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POLYOLEFIN ELASTOMERS

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POLYOLEFIN ELASTOMERS

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NAZARENO CAMELI and VITTORIO TURBA

At the First International Synthetic Rubber Symposium one of us described for the first time the properties of a new class of synthetic elastomers based on ethylene and propylene.⁽¹⁾ Subsequently, several papers on this subject have been published by us and by others,⁽²⁾ showing the great interest of both producers and consumers.

These rubbers are not only of theoretical interest, but are also of enormous importance for their practical applications. The industrial production of these rubbers is already carried on in some countries, whilst in others the study of their applications is being successfully developed. These new elastomers are already being referred to as potential general purpose rubbers.

Elastomers are now available consisting of binary ethylene-propylene copolymers, and of terpolymers containing small amounts of unsaturations in addition to ethylene and propylene.

The vulcanisation of binary copolymers is usually carried out with the aid of organic peroxides, while terpolymers are vulcanised by more conventional recipes, based on sulphur and accelerators.

Although, for several reasons, the preference is now given to terpolymers, it must be borne in mind that the vulcanisation of binary copolymers is now possible with the aid of various organic peroxides.⁽³⁾

The drawback of vulcanisate odour has been overcome,⁽⁴⁾ and the field of applications of the saturated copolymers is widening rapidly.

Introduction of Unsaturation

To make possible the use of the recipes and conditions normally employed in the Rubber Industry, the introduction of double bonds into the binary ethylene-propylene (EP) copolymers has been considered of interest.

For this purpose we have examined for a long time the synthesis of terpolymers, consisting essentially of ethylene and propylene, together with small amounts of unsaturation derived from a third, dienic monomer.

In order not to affect the excellent characteristics of resistance to oxygen, ageing and chemicals exhibited by the EP copolymers, it was necessary to obtain terpolymers having unsaturations (normally of low level) not contained in the main chain of the elastomer.

In order to obtain vulcanisates with good properties, unsaturations had to be homogeneously distributed along the copolymer chains. To avoid the formation of branches or cross-links, the residual double bond of the diene entering the polymer chain should not react further during polymerisation.

Our research led to a number of classes of termonomers copolymerisable with ethylene and propylene. One of the classes examined by us is that of monocyclic diolefins, such as cis-cis-cyclo-octadiene 1-5^(5, 6, 7) and cycloheptadiene 1-4 (Fig. 1). A second class comprises polyalkenylcycloalkanes, such as trans 1-2 divinylcyclobutane and 1-2-4 trivinylcyclohexane⁽⁷⁾ (Fig. 2). A third class is formed by bicyclic dienes, such as bicyclo [4,3,0] nonadiene 3-7 (4,7,8,9, tetrahydroindene), bicyclo [4,2,0] octadiene⁽²⁻⁷⁾ and bicyclo [3,2,0] heptadiene 2-6⁽⁸⁾ (Fig. 3).

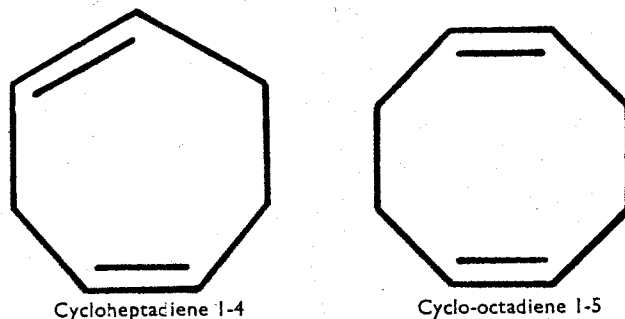


Fig. 1. Monocyclic diolefins used as termonomers in ethylene-propylene-terpolymerisation

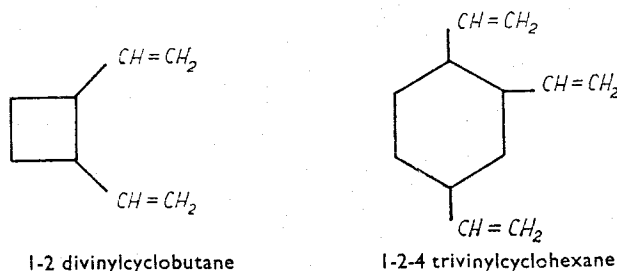


Fig. 2. Polyalkenylcycloalkanes used as termonomers in ethylene-propylene terpolymerisation

The vulcanisates obtained from these terpolymers possess excellent mechanical and dynamic properties. Terpolymers having a sufficiently high Mooney viscosity can incorporate remarkable amounts of oils.

The production of EP terpolymers containing various kinds of termonomers enabled us to compare for the first time the reactivities of different kinds of double bonds in vulcanisation.

