the main chain, but not long enough to allow even a partial crystallisation.

Our provisions in this connection have been proved in practice by copolymerising ethylene with α -olefins, and in particular with propylene, using certain types of catalysts acting with an anionic co-ordinated mechanism^(3, 7).

Not all the catalysts which homopolymerise both monomers are able to give in copolymerisation unequivocally random distribution of the monomeric units.

Homogeneity of composition of the macromolecules is necessary to avoid crystallisation of the polymers. Crystallinity can be observed either when long

regular sequences of $\text{CH}_2\text{-CH}_2$ units are present somewhere in the copolymer or when, by using stereospecific catalysts, sterically regular sequences of $\text{CH}_2\text{-CHR}$ units are formed. The use of non-stereospecific catalysts able to polymerise α -olefins, and in particular, the use of catalysts which can be defined as kinetically homogeneous (showing, that is, active centres of only one type with regard to the reactivity ratios of the two monomers) allows amorphous copolymers to be obtained, provided that these contain less than 75-80 per cent moles of ethylene, and also a limited dispersion of the composition of all the macromolecules. All these copolymers show good elastic properties, the dynamic properties increasing with the ethylene content in the copolymer⁽⁸⁾.

As we have previously mentioned in this communication, we will deal here only with the properties of ethylene-propylene copolymers produced at the Ferrara plant.

Viscoelastic Properties

Ethylene-propylene copolymers are typical rubber-like substances which look very similar to the best known synthetic rubbers. Their viscoelastic behaviour, which is substantially analogous to that of other elastomers, is connected with the intrinsic properties of the macromolecular chains of the copolymer itself. Viscoelastic properties of these new elastomers are mainly influenced by:

- (1) Average chemical composition;
- (2) Homogeneity of such composition;
- (3) Average molecular weight of the polymer;
- (4) Distribution of molecular weights.

The chemical composition can be estimated using different I.R. methods of evaluation⁽³⁾; when higher accuracy is required labelled monomers can be used.

The regularity of distribution of the composition may be determined by extraction with solvents⁽³⁾. When operating under suitable polymerisation conditions, using catalysts containing only one type of active centre, it is possible to obtain copolymers which show only a limited dispersion in their chemical composition. In Figs. 1 and 2 we report the curves of distribution of the composition of two ethylene-propylene copolymers containing respectively 45 per cent and 20.5 per cent of ethylene in moles. As it can be seen from these figures, the distribution of composition is rather narrow. It is also possible to observe that a copolymer containing 20.5 per cent moles of ethylene has a narrower distribution in

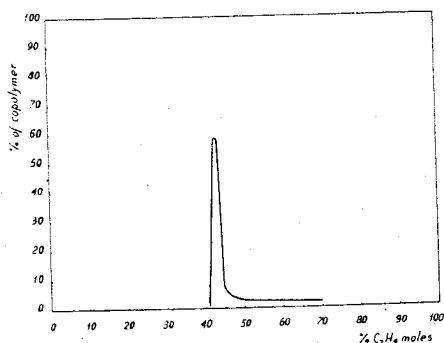


Fig. 1. Distribution Curve for Ethylene-Propylene Copolymer Containing 45 per cent Moles Ethylene

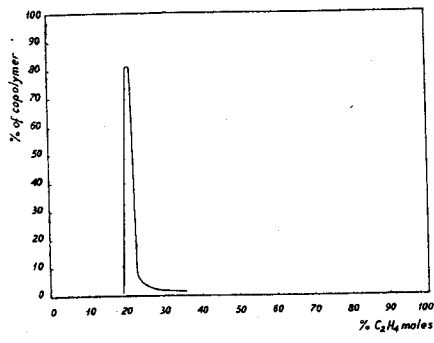


Fig. 2. Ethylene Propylene Distribution Curve for Copolymer with 20.5 per cent Ethylene

comparison with a copolymer containing 45 per cent moles of ethylene. This agrees with the results of a merely statistical calculation, comparing copolymers of different compositions(7).

