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Properties of Ethylene–Propylene Copolymers and of Terpolymers Containing Unsaturation*

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Introduction

In previous papers we described the preparation of linear amorphous high molecular weight copolymers of ethylene with α-olefins by means of anionic coordinated polymerization processes[1] as well as the properties of these copolymers as related to their composition and molecular weight;[2] these products are suitable for obtaining vulcanized rubbers with good mechanical properties and aging resistance.[3]

The class of amorphous copolymers of ethylene with other olefin hydrocarbons now includes a new category of products, namely that of copolymers of ethylene with olefins having an internal double bond. The products obtainable with the aid of catalysts, which do not homopolymerize the olefins with an internal double bond, may have a composition ranging from 50 to 100 mole-% of ethylene.

The polymers having a higher content of monomeric units of such olefins, obtained with the aid of stereospecific catalysts, are crystalline and have the highest crystallinity when their composition is similar or equal to that of the alternating copolymer. For instance, in the case of the ethylene–butene-2 copolymer, crystalline alternating copolymers with a *threo*-diisotactic structure have been so obtained.

In the presence of nonstereospecific catalysts or by increasing the ethylene content amorphous copolymers with elastomeric properties have been obtained.

The slower polymerization rate of the olefins with an internal double bond, in particular of those having a *trans* configuration, makes one foresee a lesser practical interest of these copolymers (with the exception of a few very particular cases) with respect to the ethylene–α-olefin copolymers. Therefore we will examine only these latter ones.

Obtaining of ethylene–α-olefin copolymers with good elastomeric properties is closely related to homogeneity of composition; in fact, the presence of macromolecules with a too high ethylene content may cause a partial crystallization, which exerts a negative influence on the quality of the elastomer, whereas the macromolecules with a high propylene content yield

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vulcanizates having poorer mechanical and elastic properties. Moreover the two comonomers must be distributed in such a way that most approaches the statistical distribution along the chain, which can be considered as deriving from the polyethylene chain in which a part of the hydrogen atoms is statistically substituted by alkyl groups.

The ethylene–propylene copolymers can be transformed into vulcanizates by two different methods: (*1*) by means of vulcanizing agents able to crosslink the saturated polymers (e.g. with suitable organic peroxides); (*2*) by introducing along the chain reactive groups able to give rise to the formation of crosslinks in the presence of the vulcanizing agents usually employed for the unsaturated rubbers.

With regard to this latter type of vulcanization, various methods have been studied in order to introduce double bonds into the macromolecules by modifying the chain of the ethylene–α-olefin copolymers (e.g. by partial chlorination and dehydrochlorination of the chain itself),[4] or else by introducing the double bonds directly in the synthesis of copolymers.[5] This has been carried out, for instance, with the production of terpolymers obtained with the use of a third monomer containing more than one double bond and able to polymerize with formation of monomeric units containing at least one unsaturated double bond.

Thus, it is not enough to have copolymers containing double bonds, but, in order to obtain good vulcanizates, it is necessary to adopt particular conditions of synthesis so that the third monomer containing more than one double bond is distributed homogeneously along all the macromolecules.

In this case the vulcanizates obtained from terpolymers have mechanical and elastic properties which are similar to those of the saturated copolymers vulcanized with organic peroxides.

Some data on the ethylene–propylene copolymers, with regard to their processability and to the properties of the vulcanizates will be reported in this paper, as well as the characteristics of terpolymers mainly consisting of ethylene and propylene as they are related to the degree of unsaturation and the homogeneity of composition.

Effect of Molecular Weight and Molecular Weight Distribution

As is known, it is particularly important in the use of the different synthetic rubbers to have a starting polymer with a suitable molecular weight; also the distribution of the molecular weight around their average value exerts a marked influence on the typical properties of the elastomer. In fact, from the point of view of vulcanization and of the properties of vulcanizates, it is better to have high molecular weight polymers. With these, it is possible to carry out the vulcanization with very low amount of vulcanizing agents, and vulcanizates with good mechanical and dynamic properties are obtained. On the contrary, the low molecular weight polymers require higher amounts of vulcanizing agents and yield vulcanizates with poor mechanical properties and especially poor dynamic properties.

On the other hand, the low molecular weight products are particularly advantageous with regard to processability (mixing, compounding, extrusion, etc.) of the elastomer.

In order to meet all the requisites of the processability and of vulcanization, an elastomer must consist of macromolecules all having about the same average molecular weight; therefore it is necessary to have a narrow distribution of the molecular weights, so that both the very high and the very low ones are absent. This result can be approached in natural rubber with a suitable mastication of the starting product, whereas with synthetic rubbers (which are less subject to degradation in the mixer) it is necessary to regulate the molecular weight in the synthesis.

Also the ethylene–propylene copolymers do not break down appreciably during the mixing; it is therefore necessary to vary the polymerization conditions in such a way as to obtain copolymers with a not too high average molecular weight which can be processed easily.

Polymers with a controlled average molecular weight are usually obtained by means of regulating agents (e.g., H_2 or other chain transfer agents), which act statistically on the growing chains, thus giving rise to the stoppage of the growth of the macromolecules. In this case, however, the polymers obtained have a wider distribution of the molecular weights, some low molecular weight polymer and a certain amount of high molecular weight material being present at the same time. The ethylene–propylene copolymers with a controlled molecular weight thus possess good processability properties and yield vulcanizates with satisfactory mechanical properties.