Ethylene-Propylene Terpolymerisation

The terpolymers described in this paper have been obtained employing catalytic systems acting through an anionic coordinated mechanism and prepared from organometallic compounds and transition metal compounds. As in the case of binary ethylene-propylene copolymerisation,⁽²⁾ the best catalytic systems are obtained from hydrocarbon soluble vanadium compounds and organoaluminium compounds. These catalysts are soluble or colloiddally dispersed in the polymerisation medium. In the presence of these catalytic systems (e.g. $VCl_4 + Al(n-C_4H_9)_3$, $VCl_4 + Al(C_2H_5)_2Cl$, $VCl_4 + Al_2(C_2H_5)_4Cl_2$, V triacetylacetonate + $Al(C_2H_5)_2Cl$, $VOCl_3 + Al(i-C_4H_9)_3$, $VOCl_3 + Al(C_2H_5)_2Cl$), copolymers and terpolymers having a narrow composition and molecular weight distribution are obtained.

The best catalytic systems for ethylene-propylene terpolymerisation must contain at least a halogen atom on the organoaluminium compound or on the transition metal compound.^(9, 10)

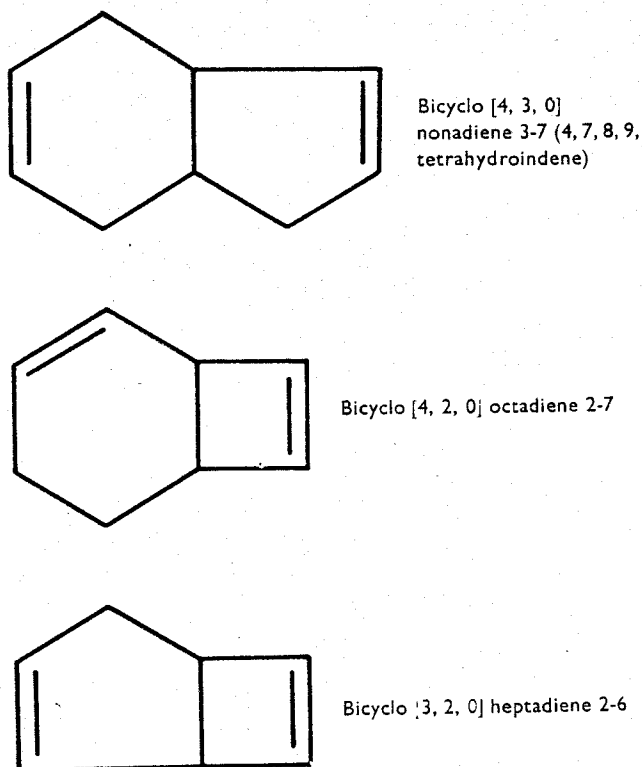


Fig. 3. Bicyclic dienes employable as monomers in ethylene-propylene terpolymerisation.

The main operating factors that influence the overall terpolymerisation rate and the molecular weight of the terpolymer are examined in more detail below.

Temperature

The temperature in general exerts a remarkable influence on the terpolymerisation rate. Using catalytic systems prepared from hydrocarbon-soluble vanadium compounds (e.g. VCl_4 , $VOCl_3$, V triacetylacetonate) and dialkylaluminiumhalides, the total monomer concentration and the other conditions being the same, at low temperature (e.g. below 0°) the overall terpolymerisation rate is higher than at room temperature. This phenomenon can be ascribed to a decrease in the ageing rate of the catalyst if the temperature decreases.

A decrease in temperature causes an increase in the average molecular weight (Mooney viscosity) of the terpolymer (see Table I).

Organoaluminium Compound/Vanadium Compound Molar Ratio

At least within a certain range, the molar ratio of organoaluminium compound to vanadium compound employed in the preparation of the catalyst exerts a certain influence on the terpolymerisation rate. In the case of ethylene-propylene-cyclo-octadiene terpolymerisation in the presence of the catalytic system $Al(C_2H_5)_2Cl + VCl_4$, a remarkable increase in rate is observed if the $Al(C_2H_5)_2Cl/VCl_4$ molar ratio is increased from 2 to 3, and a moderate increase if the ratio is increased from 3 to 10 (see Fig. 4). As can be seen from Fig. 5, an increase in the $Al(C_2H_5)_2Cl/VCl_4$ molar ratio causes a decrease in the Mooney viscosity of the terpolymer. This shows the existence of a process of chain transfer with the alkylaluminium compound.

The molar ratio of alkylaluminium compound to transition metal compound does not exert an appreciable influence on the terpolymer composition.