The influence exerted by the dispersion of the composition upon the viscoelastic properties appears to be important, only in the case that crystallisable chain segments are present. In fact, our experiments prove that the properties of non-crystallisable copolymers consisting of different macromolecules—differing from each other in chemical composition by about 10–15 per cent—do not differ in practice from the properties of more homogeneous copolymers. Plotting rebound versus temperature for a mixture of two homogeneous copolymers of different chemical compositions, one obtains values which are intermediate between those corresponding to the two homogeneous copolymers. Moreover, the rebound curve of the mixture shows only one minimum, contrary to what generally happens for mixtures of two different elastomers(8).

In order to study the viscoelastic characteristics of amorphous polymers, it may be useful to examine the stress relaxation, as a function of time, for a wide range of temperatures(9). The determination of the relaxation modulus at different times is useful to determine

the behaviour of the polymers as a function of the two main parameters: time and temperature.

Fig. 3 shows the relaxation moduli which have been determined for an ethylene-propylene copolymer containing 47 per cent moles ethylene at temperatures ranging from $-60^{\circ}\text{C}.$ to $+45^{\circ}\text{C}.$ for three different lengths of time (10 secs., 100 secs., 1,000 secs.). The modulus-temperature curves show a very marked kink, at $-35^{\circ}\text{C}.$ in the case considered in Fig. 3, corresponding to a beginning of transition temperature and to a minimum of the rebound.

At temperatures below $-50^{\circ}\text{C}.$, moduli taken at different times almost coincide; moreover, when lowering the temperature, modulus increases at a lower rate, reaching the values of the vitreous state (10^{10} – $10^{10.5}$ dynes/cm²) at extremely low temperatures. In fact, the glass transition temperature, determined by brittle point measurements, has values of about $-100^{\circ}\text{C}.$ for ethylene-propylene copolymers containing about 50 per cent of ethylene moles.

A similar behaviour is shown by the stress-elongation curves taken at different temperatures. Fig. 4 shows these curves for the same ethylene-propylene copolymer in Fig. 3, with an almost constant elongation rate ($R=0.2$ sec.⁻¹).

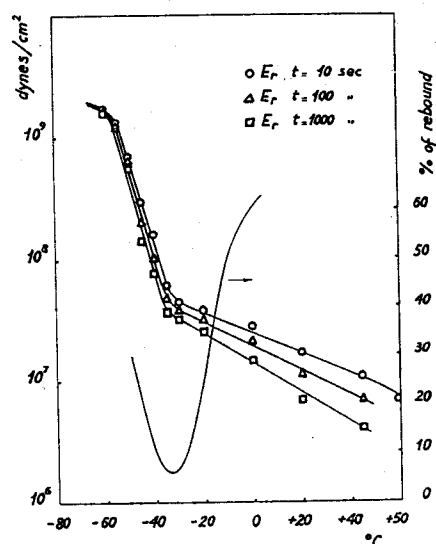


Fig. 3. Relaxation Moduli for Ethylene Propylene Copolymer Containing 47 per cent Moles Ethylene

From this figure it can be easily observed that the initial elastic modulus shows a rapid variation at a temperature of about $-35^{\circ}\text{C}.$ The elongation at break of ethylene-propylene copolymers, also at the temperature of $-60^{\circ}\text{C}.$ is high (300 per cent at a test rate of 500 mm./min.), and it proves that this temperature is very far from the brittle point. Furthermore, properties at low temperature improve when the content of ethylene increases, as described in other papers of ours(8).

The viscosity of the copolymer and, therefore, its processability, depend on its average molecular weight and on the distribution of molecular weights. It is difficult to process copolymers of high molecular weight, because in practice they do not undergo the usual breakdown processes (e.g. by prolonged mastication in mixers). Therefore it becomes necessary to produce, directly in the polymerisation, copolymers having a molecular weight suitable for a good processability (with machinery commonly used in the rubber industry), and having good mechanical and elastic properties after vulcanisation.

Processing of Ethylene-Propylene Copolymers

Speaking of the processing of ethylene-propylene copolymers, we shall refer here only to polymers having a Mooney viscosity in the crude of about 50 (ML1+4).

Processing of these polymers in the roll mixer is not difficult; they form an easily processing smooth band which incorporates vulcanising agents and fillers without difficulty. The addition of suitable plasticisers furnishes a mix with excellent fluidity qualities.