Even better results, from the point of view of processability, can be ob-

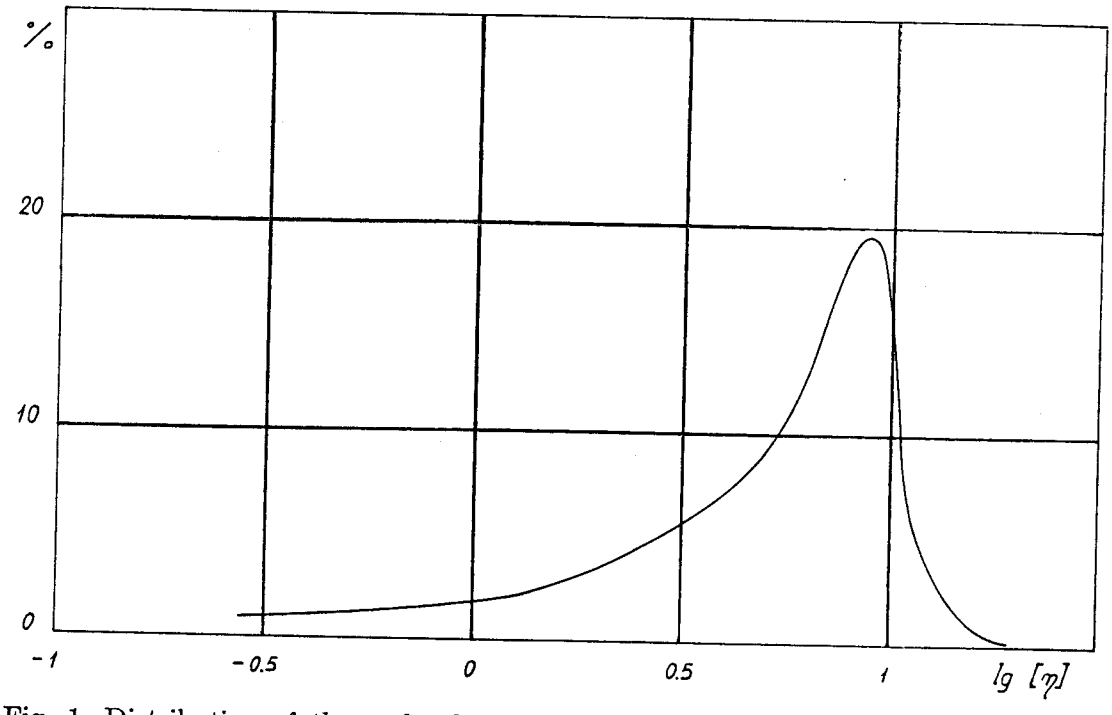

Fig. 1. Distribution of the molecular weights of a high molecular weight ethylene–propylene copolymer. Intrinsic viscosity $[\eta]$ in toluene at 30°C.

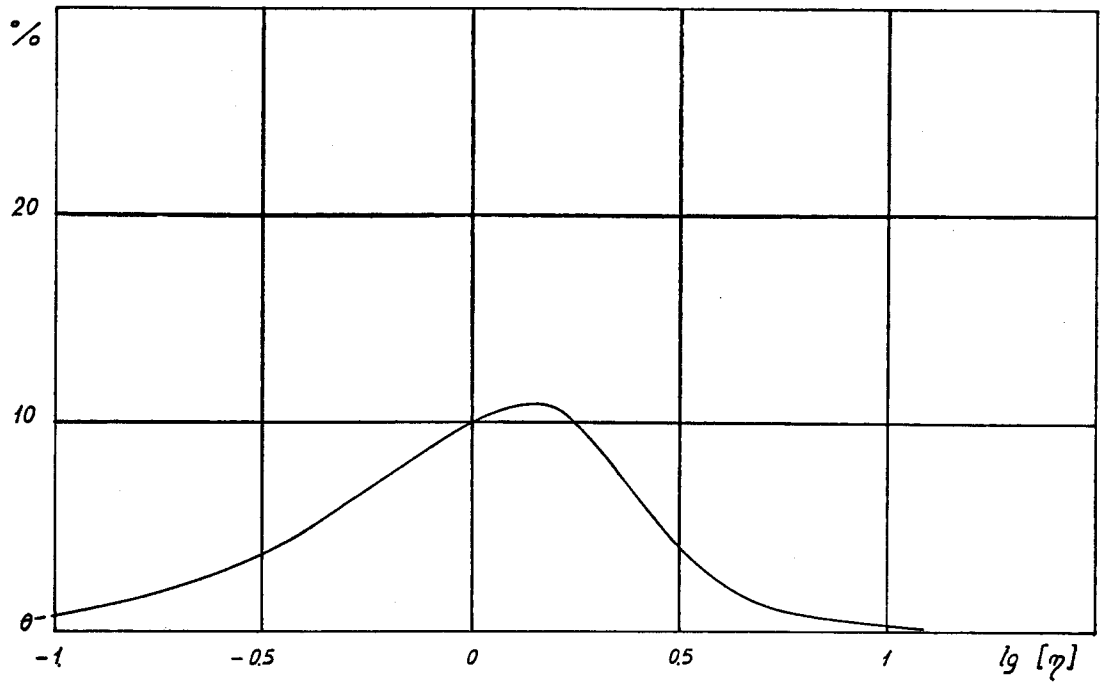

Fig. 2. Distribution of the molecular weights of an ethylene–propylene copolymer having molecular weight controlled with chain transfer agents. Intrinsic viscosity [η] in toluene at 30°C.