Catalyst Concentration

An increase of catalyst concentration causes an increase in terpolymerisation rate and a decrease in intrinsic viscosity. This last fact shows the existence of transfer processes between

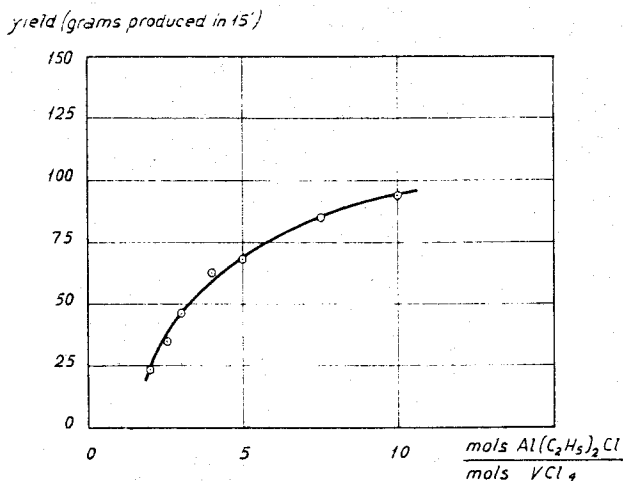


Fig. 4. Dependence of ethylene-propylene-cyclo-octadiene terpolymer yield (grams of terpolymer obtained in 15 min.) on the molar ratio $Al(C_2H_5)_2Cl/VCl_4$. Experimental conditions: polymerisation temperature = $-20^\circ C$.; abs. pressure = 1 atm.; solvent, n-heptane; weight % C_3H_6 in the terpolymer = 53; weight % COD in terpolymer = 1,8; molar ratios $C_3H_4:C_3H_6:COD$ and VCl_4 concentration are the same in each run.

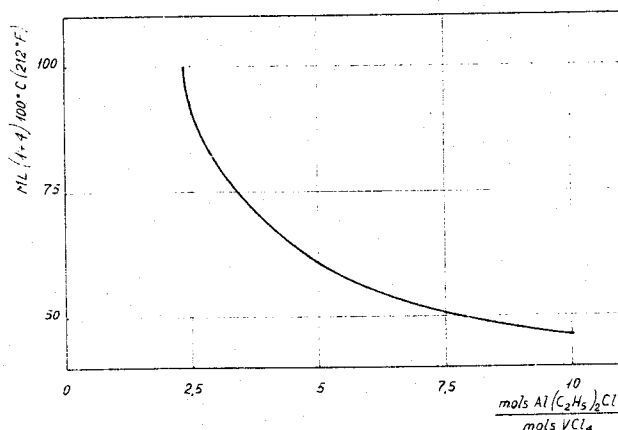


Fig. 5. Dependence of Mooney viscosity of ethylene-propylene-cyclo-octadiene terpolymer on $Al(C_2H_5)_2Cl/VCl_4$ molar ratio.

TABLE I

Influence of temperature on Mooney viscosity of ethylene-propylene-cyclooctadiene terpolymers prepared at constant ethylene : propylene : cyclooctadiene molar ratios in the reacting phase, in presence of catalytic system $Al(C_2H_5)_2Cl + VCl_4$ at atmospheric pressure

T ($^\circ C$)	Operating conditions		Properties of the terpolymer	
	C_3H_6/C_2H_4 molar ratio in the gaseous feed	COD cm^3	C_3H_6 wt. %	Mooney $ML(1+4)$ at $100^\circ C$.
0	2.5	25	51	39
-10	2.35	34	51	47
-20	2	50	51	52.5
-30	1.65	77	55	80

the growing polymer chains and the catalytic system present in solution. The catalyst concentration does not exert an appreciable influence on the terpolymer composition.

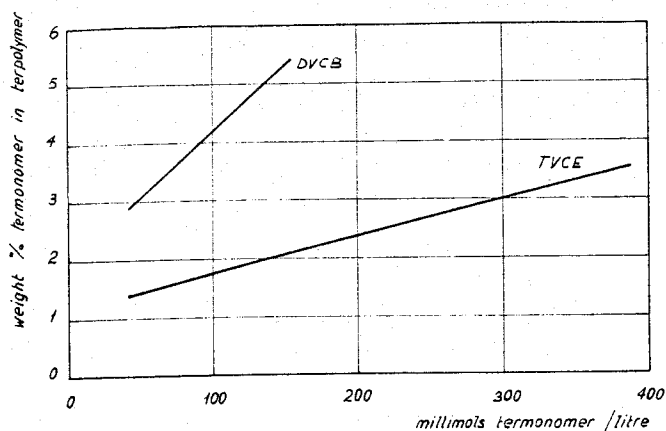


Fig. 6. Dependence of content of divinylcyclobutane and trivinylcyclohexane in terpolymer on the termonomer concentration in reacting phase.

