Influence of the termonomer on the synthesis and properties of ethylene-propylene polymers

Carlos M. R. Santanna[1], Elisabeth Ermel[1], and Juan R. Quijada[1,2]

[1]Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, P.O. Box 68525, Rio de Janeiro, 21945, RJ, Brazil
[2]PPH – Cia. Industrial de Polipropileno, Porto Alegre, 90020, RS, Brazil

ABSTRACT

EPDM elastomers have been synthesized by the Ziegler-Natta catalytic system $VOCl_3/Al_2Et_3Cl_3$ with the objetive of verifying the influence of termonomers on terpolymer synthesis and on the properties of peroxide-vulcanized terpolymer compositions. Two groups of termonomers have been studied. Dienes, i.e., dicyclopentadiene (DCP), 5-ethylidene-2-norbornene (ENB) and limonene, and aromatic compounds, i.e., indene (IND) and styrene (ST). The influence on the synthesis has been verified by yield, termonomer incorporation, and molecular weight distribution. The vulcanizate properties have included mechanical and electrical properties.

INTRODUCTION

Besides highly crystalline polymers, Ziegler-Natta catalysts can produce amorphous materials with elastomers. In this second group of materials are EPM copolymers which are synthesized from ethylene and propylene.

Suitable Ziegler-Natta catalysts for the synthesis of EPM elastomers are based on vanadium compounds which produce homogeneous catalytic sites. These soluble sites allow random monomer insertion in the growing chains, a pre-requisite for good elastomeric behaviour (1).

EPM elastomers show high thermal and oxidative resistance because of the virtual absence of unsaturation. This characteristic, however, causes difficulties with the vulcanization process of these rubbers.

To solve this problem, the next step in the development of the ethylene-propylene elastomers was the addition of a third monomer (a diene) which provided controlled unsaturation levels, henceforth named EPDM rubbers (1,2).

The termonomer is generally a non-conjugated diene with one of its unsaturations more active towards the polymerization catalyst. Besides, an useful termonomer should not reduce the catalytic activity and should not change the good mechanical and electrical properties of the ethylene-propylene rubbers.

Two dienes that have achieved industrial success are DCP and ENB (Figure 1). However, they are expensive and so it is of interest to find other compounds which can match the good properties but which will permit a lower price of the rubber. Abundant natural dienic compounds, such as limonene (Figure 1), deserves some interest.

As the secondary unsaturation of the most common dienic

termonomers are not completely unreactive towards the polymerization catalyst, branching and even gelled EPDM are sometimes observed (1,2). The aromatic rings of some compounds can act as vulcanization activators in the same way as the secondary unsaturation of the dienic termonomers but, unlike these unsaturations, they are not able to take part in the polymerization process. Besides, aromatic rings can improve the dielectric strength (3) and they provide sites for chemical modifications. So, compounds such as indene and styrene (Figure 1) also deserve some interest.
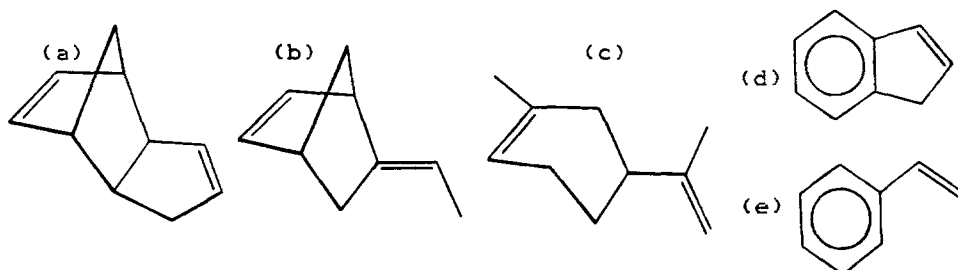

Figure 1. Compounds employed as termonomers in the synthesis of EPDM elastomers: (a)DCP, (b)ENB, (c)Limonene, (d)IND, (e)ST.

EXPERIMENTAL

Gaseous monomers (polymer grade) and nitrogen were used after passing through 4A molecular sieves columns. Termonomers were doubly vacuum-distilled before use and stored in a dry box. The catalytic system components, vanadium oxytrichloride and aluminum ethyl sesquichloride, were high purity and used as received.

Glassware was thoroughly cleaned and dried. Dried, purified n-hexane (0.3 l) was pumped to a 0.5 l reactor (4), fitted with mechanical stirrer, thermometer, manometer, and a gas inlet tube. Apparatus was assembled and placed in a bath at $15°C$. Gaseous monomers (100 mmHg) were continuously introduced throughout the polymerization reactions and their molar ratio (1:1) were kept constant by means of flowmeters. Polymerizations were stopped by adding 20 ml of 10% w/w hydrochloric acid solution in methanol.