tained by thermal degradation (at temperatures above 250°C.) of the high molecular weight ethylene–propylene copolymers. In this way, a degradation of the high molecular weight material occurs, without an especially marked increase of the very low molecular weight fractions. Figure 1 shows the curve of distribution of the molecular weights of an average high molecular weight ethylene–propylene copolymer. This copolymer has a very poor processability, whereas the vulcanizates show excellent mechanical and dynamic properties. If a regulating agent of the molecular weights is employed in the same polymerization systems, a copolymer with the distribution of molecular weights indicated in Figure 2 is obtained. In this case, the processability is improved, whereas the properties of the vulcanizate have sufficiently good values (Table I).

TABLE I

Characteristics of Vulcanizates Obtained from Ethylene–Propylene Copolymers (Dutral N) having Mooney Viscosity of 40–50 (ML 1 + 4 at 100°C.)[a]

Tensile strength, kg./cm.^{2}	180–200
Elongation at break, %	350–450
100% Modulus, kg./cm.^{2}	16–20
300% Modulus, kg./cm.^{2}	120–135
Tear strength, kg./cm.^{2}	40–50
Tension set, %	6–7
Hardness, IRHD	57–62

[a] Recipe: Dutral N, 100.0 parts; HAF black, 50.0 parts; sulfur, 0.30 parts; dicumyl peroxide, 2.6 parts; vulcanization at 165°C. for 30 min.

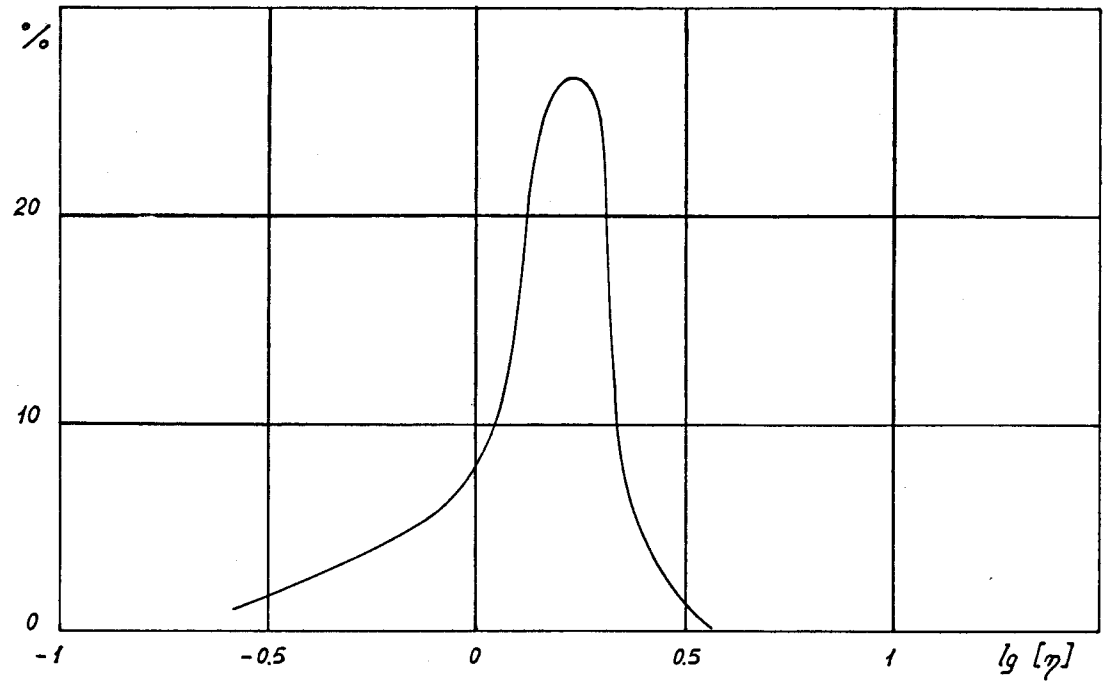

Fig. 3. Distribution of the molecular weights of an ethylene–propylene copolymer obtained by degradation of the copolymer given in Figure 1. Intrinsic viscosity [η] in toluene at 30°C.