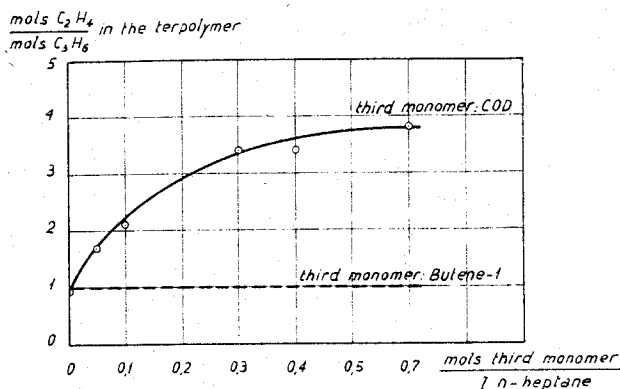


Fig. 7. Terpolymerisation of ethylene and propylene with a third monomer. Dependence of C_2H_4/C_3H_6 molar ratio in terpolymer on concentration of the third monomer in reacting phase. Solid line: ethylene-propylene-cyclo-octadiene terpolymerisation. Experimental conditions: $T = -10^\circ C$.; abs. pressure = 1 atm.; solvent, *n*-heptane; moles C_3H_6 /moles C_2H_4 in the gaseous feed = 2; $VCl_4 = 0.5$ mmole/l *n*-heptane; moles $Al(C_2H_5)_2Cl$ /moles $VCl_4 = 5$. Dotted line: ethylene-propylene-butene-1 terpolymerisation. Experimental conditions: $T = 25^\circ C$.; abs. pressure = 1 atm.; solvent, *n*-heptane; moles C_3H_6 /moles C_2H_4 in the gaseous feed = 2; $VCl_4 = 1$ mmole/l *n*-heptane; moles $Al(n-C_6H_{13})_3$ /moles $VCl_4 = 2.5$.

TABLE II

Influence of ethylene/propylene molar ratio on ethylene-propylene-cyclooctadiene terpolymerisation, in the presence of the catalytic system $Al(C_2H_5)_2Cl + VCl_4$ at $-20^\circ C$

Operating conditions		Properties of the terpolymer		
C_3H_6/C_2H_4 molar ratio in the gaseous feed	Polymerisation time min.	g	Mooney ML(1+4) at $100^\circ C$.	C_3H_6 wt. %
2	13.5	44	62.5	51
1.5	8	42	67	47
1.25	7	40	87	41.5
1	5	37	102	36

Relative Monomer Concentrations in the Reacting Phase

An increase in the ethylene/propylene molar ratio in the reacting phase causes an increase in polymerisation rate and in molecular weight.

Table II shows the dependence of the polymerisation rate and Mooney viscosity on ethylene/propylene molar ratio, in the case of the ethylene-propylene-cyclooctadiene terpolymerisation.

The concentration of the termonomer in the terpolymer increases as its concentration in the reacting phase increases. In Fig. 6 the unsaturation contents of ethylene-propylene trivinyl-cyclohexane and ethylene-propylene-trans 1-2 divinyl-cyclobutane terpolymers are plotted against the termonomer concentration in the reacting mixture.

Unlike in the terpolymerisation of ethylene and propylene with higher α -olefins (e.g. butene-1),⁽¹¹⁾ in the terpolymerisation with cyclo-octadiene, the other factors being constant (i.e. with a constant ethylene/propylene molar ratio in the reacting phase), an increase in diolefin concentration in the reacting phase causes an increase in ethylene/propylene molar ratio in the terpolymer (see Fig. 7).

Such a remarkable influence cannot be explained by the mere hypothesis that, owing to steric hindrances, addition processes leading to direct linking between two cyclo-octadiene units or one cyclo-octadiene and one propylene unit may not take place: It should be rather assumed that the phenomenon is due to an interaction (e.g. complexing) of cyclo-octadiene with the catalyst.

Properties of Uncured Terpolymers

As already reported in previous papers,^(5, 6, 12, 13, 14) the viscoelastic properties of the terpolymers are not substantially different from those of ethylene-propylene copolymers; in fact the amount of termonomer contained in these elastomers is rather low and therefore it does not practically exert any influence on the characteristics of the macromolecules.

The viscoelastic behaviour (Mooney viscosity, processability, dynamic characteristics, etc.) depends, as in the case of the copolymers, on the average molecular weight, molecular weight distribution, ethylene/propylene ratio and composition distribution.

Generally, terpolymers can be produced in a large range of compositions and of average molecular weights: the synthesis of terpolymers having a molecular weight controlled during polymerisation is generally preferred, as there is no appreciable degradation during subsequent rubber processing.