Flow curves at different temperatures and at different flow speeds were determined with a modified Mooney type viscometer fitted with a biconical rotor (in order to obtain the same shear speed in all parts of the sample). The curves reported in Fig. 5 have been determined

TABLE I
Extrusion test with Garvey die (at $100^{\circ}\text{C}.$)

	Ethylene-propylene rubber		SBR rubber
	Cable	Extruded shape	Tread compound
Rating	13½	14½	15
Extrusion velocity	0.54 m/min.	0.45 m/min.	0.45 m/min.
Swelling	12%	32%	39%
Cable compound:	Extruded shape compound:		
Copolymer	Copolymer	SBR tread compound:	
ML(1+4)=20 100	ML(1+4)=50 100	SBR	100
Hard clay ... 100	FEF black ... 70	HAF black	50
ZnO 5	Sulphur 0.24	Circosol 214	10
DPG 1	Dicumylperoxide 2	Nonox B	1
Sulphur 0.4		Stearic acid	2
Dicumylperoxide 3.3		ZnO	5
		Santocure	1
		Sulphur	1.75

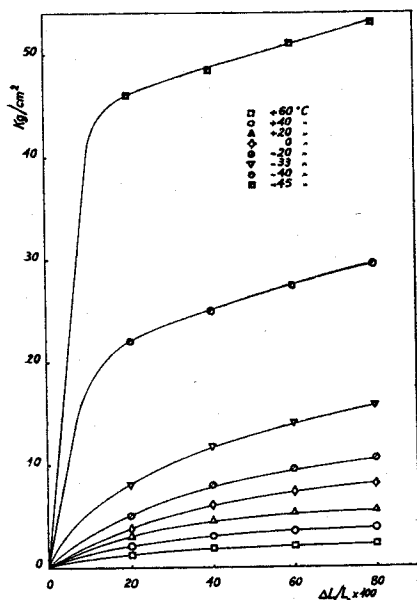


Fig. 4. Stress/Elongation Shown by Ethylene-Propylene Copolymer of Fig. 3.

at temperatures varying from 70°C. to 160°C., with rotation speeds ranging from 0.2 to 4 revs./min. They give an indication of the processability of the ethylene-propylene copolymers at different shear speeds and at different temperatures. The influence of shear speed on viscosity decreases with an increase of temperature.

Also the extrusion of ethylene-propylene copolymer is relatively easy when operating on suitable mixes. In Table I we report extrusion data, determined by the Garvey method, on two mixes: the first corresponding to a typical compound employed for electrical insulation cables, the second suitable for obtaining extrusion products having complex sections. As a comparison, we report analogous data for a mix of SBR rubber. From this table the good value reached by the Garvey index and the fairly good output per hour can be observed.

It is thus clear that processability of the considered ethylene-propylene copolymer is very similar to that of the most common synthetic rubbers. We believe that further research now in progress will overcome some inconveniences (e.g. lack of tackiness), and provide a satisfactory rubber for a vast number of applications.

Vulcanisation

Owing to the absence of unsaturation, and to the lower reactivity of the hydrogen atoms bound to tertiary carbons in comparison with that of allylic hydrogen, vulcanisation of chemically non-modified ethylene- α -olefin copolymers, in particular of ethylene-propylene copolymers, cannot be carried out with the aid of the ingredients usually employed for unsaturated rubbers.

The problem of transforming copolymers in cured rubbers was at first faced using methods similar to those

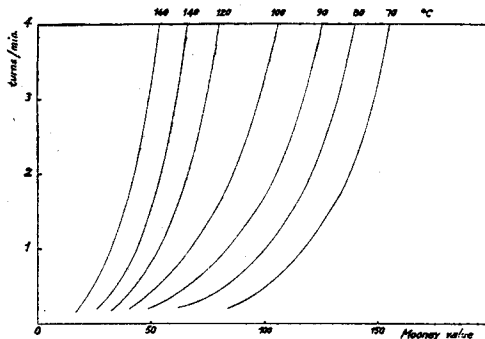


Fig. 5. Viscosity Variation with Temperature and Rotational Speed Change

already employed in the case of polyethylene. Later on we studied new cross-linking methods which provided products of improved characteristics⁽¹⁰⁾. Some of these methods have been described in a previous paper⁽¹¹⁾, in which we have also reported the results obtained on the cured products. In this paper we mainly report the data obtained in the cross-linking of pure ethylene-propylene copolymers by means of organic peroxides. We shall not report the data obtained on copolymers modified by the introduction of chemically reacting groups in the macromolecules.