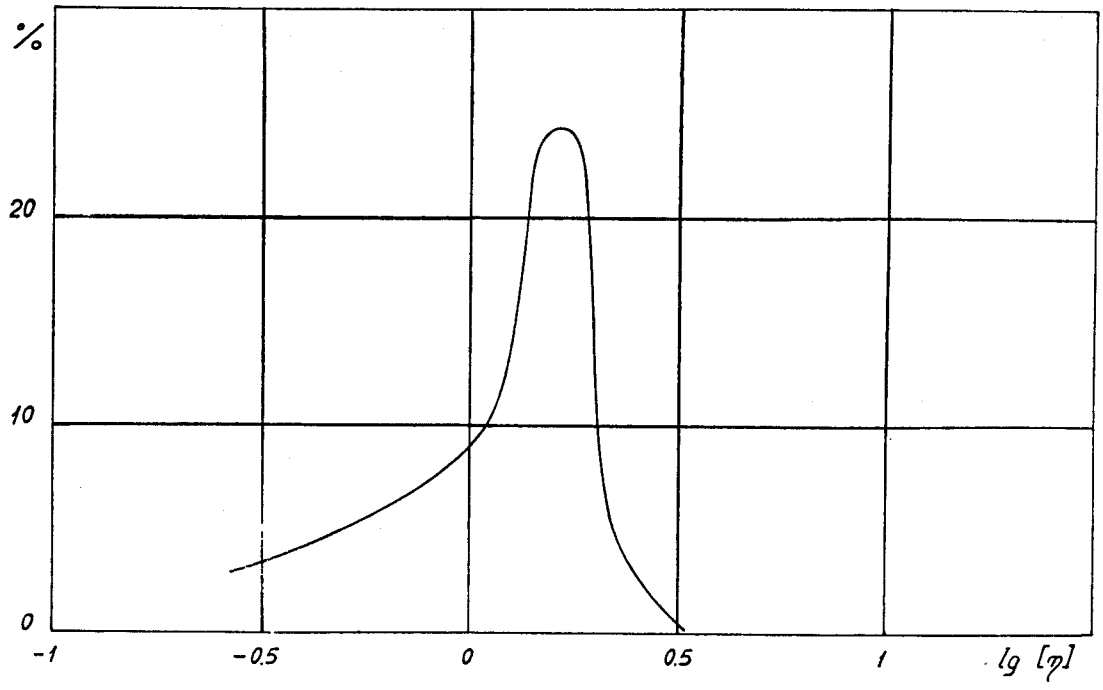

Fig. 4. Distribution of the molecular weights of an ethylene–propylene copolymer as obtained directly in synthesis. Intrinsic viscosity [η] in toluene at 30°C.

By thermal degradation in an inert atmosphere (at temperatures of 280°C. for 6 hr.) of the copolymer of Figure 1, a product was obtained whose curve of distribution of molecular weights is reported in Figure 3. As is seen in this Figure, there is a more narrow distribution of the molecular weights; in addition, it can be observed that the high molecular weight ma-

terials, which have a negative influence on the processability, are almost completely absent. The copolymer can be very well processed; with regard to the properties of the vulcanizate, only a slight worsening of the dynamic properties occurs.

By operating with suitable catalytic systems directly in the synthesis, ethylene–propylene copolymers, called Dutral P, have been obtained by Montecatini. Their molecular weight distribution curve is similar to that shown in Figure 3. The characteristic curve of the copolymers obtained in this way is shown in Figure 4; it is thus clear that this curve is very similar to that reported in Fig. 3, as it differs only for the slightly higher content of the low molecular weight fractions. However, also in this case, the very high molecular weight polymers are absent. The ethylene–propylene copolymers obtained with the aid of these catalytic systems have an excellent processability on the mixer, can be easily extruded with sharp and smooth surface, and have a sufficient tack for the shaping of composite articles. The mechanical properties of the vulcanizate are satisfactory (Table II), but the dynamic properties are not very good. Probably the content of very low molecular weight fractions in these copolymers is rather high, and viscous components due to noneffective crosslinks, are present in the three-dimensional network.

TABLE II
Characteristics of Vulcanizates Obtained from Ethylene–Propylene Copolymers (Dutral P) Having Mooney Viscosity of 20–30 (ML 1 + 4 at 100°C.)[a]

Tensile strength, kg./cm.^{2}	170–180
Elongation at break, %	350–400
100% Modulus, kg./cm.^{2}	20–22
300% Modulus, kg./cm.^{2}	125–140
Tear strength, kg./cm.^{2}	50–60
Tension set, %	7–8
Hardness, IRHD	60–65

[a] Recipe: Dutral P, 100.0 parts; HAF black, 50.0 parts; sulfur, 0.4 parts; dicumyl peroxide, 3.3 parts; vulcanization at 165°C. for 30 min.

Homogeneity Problems of Terpolymers

When considering terpolymers, consisting predominantly of ethylene and propylene and small amounts of monomer containing more than one double bond, it is clear that in this case it is necessary to satisfy various conditions in order to obtain an elastomer of good properties. First of all, the conditions previously described for the ethylene–propylene copolymers must be met: (*1*) homogeneity of composition; (*2*) statistical distribution of the two olefin monomers along each macromolecule; (*3*) not too high average molecular weight; (*4*) a sufficiently narrow distribution of the molecular weights.

To these must be added the conditions of the regularity of distribution of the third monomer, which can be summarized as follows: (*5*) a statistical

distribution in each chain of the monomer containing more than one double bond; (*6*) all the macromolecules forming the raw product must contain about the same number of double bonds per 100 monomeric units.