To have good processability Mooney viscosity (ML(1+4) at $100^\circ C$) of the crude terpolymer must be between 30 and 60; terpolymers with a higher Mooney viscosity (>80) are particularly suitable for oil extension. The addition of oils gives an easy processing rubber which, after vulcanisation, exhibits excellent mechanical and dynamic properties.

Recipes and Vulcanisation

Vulcanisation of these elastomers can be carried out using the double bonds present along the polymer chains. The vulcanisation systems can be based on the use of sulphur and accelerators, quinone compounds, phenol resins, and peroxides.

As these elastomers possess a limited number of double bonds, it is best to use recipes containing ultra-fast accelerators, either alone or preferably in combination with secondary accelerators. Among the ultra accelerators normally used are tetramethylthiuram mono- and disulphide, zinc diethyl dithiocarbonate, tellurium diethyl dithiocarbonate, etc.

In the recipes employed the addition of zinc oxide in normal amounts (5 parts) is very useful, whereas stearic acid is not indispensable to obtain a good vulcanisation.

The vulcanisation of these elastomers can be conveniently carried out at temperatures between 150 and $180^\circ C$; the temperature of $150^\circ C$, although not completely satisfactory from a practical point of view, has often been adopted by us for useful comparison among the vulcanisations of the different kinds of terpolymer.

Vulcanisate Properties

Unlike the low unsaturation elastomers known up to now, the terpolymers based on ethylene and propylene can undergo

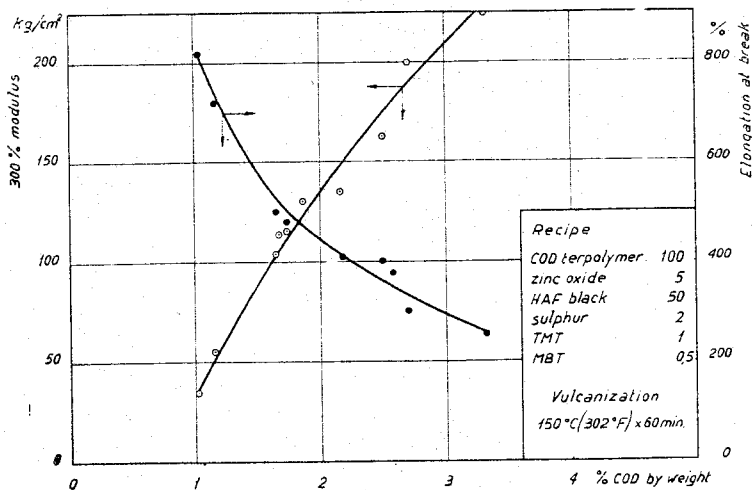
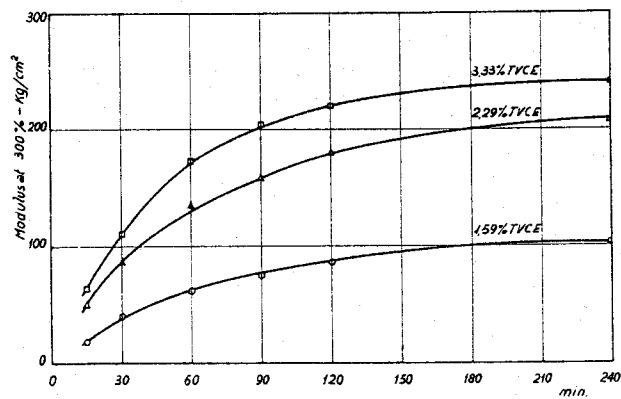
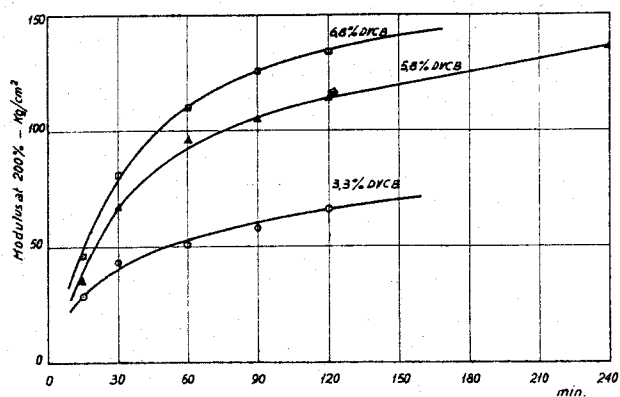


Fig. 8. Influence of cyclo-octadiene content in ethylene-propylene cyclo-octadiene terpolymers on vulcanisate properties.

Fig. 9. (below left) Modulus at 200% of vulcanisates obtained from increasingly unsaturated ethylene-propylene-divinyl-cyclobutane terpolymers as function of vulcanisation time.