Vulcanisation of Organic Peroxides

The mechanism of cross-linking of saturated polymers by means of peroxides is already known in its fundamental outlines.

An organic peroxide, when heated at a certain temperature, is decomposed into two free radicals. These radicals react in the presence of saturated hydrocarbons, abstracting a hydrogen atom from the polymer chain, and forming an induced radical on the chain. Two induced radicals of this type on different chains may join together, giving a cross-linking bond.

Together with these reactions which are useful for cross-linking the polymer, other parasitic reactions may obviously take place which cause a decrease of the cross-linking yield. These reactions are of different types, and may depend on the reactivity of the radicals formed by decomposition of the peroxide, on the reactivity of radicals induced on the polymeric chains, and on the tendency of the polymeric chain to depolymerise, especially by action of oxidation agents.

Parasitic reactions also take place in the case of cross-linking of ethylene-propylene copolymers by means of organic peroxides; generally it is rather difficult to obtain vulcanisates with good mechanical properties using only peroxides.

However, if the copolymer is cured with organic peroxides, in the presence of small amounts of sulphur, a high

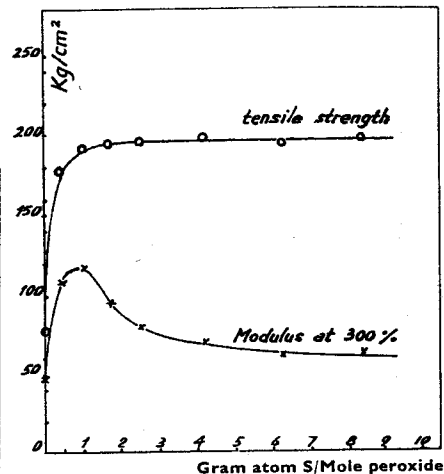


Fig. 6. Effect of Sulphur on Tensile and Modulus

cross-linking yield (essentially due to a decrease of side reactions) and a remarkable improvement of the physical properties of the vulcanisates are obtained.

Figs. 6 and 7 show the effect of sulphur on the main physical properties of the vulcanisate (165°C., 45 min.). Assuming as index of the cross-linking degree the modulus at 300 per cent, one can observe that, at the beginning, an increase of the sulphur concentration causes a rapid increase of the cross-linking degree, up to a concentration of 0.2 per cent of sulphur. Beyond this limit, an increase of sulphur concentration causes a marked decrease of the cross-linking degree.

In Table 2 the characteristics of vulcanisates obtained in the presence and in the absence of sulphur, with different concentrations of peroxide, are described. It can be observed that the increase of the peroxide concentration is not sufficient to furnish mechanical properties comparable with those obtained in the presence of sulphur. This

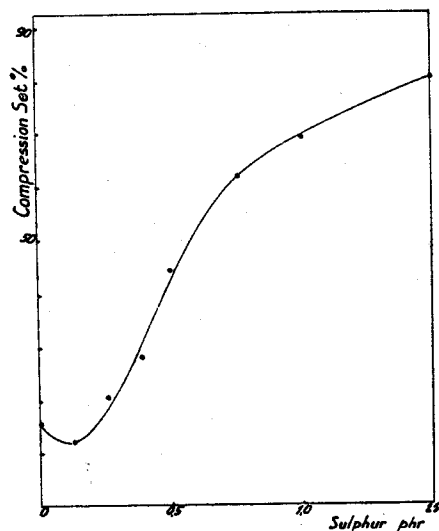


Fig. 7. Effect of Sulphur on Compression Set

TABLE II
Comparison between vulcanisates, in the presence or absence of sulphur

Ethylene-propylene copolymer	100	100	100	100	100	100	100	100	100
HAF—black	50	50	50	50	50	50	50	50	50
Sulphur	0.24	—	0.3	—	—	—	—	—	—
<i>tert.</i> -Butyl-cumyl-peroxide	1.54	1.54	2	2	2.5	3	3.5	4	4
Vulcanisation time: 45 min. at 165°C.									
Tensile strength kg./cm. ²	202	76	184	133	124	135	130	132	132
Elongation at break %	470	475	380	390	350	315	270	—	240
Modulus at 300%, kg./cm. ²	117	46	132	78	107	131	—	—	—
Tension set at 200%	8	31	6	21	13.5	11	broken	broken	—

leads one to believe that, in the absence of sulphur, side reactions which can also cause copolymer breakdown take place.