When all the above conditions are satisfied, a terpolymer can be obtained which, when vulcanized with recipes based on sulfur and accelerating agents, has the same mechanical and dynamic properties as the ethylene–propylene copolymers vulcanized by means of organic peroxides. Various diolefinic compounds, such as aliphatic, nonconjugated diolefins and *endo*-methylenic compounds, have been proposed for use as monomers containing more than one double bond in this synthesis; each diolefin generally requires a suitable choice of the catalyst and of the polymerization conditions.

Under suitable polymerization conditions, it was possible to obtain with certain monomers crude terpolymers containing about the same content of double bonds in all the fractions, regardless of their different molecular weights. Table III shows the double bond content per 100 monomeric units in the various fractions of a terpolymer, which has a content, determined on the total polymer, of 3.8 double bonds per 100 monomeric units.

TABLE III
Double Bond Content of Various Fractions of a Terpolymer Having a Total Content of 3.8 Double Bonds per 100 Monomeric Units

Fraction number	% of total terpolymer	Double bond content per 100 monomeric units
1	12.7	3.75
2	20.8	3.85
3	29.5	3.85
4	37.7	3.80
5	46.4	3.80
6	58.5	3.85
7	65.0	3.70
8	70.0	3.60
9	76.0	3.70
10	82.6	3.85
11	91.5	3.70
12	99.5	3.80

As can be observed, the various fractions contain practically the same number of double bonds, the reported variations being within the limits of the experimental error. The properties of the vulcanizates obtained from these terpolymers are shown in Figure 5, for different types with a different degree of unsaturation and Mooney viscosity (ML 1 + 4 at 100°C.) ranging from 20 to 30. The crosslinking degree regularly increases with the unsaturation degree. Vulcanizates with good properties have been obtained also from terpolymers, containing 1–1.5 double bonds per 100 monomeric units, in which the above-mentioned conditions are satisfied.

The same considerations as those stated for the ethylene–propylene copolymers are valid also with regard to the processability of these terpoly-

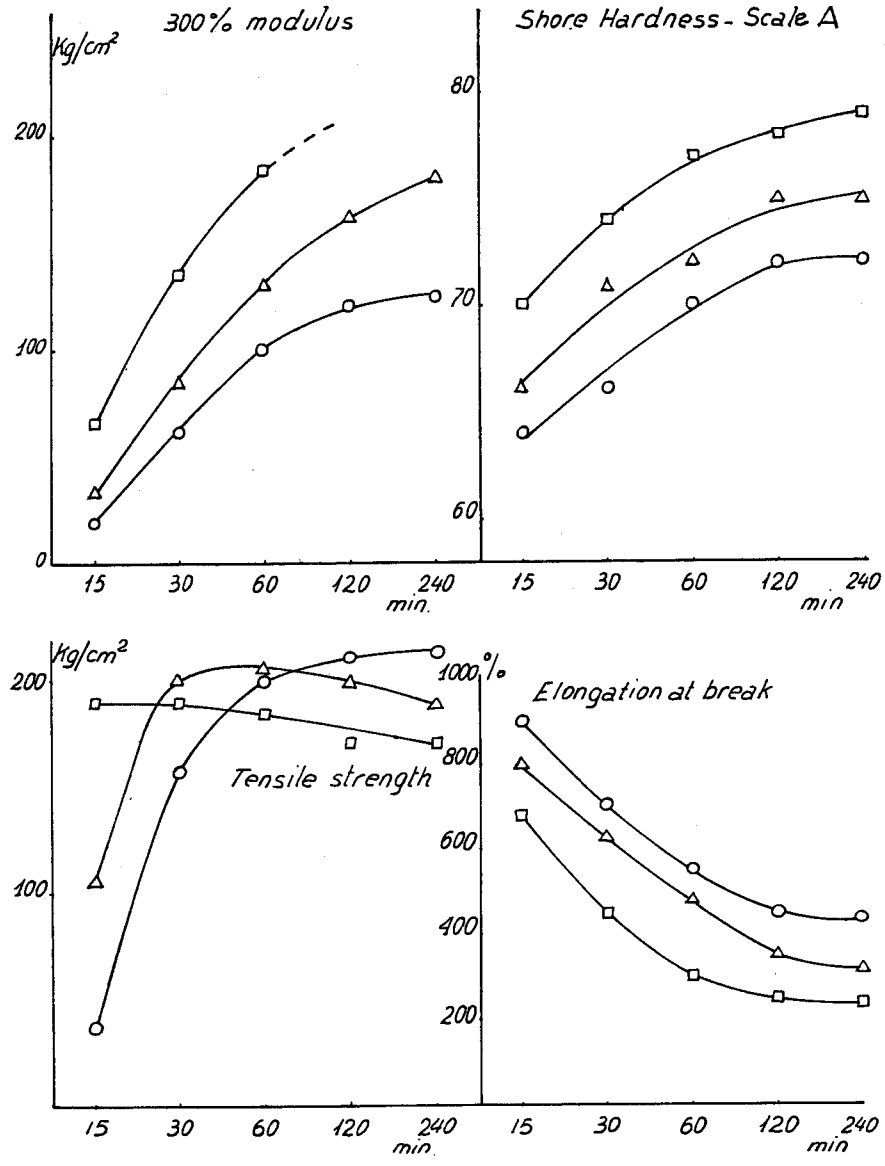

Fig. 5. Characteristics of vulcanizates versus vulcanization time (at 150°C.) for different copolymers: (O) unsaturation 1,4%; (△) unsaturation 2,2%; (□) unsaturation 2,7%.