Fig. 10. (below right) Modulus at 300% of vulcanisates obtained from increasingly unsaturated ethylene-propylene-trivinyl-cyclohexane terpolymers as function of vulcanisation time.



wide variations in composition, average molecular weight, amount and kind of unsaturations.

The parameters most influencing the properties of the vulcanisates are the double bond content and the average molecular weight (expressed as Mooney viscosity). The ethylene/propylene ratio does not influence the properties, at least for ethylene contents not so high as to give polyethylene-type crystallinity. The double bond content exerts considerable influence on the cross-linking degree of vulcanised products. In Fig. 8 values for 300 per cent modulus and elongation at break are reported for vulcanisates, obtained, under the same conditions, from terpolymers containing different amounts of cyclo-octadiene.

An increase in unsaturation content exerts a great influence on properties; a weight content of about 3 per cent is enough to give vulcanisates having excellent mechanical properties.

In Fig. 9 the 200 per cent modulus is plotted against the vulcanisation time at 150° for terpolymers containing different amounts of divinylcyclobutane, and in Fig. 10 the 300 per cent modulus for terpolymers containing different amounts of trivinylcyclohexane is reported.

The marked influence of the unsaturation content on the properties of the end product and the high values of the moduli, even for comparatively low unsaturation contents, can be seen.

The average molecular weight is another factor exerting a strong influence on the properties of the vulcanisates.

Previous papers (5, 6, 12, 13, 14) have shown the influence of Mooney viscosity of the base elastomer on the properties of vulcanisates in the case of cyclo-octadiene containing terpolymers. The same influence is exerted in the case of other types of terpolymer: in Fig. 11 the values for 200 per cent modulus are plotted against vulcanisation time for terpolymers of different Mooney viscosity containing approximately the same amount of divinylcyclobutane.

The terpolymers having a high Mooney viscosity (> 80) are very interesting from a commercial point of view, owing

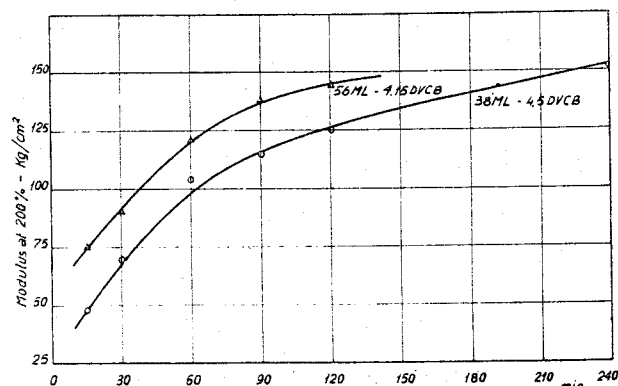


Fig. 11. Influence of Mooney viscosity on modulus at 200% of vulcanisates obtained from ethylene-propylene-divinylcyclobutane terpolymers.

to the possibility of extension with remarkable amounts of oils. These elastomers are compatible with oils of different kinds, which can be added in great amounts without affecting considerably the properties of the products.

The influence of the amount and kind of oil on the properties of the vulcanisates has already been described (5, 6, 7, 15, 16, 17, 18, 19). Amounts of oil as high as 100 per cent with respect to the terpolymer can be added, and yet the mechanical properties of the vulcanisates are satisfactory.

Vulcanisation Rate

It is interesting to compare terpolymers containing different kinds of monomers from the point of view of vulcanisation rate. As an index of vulcanisation rate we can assume the time necessary to reach the vulcanisation maximum; the cross-linking degree is usually measured through the values for moduli (at 200 per cent or 300 per cent) of the vulcanisate.

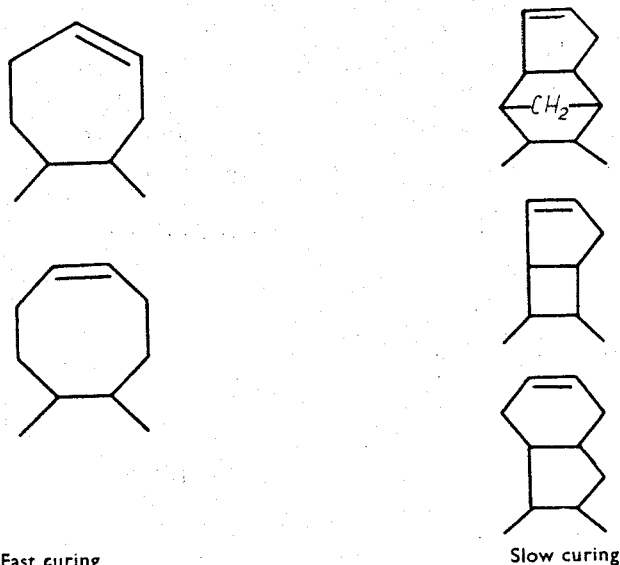


Fig. 12. Fast and slow curing termonomer units.