Characteristics of the Vulcanisation with Peroxides

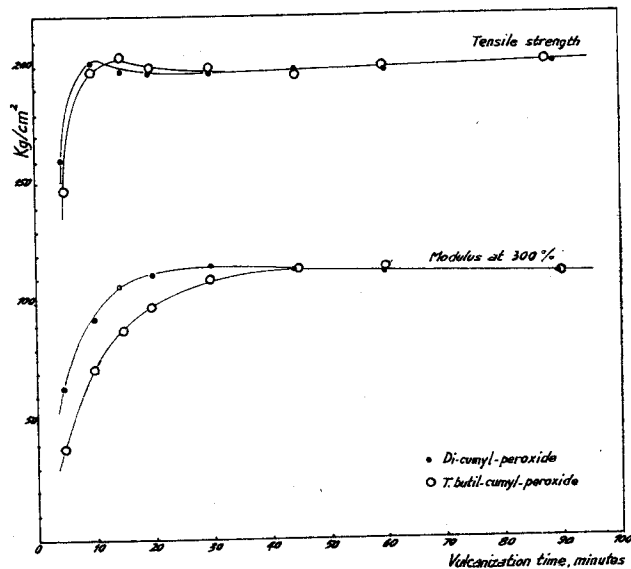
In Fig. 8 are shown some vulcanisation data obtained from compounds of copolymers containing HAF carbon black. It can be observed that these vulcanisates have good characteristics, even for long vulcanisation times. That is essentially due to the fact that during vulcanisation with organic peroxides reversion or breakdown reactions do not take place.

It is therefore possible to perform the vulcanisation at very high temperatures, without damaging the physical properties of the products.

This makes it possible to accelerate the vulcanisation by an increase in temperature, because an increase in temperature accelerates the monomolecular homolytic decomposition of the peroxide, without varying the mechanism. The vulcanisation curves of Fig. 9 show the behaviour of a copolymer at different temperatures; the vulcanisation compound contains 50 parts of HAF, 1.54 per cent of *tert*-butyl-cumyl-peroxide, and 0.2 per cent of sulphur.

Auxiliary curing agents, which may be added to the mixes, may exert a re-

Fig. 8.
Vulcanisation Data for Compounds Containing HAF Black



markable influence on the vulcanisation of ethylene-propylene copolymers.

In fact, the high reactivity of peroxides, which makes them suitable for the cross-linking of saturated polymers, favours their reaction with other substances and therefore lowers the

specificity of peroxides with regard to the vulcanisation of the polymer.

Thus all the substances able to react with free radicals, lower the vulcanisation yield obtainable with peroxides. This happens, for instance, with carbon black, with antioxidants and hydro-

TABLE III
Ageing of vulcanisate in circulating air at high temperature

Copolymer (Mooney 50)	100	100	100	100	100	100	100	100	100
HAF black	50	50	50	50	50	50	50	50	50
Phenyl-beta-naphthylamine	—	—	—	—	—	—	—	—	—
TPL—Agerit Superlit (1:1)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Sulphur	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
Dicumylperoxyde	—	—	—	—	—	—	—	—	—
	Tensile strength kg./cm. ²	Elong. at break %	Mod. at 300% kg./cm. ²	Tensile strength kg./cm. ²	Elong. at break %	Mod. at 300% kg./cm. ²	Tensile strength kg./cm. ²	Elong. at break %	Mod. at 300% kg./cm. ²
After curing for 20 min. at 165°C....	180	390	122	185	520	90	192	450	108
After ageing in air oven at:									
125° after 4 days	182	370	125	184	460	116	187	420	121
125° after 8 days	174	370	128	185	460	114	180	410	118
125° after 16 days	65	300	—	155	440	104	148	380	96
150° after 1 day	176	360	110	178	460	96	172	400	100
150° after 2 days	142	360	80	153	430	79	149	360	92
150° after 4 days	38	240	—	80	400	55	65	310	60

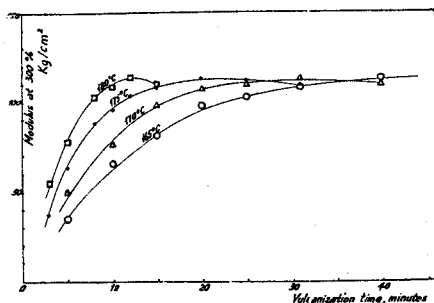


Fig. 9. Modulus/Vulcanisation Time for Compound with 50 Parts HAF, 1.54 per cent TBCP, 0.2 per cent Sulphur

carbon plasticisers, especially if they are unsaturated. Fig. 10 shows that the inhibitory effect of alkaline ("furnace") carbon blacks is fairly limited and detectable only for very fine blacks.