mers. In fact, in this case also, it is preferable to have rubbers with a narrow molecular weight distribution, particularly if high molecular weight fractions are absent. This result can be directly achieved in the synthesis by operating under suitable polymerization conditions, in order to obtain not only the regulation of the molecular weight, but also a homogeneous composition both with regard to the ethylene–propylene ratio and to the double bond content in the various fractions. Figure 6 shows the distribution curve of the molecular weights of a terpolymer which meets the above-mentioned requisites and which contains 1.7 double bonds per 100 monomeric units, whereas Table IV shows the ethylene content and the double bond content in the various fractions. As it can be observed from Figure 6 and Table IV, the terpolymers obtained under these conditions, show a rather narrow distribution of the molecular weights and an excellent homogeneity of composi-

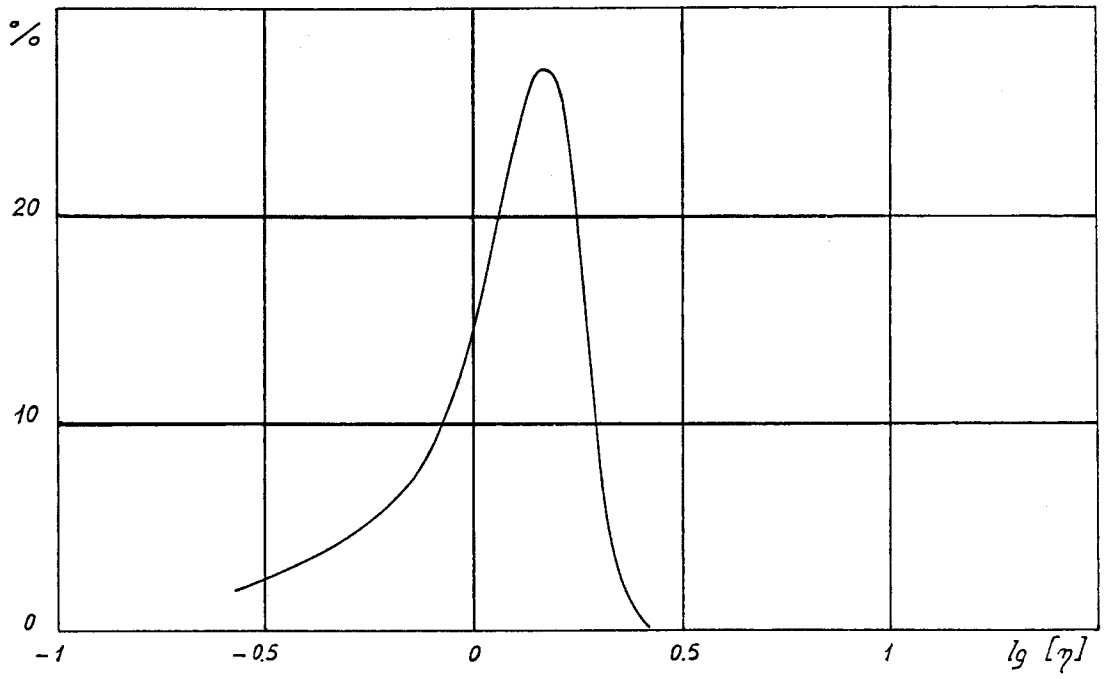

Fig. 6. Distribution of the molecular weights of a terpolymer. Intrinsic viscosity [η] in toluene at 30°C.

tion. The processability of these elastomers is very good, while the mechanical properties of the vulcanizate are, on the whole, satisfactory.

It is sometimes difficult to obtain a good homogeneity of composition with some types of monomers containing more than one double bond. These terpolymers generally show poorer properties after vulcanization. The presence in the raw terpolymer of a limited percentage (of the order of 5–10%) of ethylene–propylene copolymer free from unsaturation, exerts a negative influence on the properties of the vulcanizate. In this case, in

TABLE IV

Composition of Various Fractions of a Terpolymer Having a Total Content of 1.7 Double Bonds per 100 Monomeric Units and of 63 Mole-% of Ethylene

Fraction number	% of total terpolymer	C_2, mole-%	Double bond content per 100 monomeric units
1	13.8	64.0	1.68
2	21.6	64.0	1.68
3	28.0	64.0	1.68
4	33.0	64.0	1.68
5	42.7	64.0	1.65
6	51.7	64.0	1.65
7	61.5	64.0	1.65
8	68.0	63.0	1.72
9	73.5	63.0	1.72
10	81.0	63.0	1.72
11	86.0	61.5	1.67
12	91.5	59.0	1.78
13	98.5	60.5	1.70