As already reported in previous papers,^(5, 6, 7, 20) the vulcanisation rate is different for the different kinds of terpolymers, depending on the nature of the termonomer, recipe and vulcanisation conditions being constant.

If the maximum value for the modulus is assumed equal to 100 and if, on this basis, the values for modulus for different vulcanisation times are calculated, a curve showing the vulcanisation rate is obtained, independent of the absolute values for modulus.

We can thus compare vulcanisation rates of different kinds of termonomers. In the case of cyclic termonomers we have noticed that ring size exerts a remarkable influence on the vulcanisation rate. In previous papers^(5, 6, 20) fast curing ethylene-propylene-cyclo-octadiene terpolymers had been compared with slow curing ethylene-propylene-dicyclopentadiene terpolymers.

In general it can be said that if the double bond is contained in a seven- or eight-membered ring, the terpolymer is fast curing, whereas it is slow curing if the double bond is in a five- or six-membered ring. In Fig. 12 some examples of the two kinds of monomer units are shown. The different ring tensions could be responsible for this difference in vulcanisation behaviour. In Fig. 13 the vulcanisation rates of terpolymers containing different kinds of cyclic termonomers are compared.

If the residual double bond is contained in an aliphatic chain its position has a remarkable influence on the vulcanisation rate. The internal double bond of a hexadiene 1-4 monomer unit is faster curing than the terminal double bond of a hexadiene 1-5 monomer unit. In Fig. 14 the vulcanisation rates of two terpolymers containing the two hexadienes are compared.

Vulcanisation rate is affected by the recipe and conditions but, in general, variations are such that it is possible to maintain, at least qualitatively, the above-mentioned differences between the different kinds of terpolymers.

Vulcanisation Study

The possibility of introducing in the ethylene-propylene copolymer chain different types of monomer units containing residual double bonds, for use in the cross-linking reaction, opens new possibilities in the study of the phenomena that occur during vulcanisation. As the double bond content of these elastomers is never higher than 3-5 mole per cent, vulcanisation is generally carried out with an excess of vulcanising agents; in this way, the cross-linking rate depends on the amount and kind of unsaturations and on the substance employed as vulcanising agent.

In Fig. 15, 300 per cent moduli are plotted against vulcanisation time at different temperatures for an ethylene-propylene-cyclo-octadiene terpolymer containing only sulphur as vulcanising agent in a black compound. In Fig. 16 corresponding curves are shown for the same terpolymer containing only tetramethylthiuram-disulphide as vulcanising agent in a black compound.

The theoretical curves derive from equations reported in a previous paper⁽²¹⁾ and based on the above-mentioned hypotheses.

Regardless of the absolute values for moduli in the two cases, we can see the different shape of the vulcanisation curves in the two figures and the different dependence of the vulcanisation rate on temperature. Similar curves have been

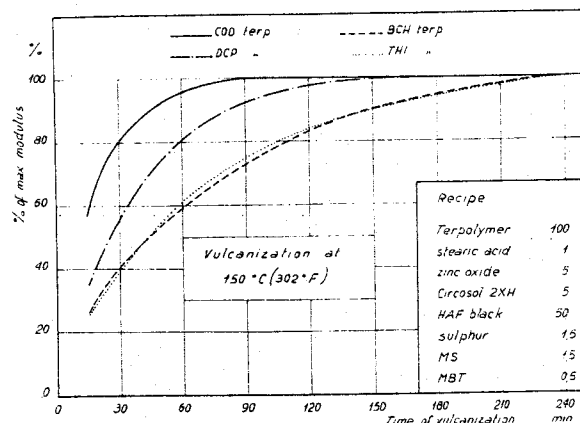


Fig. 13. Comparison between vulcanisation rates at 150°C. of ethylene-propylene terpolymers containing different kinds of cyclic termonomers. 1-5 cyclooctadiene (COD) terpolymer ———; dicyclopentadiene (DCP) terpolymer — · — ·; 4,7,8,9 tetrahydroindene (THI) terpolymer ·······; bicyclo [3,2,0] heptadiene 2-6 (BCH) terpolymer - - - -.