In any case, the inhibitory effect of the finest carbon blacks and of antioxidants may be suitably corrected by slightly increasing the concentration of peroxide.

There are also substances having an acidic character which may inhibit the vulcanisation of ethylene-propylene copolymers, especially when using aralkyl peroxides, since these substances can cause anionic decomposition of these peroxides with a corresponding disappearance of free radicals. This effect is observed, for instance, with channel blacks and siliceous fillers which possess a certain acidity. Moreover, the negative influence of these substances may be easily corrected, either by employing peroxides which undergo heterolytic reactions in a more difficult way, or adding suitable alkaline substances in the mixes.

Characteristics of Vulcanisates

Vulcanisates obtained from ethylene-propylene copolymers in the presence of reinforcing fillers show mechanical characteristics which are analogous to or even better than those of vulcanisates obtained from the best known synthetic rubbers.

The most important mechanical properties have already been described in previous figures and tables. In Fig. 11

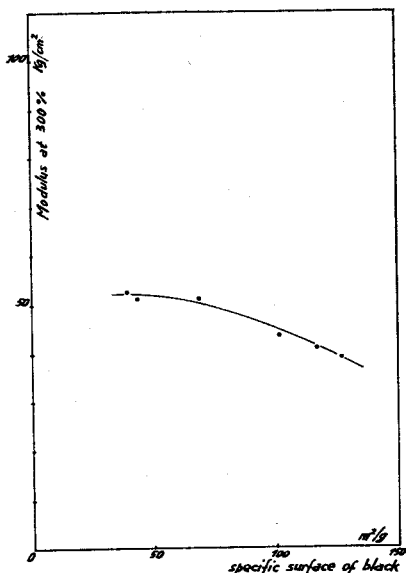


Fig. 10. Slight Inhibition Effect of Furnace Blacks

we report the variation of tensile strength versus temperature, and in Fig. 12 the analogous variation for tear strength. Curve II of the latter figure refers to a slightly undercured product.

Resistance to ageing is clearly a characteristic of this new class of elastomers. The main characteristics of vulcanisates aged in an air oven at temperatures of 125°C. to 150°C. are reported in Table III. The thermal stability of these vulcanisates is very high, in particular if compared with that shown by conventional synthetic elastomers.

In Table IV we report the characteristics of vulcanisates obtained in the presence of white fillers. If we consider the excellent electric properties of the copolymer and its resistance to ageing, we can foresee that these elastomers will acquire a particular importance in the field of cables. In fact, their resistance to ozone is also excellent. Vulcanised samples tested at an elongation of 25 per cent, subjected to an ozone concen-

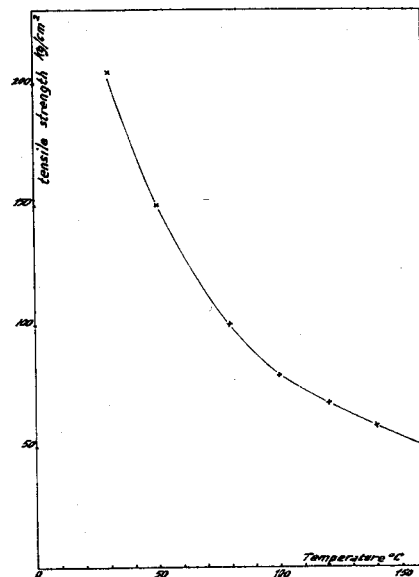


Fig. 11. Tensile Strength/Temperature for Filled Copolymer

tration of 150 ppm. at 50°C., do not show, after 200 hours, any appreciable decrease in mechanical properties. Fig. 13 (overleaf) compares the behaviour of a copolymer after a 200-hour treatment (I), and of butyl rubber (II), natural rubber (III), SBR rubber (IV), when subjected to the same ozone concentration for 24 hours.