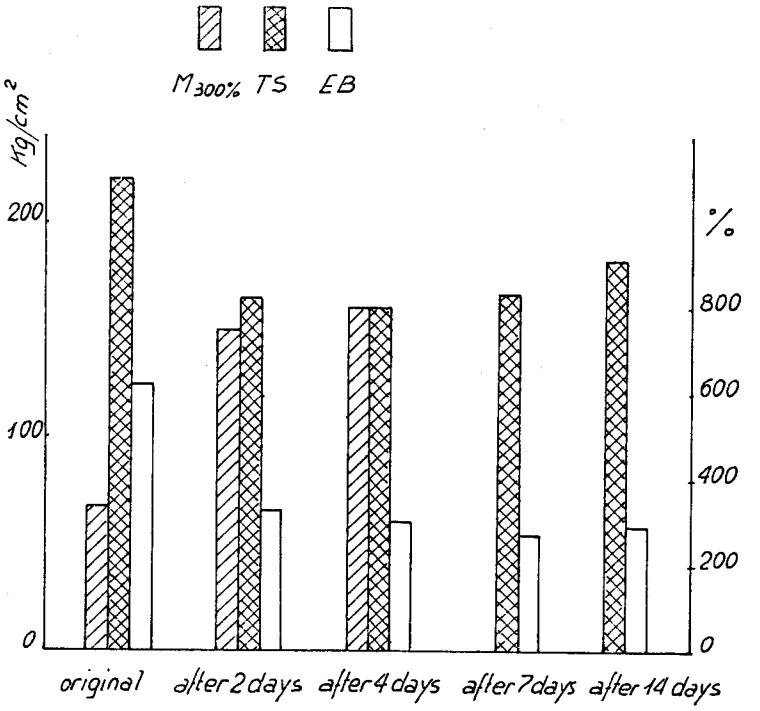

Fig. 7. 300% Modulus ($M_{300\%}$), tensile strength (TS) and elongation at break (EB) of vulcanized terpolymer after aging at 125°C.

order to obtain low tension set in the vulcanizate, it is necessary to crosslink the terpolymer considerably, thus obtaining fairly high moduli and hardness values with respect to those usually obtained with the ethylene–propylene copolymers or with the terpolymers with a good homogeneity of composition.

It is interesting to point out that the presence of double bonds along the chains of the ethylene–propylene copolymers does not exert a negative influence on the excellent aging resistance which is typical of the saturated copolymers.

Figure 7 shows the results after aging at 125°C. in a circulating air oven of a terpolymer with an initial Mooney viscosity (ML 1 + 4 at 100°C.) of 30 and an unsaturation content of 1.85%. From these data and from the data published on the saturated polymers,[3] it can be observed that also in the terpolymers, the good aging resistance which is characteristic of the ethylene–propylene copolymers is kept practically unaltered.

Conclusion

The random distribution of a certain percentage (1–3%) of unsaturated monomeric units, in the ethylene–α-olefin copolymers obtained by copolymerizing ethylene with an α-olefin and suitable diolefin monomers under particular polymerization conditions gives elastomers which can be vulcanized by the traditional methods known for low-unsaturation rubbers; the vulcanized products with good mechanical and dynamic properties, keep practically unchanged the excellent aging resistance properties of the saturated ethylene–α–olefin copolymers.

A narrow distribution of molecular weights was obtained in the polymerization, and this appeared to be necessary in order to obtain good properties of the vulcanizates, whereas a not too high average molecular weight (values of Mooney viscosity ranging from 20 to 40) is useful in order to have a good processability. Examples of copolymers corresponding to these requisites and their properties have been reported.

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Synopsis

The elastomeric properties of amorphous ethylene–α-olefin copolymers have been described in previous papers, as well as the importance of both the homogeneity of composition of each macromolecule forming the raw polymer and the statistical distribution of the two comonomers. It has been observed that a narrow distribution of the molecular weights is very important with regard to the mechanical properties of the cured synthetic rubbers obtained from the ethylene–propylene copolymers, whereas a not too high average molecular weight is important as far as the processability is concerned. One of the most interesting properties of the ethylene–propylene copolymers is their good aging resistance which is due to the saturated nature of the polymeric macromolecules. It has been observed that these properties are substantially shown also by those terpolymers consisting predominantly of ethylene and propylene (or other α-olefins), and in addition a small amount of a monomer whose molecule contains more than one double bond; on polymerization these last monomers yield monomeric units still containing a double bond. A great number of monomers are well suited for the production of terpolymers with a low degree of unsaturation, which is sufficient for the conventional vulcanization methods adopted for other rubbers, particularly for those containing a low degree of unsaturation. It is quite essential, in order to obtain good vulcanizable products, that the unsaturation is regularly distributed in all the macromolecules, and that in each of these they are distributed at random. Probably, the differences observed with various monomers depend primarily on the ability of each monomer and of the copolymerization system adopted to meet to these requirements. This is the reason why we shall discuss the properties of those products in which a considerable homogeneity of distribution has been achieved. The mechanical and dynamic properties will be related to the degree of unsaturation. The results obtained from the use of such terpolymers for the production of elastomers have demonstrated that the elastic, dynamic, and aging properties remain essentially the same as those for the ethylene–propylene copolymers when the degree of unsaturation does not exceed 2–3%, expressed as number of double bonds per hundred monomeric units.