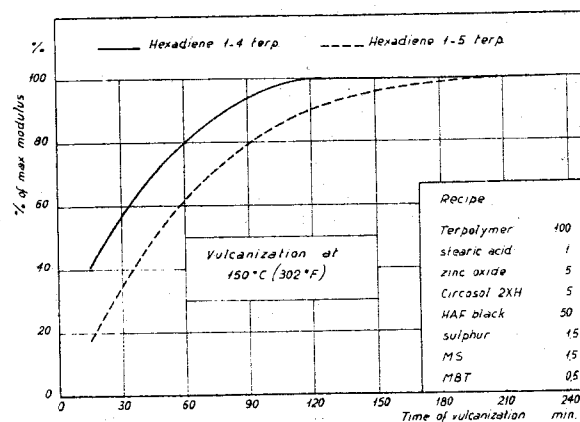


Fig. 14. Comparison between vulcanisation rates at 150°C. of ethylene-propylene-hexadiene 1-4 and ethylene-propylene-hexadiene 1-5 terpolymers. Solid line: hexadiene 1-4 terpolymer; dotted line: hexadiene 1-5 terpolymer.

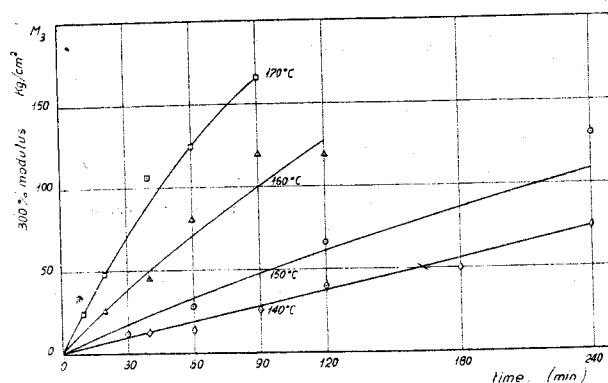


Fig. 15. Vulcanisation rate at different temperatures of ethylene-propylene-cyclo-octadiene terpolymer. Vulcanising agent: sulphur.

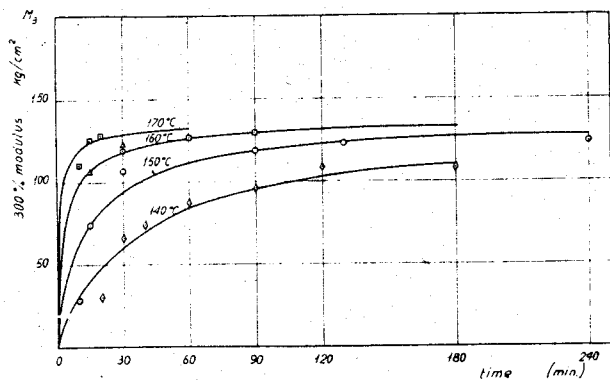


Fig. 16. Vulcanisation rate at different temperatures of ethylene-propylene-cyclooctadiene terpolymer. Vulcanising agent: tetramethylthiuramdisulphide.

determined for other terpolymers having different kinds of unsaturated monomer units and for other vulcanisation systems. The possibility of studying the vulcanisation reaction with different terpolymers enables us to establish the influence of different parameters (e.g. position of the double bond, kind and amount of the substituents etc.) on this reaction and to examine the most suitable monomers for the production of these elastomers.

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DISCUSSION

Dr. L. S. Citarel, Thiokol Chemical Corp.

Q.—Because EPT contains pendant double bonds which can be vulcanised either by sulphur or peroxide cure systems, would you comment on the difference in physical properties obtained from the use of each cure system, especially with regard to heat age performance?

A.—In mechanical properties we do not see any relevant difference between the two systems, except that compression set in the peroxide cure always gave lower compression set than the sulphur cure.

Q.—Are the tensile strengths as high with peroxide?

A.—The tensile strengths are somewhat lower but quite satisfactory.

Q.—In automobile tyres one of the major problems with the processing of EPT is the development of tack or self-adhesion. Has there been any progress in this area recently?

A.—I would say it is still one of the big problems.

H. Weber, Chemische Werke Hüls AG

Q.—Have you any explanation why ring size has such a big influence on cure rate?

A.—We are now investigating vulcanisation phenomena and I said in my paper that not only the ring size has an influence but also the position of the double bond and the substituents that you have at the double bond. We think that the 5 and 6 membered reacts with sulphur more easily, but the vulcanisation rate is a compromise between vulcanisation and reversion. So perhaps the vulcanisation reaction is very fast and the reversion reaction very slow.

J. C. Soeterbroek, Staatsmijnen

Q.—You talked about the difference in behaviours during terpolymerisation with cyclo-octadiene and butene 1. Do you know what kind of complex is formed between cyclo-octadiene and the catalyst during terpolymerisation?

A.—We only know that by using cyclo-octadiene to give an unsaturation content of about 2 or 3 per cent of the polymer, there is an interaction between monomer and catalyst, but we do not know what kind of complex is formed.

Marshall Sittig (Princeton)

Q.—Have you any indications of the behaviour of cyclo-dodecatriene or other C₁₂ chains?

A.—If I remember correctly it hardly copolymerises with ethylene and propylene.