One should also mention the good resistance of this rubber to chemical reagents, such as concentrated sulphuric acid and nitric acid. After a 60-day immersion in concentrated sulphuric acid, a cured ethylene-propylene copolymer only loses 25 per cent of its tensile strength and of its elongation at break.

Conclusions

From the above-mentioned data it follows that the chain backbone of an ethylene-propylene copolymer is a

TABLE IV
Characteristics of vulcanisates with white fillers

Compound	For cable	For technical articles	A.S.T.M.
Ethylene-propylene copolymer	100	100	
Hard clay	100	—	
Ultrasil	—	30	
PbO	3	—	
Plasticiser (Buna 32)	—	10	
Diphenylguanidine	1	—	
tert.-butyl-cumylperoxide	2.5	2.5	
Sulphur	0.4	0.4	
Cure time: 40 min. at 165°C.			
<i>Mechanical Properties:</i>			
Tensile strength (kg./cm. ²)	55	120	D 142
Elongation at break (%)	500	500	"
Modulus at 300% (kg./cm. ²)	30	50	"
Tear strength (type B) (kg./cm. ²)	22	22	D 624
Hardness, Shore A	55	60	D 676

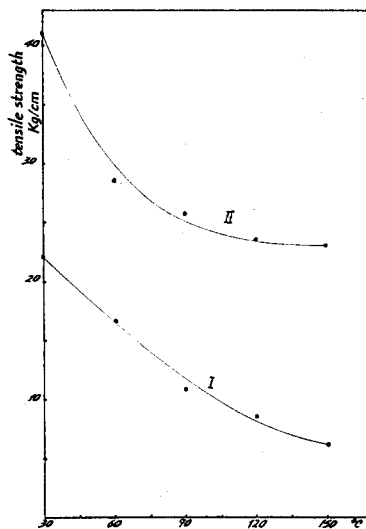


Fig. 12. Tear Strength/Temperature Relationship

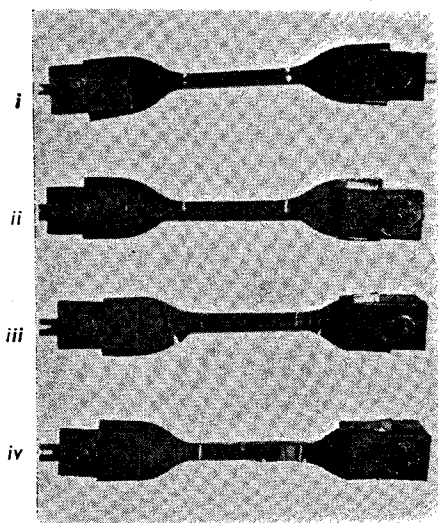


Fig. 13. Ozone Resistance of Ethylene-Propylene Copolymer

raw material very suitable for the production of elastomers.

The vulcanisation system which has been considered in this communication is, in fact, the one which least modifies the nature of the main chain.

Among other methods studied by us for the vulcanisation of ethylene-propylene copolymers, we will just mention here the most interesting ones:

(1) Chlorosulphonation, up to a content of 2-3 per cent by weight of chlorine, which is much lower than the amount of chlorine present in chlorosulphonated polyethylene.

(2) Chlorination (5-15 per cent of Cl by weight) and vulcanisation in the presence of inorganic bases, using butyl rubber recipes.

(3) Introduction of small amounts of double bonds, either by copolymerisation or by chemical reactions on the preformed copolymers.

(4) Grafting of reactive groups (for instance grafting maleic acid or its derivatives).

(5) Cross-linking by using monomers, which undergo free radical polymerisation.

These different vulcanisation processes allow the use, in some cases, of conventional vulcanisation methods, and they confirm the good elastic properties of the chains consisting essentially of ethylene-propylene copolymers.

Discussion

R. L. Zapp, Esso Research and Engineering:

Q.—What is the role of sulphur in the crosslinking?

A.—The role of sulphur is to protect the copolymer from breakdown reaction.

Q.—Does a small amount of sulphur enter the cross-link?

A.—We believe the sulphur enters the cross-link and that in the case of vulcanisation with peroxide and sulphur we have some sulphur bridge.