Résumé

Dans des publications précédentes, on a décrit les propriétés élastomères de copolymères amorphes d'éthylène avec une α-oléfine, ainsi que l'importance de l'homogénéité et de la composition de chaque macromolécule formant le polymère brut, et de la distribution statistique des deux monomères. On a observé qu'une distribution étroite des poids moléculaires est très importante pour les propriétés physiques des caoutchoucs synthétiques traités, obtenus à partir des copolymères éthylène–propylène. D'autre part il est très important que le poids moléculaire ne soit pas trop haut dans le mesure où il s'agit de la possibilité du "processing." La bonne résistance au vieillissement, due à la nature saturée des macromolécules, est une des propriétés les plus intéressantes des copolymères éthylène–propylène. On a observé que ces propriétés se manisfestent aussi dans le cas de polymères ternaires qui contiennent en majeure partie de l'éthylène et du propylène (ou d'autres α-oléfines) et en outre de faibles quantités d'un monomère dont la molécule a plus d'une double liaison. Ces derniers monomères donnent dans la polymérisation des unités contenant encore une double liaison. Un grand nombre de monomères sont aptes à la production de polymères ternaires avec faible degré d'insaturation, celui-ci étant suffisamment élevé pour les méthodes conventionnelles de vulcanisation, employées pour les autres caoutchoucs, notamment ceux qui ont un faible degré d'insaturation. Pour obtenir des produits pouvant être facilement vulcanisés, il est essentiel que l'insaturation soit distribuée régulièrement sur toutes les macromolécules, et dans chacune d'une façon statistique. Il est possible que les différences observées pour les différents monomères dépendent en premier lieu de l'aptitude de chaque monomère et de chaque système de copolymérisation à satisfaire à ces exigences. C'est pour cette raison que nous allons discuter les propriétés des produits dans lesquels on a obtenu une homogénéité de distribution considérable. Les propriétés mécaniques et dynamiques sont reliées au degré d'insaturation. Les résultats obtenus par l'emploi de ces copolymères ternaires, pour la production d'élastomères, ont démontré que les propriétés élastiques, dynamiques et la résistance au vieillissement restent les mêmes que celles des copolymères éthylène–propylène pour autant que le degré d'insaturation ne dépasse pas 2 à 3 %. Ce pourcentage indique le nombre de double soudures par cent unités monomériques.

Zusammenfassung

Die elastischen Eigenschaften amorpher Äthylen-α-Olefincopolymerer sowie die Bedeutung der Zusammensetzungshomogenität der einzelnen Makromoleküle im Rohpolymeren und der statistischen Verteilung der beiden Comonomeren wurden in früheren Arbeiten beschrieben. Es zeigte sich, dass eine enge Molekulargewichtsverteilung für die mechanischen Eigenschaften der aus den Äthylen-Propylencopolymeren erhaltenen Vulkanisaten ausschlaggebend ist, während für die Verarbeitbarkeit ein nicht zu hohes mittleres Molekulargewicht wichtig ist. Eine der interessantesten Eigenschaften der Äthylen-Propylencopolymeren bildet ihre gute Alterungsbeständigkeit, die in der gesättigten Natur der Polymermoleküle begründet ist. Diese Eigenschaft besitzen im wesentlichen auch solche Terpolymere, die vorwiegend aus Äthylen und Propylen (oder anderen α-Olefinen) bestehen und zusätzlich kleine Mengen eines Monomeren mit mehr als einer Doppelbindung enthalten. Bei der Polymerisation liefern diese Monomeren Einheiten, die noch eine Doppelbindung enthalten. Eine gross Zahl Monomerer ist zur Erzeugung von Terpolymeren mit einem geringen, für die konventionellen Vulkanisationsmethoden ausreichenden Grad an Ungesättigtheit geeignet. Es kommen vor allem Methoden in Frage, die für Kautschuke mit geringem Grad an Ungesättigtheit ausgearbeitet wurden. Zur Erreichung gut vulkanisierbarer Produkte ist es ganz wesentlich, dass die Ungesättigtheit über alle Makromoleküle gleichförmig und in edem einzelnen Makromolekül statistisch verteilt ist. Wahrscheinlich sind die bei verschiedenen Monomeren beobachteten Unterschiede primär durch die Fähigkeit eines Monomeren und eines gewählten Copolymerisationssystems,

diesen Erfordernissen zu entsprechen, bedingt. Aus diesem Grund wird über die Eigenschaften solcher Produkte berichtet, bei denen eine beträchtliche Verteilungshomogenität erreicht wurde. Die mechanischen und dynamischen Eigenschaften werden in Beziehung zum Ungesättigtheitsgrad betrachtet. Die Ergebnisse bei der Verwendung solcher Terpolymerer für die Erzeugung von Elastomeren haben gezeigt, dass die elastischen, dynamischen und Alterungs-Eigenschaften bei einem Ungesättigtheitsgrad, ausgedrückt als Zahl der Doppelbindungen pro hundert Monomereinheit, nicht über 2–3% im wesentlichen die gleichen wie die der Äthylen-Propylencopolymeren sind.

End of Symposium