Dr. D. Thoenes, State Mines, Holland:
Dr. Crespi emphasised that the distribution of ethylene and propylene units in the copolymer should be random in

order to make a good elastomer. Now, if conditions could be found where the product of the two "reactivity ratios" (as defined by Natta and co-workers) is much smaller than one, a copolymer could be obtained consisting of alternate ethylene and propylene units. Such a polymer would be identical with hydrogenated polyisoprene. What would, in Dr. Crespi's opinion, be the properties of such a copolymer?

A.—The distribution of the monomeric units of the ethylene-propylene copolymers have been investigated, and it has been established that the copolymers prepared using catalytic systems from VCl₄ have a distribution of the monomeric units which is very near to the completely statistical one. In the case of copolymers prepared using these catalysts and using all the catalytic systems, the product of the reactivity ratios of which is very near to 1, most sequences of monomeric units in a 50:50 copolymer are therefore formed either by one molecule of ethylene or of propylene respectively.

Obviously sequences containing more than 1 monomeric unit are also present. When the product of the reactivity ratios tend to 0, the alternance of the monomeric units approaches the maximum, and a 50:50 copolymer tends to assume the chemical structure of hydrogenated polyisoprene.

Since the product of the reactivity ratios, for the best catalytic system which can be employed for the C₂C₃ copolymers, is always very near to 1, up to now it is impossible to synthesise, directly by copolymerisation, a product having exactly this chemical structure.

We have examined other methods to produce this hydrogenated polyisoprene, but we cannot describe yet the properties of this product.

Dr. R. S. Voris, Hercules Powder Co., Wilmington, Del.:

Q.—Dr. Crespi has described an interesting field of elastomers and made the point that we are dealing here with a family of copolymers and not just a single rubber. It is interesting to note that we have concentrated our efforts on copolymers with lower propylene content, i.e. in the range of 30-40 per cent propylene and with a viscosity somewhat lower than that which you have used in most of your work, i.e. in the Mooney (ML-4, 212°F.) range of 30-40. This material also has the outstanding properties you have shown. At higher molecular weight this rubber also becomes oil-extendable, provided a saturated oil is used to avoid interference with the curing system.

Would Dr. Crespi comment on the variations in properties of products with various ethylene contents, and particularly the effect of sulphur "demand" and "Dicup"/5 ratio and ethylene content change?

A.—I believe that the sulphur/peroxide ratios are not very different for different copolymers. Using a copolymer with greater ethylene content it may perhaps be that you can use a smaller quantity of sulphur.

Dr. Sei Otsuka, Japan Synthetic Rubber Co. Ltd.:

Q.—Your data and various tables are based on the 50:50 copolymer. What

is the effect of the percentage of propylene on the rate of vulcanisation?

A.—We have not studied the rate of vulcanisation very much at this stage. The rate of vulcanisation is rather low, depending upon the peroxide that you use. When you are using, for instance, dicumyl peroxide you have a good vulcanisation with a temperature of 165°C. for 40 minutes, but when you use a different peroxide you have a different cure rate, at the same curing temperature.
D. E. Knibbe, Koninklijke/Shell Laboratorium, Amsterdam:

Q.—In the beginning of your lecture you mentioned that rubbers with too high molecular weight are not very well processed. Do you have any particular molecular weight in mind that you might say—this is still a good rubber, and easy to process?

A.—Yes, molecular weight determination is in the numerical values not very easy to make. We have some intrinsic viscosity values in tetralin by 135°C. and for a polymer having about 50 Mooney value, the intrinsic viscosity is about 2, but we have no good correlation up to date between intrinsic viscosity and molecular weight.

T. Liggins, Precision Rubbers Ltd.:

Q.—You appear to have done some work on antioxidants. Could you tell us the ones which you have found suitable for improving the heat ageing resistance, and at what levels they would be effective?

A.—We use several antioxidants. You can use a phenolic antioxidant or an aminic antioxidant. It is the same when you use a PBN or phenolic type antioxidants for a good ageing resistance.
J. Hyllsted, Linatex Ltd., Denmark:

Q.—What is the effect of sulphur on vulcanisation?

A.—We put sulphur in the vulcanisation compounds and we found that sulphur has a good influence on the mechanical properties up to a certain content, that is, about 1 atom sulphur, 1 mol. peroxide.

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