Dienic termonomer incorporation was determined by the iodine index method(5). Ethylene/propylene ratios were obtained using infrared spectrometry (Perkin Elmer, 283B, infrared spectrophotometer) according ASTM D3900-86. Aromatic termonomer incorporation was determined by UV spectrometry (Varian, Cary 17, UV spectrophotometer), using as solvent a cyclo-hexane/di-chloromethane (9:1 by volume) mixture. The measurements were carried out by means of calibration curves using polyindene (274nm absorption) and polystyrene (254nm absorption) as standards. Intrinsic viscosity was determined at $135°C$ (ASTM D2857-87), with decaline as solvent (K and a values of 3.8×10^{-4} dl/g and 0.74 respectively) (1,2). Molecular weight distribution was determined by GPC (Waters Associates, model 150C), operating with 500, 10^4 and 10^5A columns, at $135°C$, with 1,2,4-trichlorobenzene (stabilized with 0.5% Irganox 1010) as solvent, and using

0.05% polymer solution. The flow rate was mantained at 1ml/min. and polystyrene standards were used for calibration purposes.

The rubber formulation employed to prepare the vulcanized compositions included EPM or EPDM elastomers (100 phr), a surface-treated clay (110 phr), zinc and lead oxides (5 phr each), paraffinic oils (17.5 phr), an organosilane (1 phr), an antioxidant (1.5 phr), and a peroxide (8 phr) for crosslinking; sulphur based crosslinking agents are not employed in compositions to be used as dielectrics, for they can react with copper wires. Hardness (ASTM D2240), tensile strength and elongation (ASTM D412-87), were measured at 23°C (Shore A Zwick durometer and Instron, model 1130 extensometer), using six measurements for each composition (4). The relative permittivity was determined by means of a Schering bridge connected to a cell with thermostatic control(ASTM D150-87). The DC dielectric strength was measured for the specimens shown in Figure 2 (6), using 20 specimens for each composition and the results were treated by Weibull distribution statistical analysis (7).
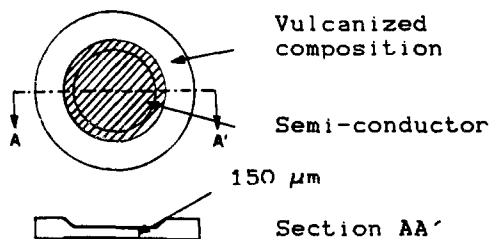

Figure 2. Schematic description of the specimens used in the dielectric strength determination of the vulcanized compositions.

RESULTS AND DISCUSSION

Termonomer incorporation

Under the reaction conditions, DCP and ENB, as expected, have been fully incorporated, and the probable mean content of monomers in each elastomer is presented in Table 1. In fact, they have showed the strongest reactivities of the compounds employed as termonomers. When they were transferred to the polymerization medium by injection of a single portion before the

Monomer	Ethylene (%)	Propylene (%)	Monomer (%)
---	48.0	52.0	---
DCP	49.0	45.1	5.9
ENB	44.0	52.5	3.5
Indene	48.0	47.4	4.6
Styrene	49.0	45.7	5.3

Table 1. Probable elastomer compositions. Mean values from three reactions.

reaction start, they reacted completely before the first 10 minutes of reaction. To improve the insertion of these termonomers

among the chains, it was necessary to divide their total a-
mounts into portions added up at every 5 minutes.

Ultraviolet spectrometry showed that indene and sty-
rene were totally consumed during the polymerization. Cyclo-
-hexane was an appropriate solvent for the elastomers obtained
using aromatic monomers, henceforth named aromatic elastomers/
rubbers, but this is not valid for the homopolymers polyindene
and polystyrene, which were soluble in di-chloromethane. For
this reason, the analysis was carried out using as solvent cy-
clo-hexane/di-chloromethane mixture to build the calibration
curves needed to measure the indene and styrene content in the
rubbers. It was observed that their addition in the rubber was
not as fast as the incorporation of DCP and ENB (Table 1).

Limonene was not incorporated, even when its concentra-
tion was increased 10 times the initial value. However, it has
reduced the intrinsic viscosity of the copolymers obtained in
its presence, as shown in Table 2. A similar behaviour was
found with 4-vinylcyclohexene as a termonomer (8).

Limonene conc. (mmol/l)	$[\eta]$ (dl/g)	$\bar{M}_v$ (10^{-3})
0	2.21	122.3
16	2.15	117.8
40	1.65	82.4
80	1.51	73.1

Table 2. Effect of the limonene concentration on the intrinsic
viscosity of the EPM rubbers.

As the reduction of the intrinsic viscosities was not
accompanied by unsaturation increase relative to the copolymer
level, probably limonene was not a chain transfer agent.

In fact, under appropriate conditions (palladium cata-
lysts), limonene is oxidized to p-cymene with liberation of hy-
drogen to reduce an unsaturated compound (9). It may be suggest-
ed that limonene was oxidized in the presence of the vanadium
catalyst, and that the liberated hydrogen was the chain trans-
fer agent.

Catalytic Activity
The influence of the incorporated monomers on the cata-

Monomer	Cat. activity (polymer g/h.V g)	$\bar{M}_w$ (10^{-3})	$\bar{M}_n$ (10^{-3})	$\bar{M}_w/\bar{M}_n$
---	161 ± 3	---	---	----
DCP	129 ± 3	442	90	4.94
ENB	147 ± 3	406	112	3.62
Indene	156 ± 3	236	79	3.00
Styrene	134 ± 3	233	82	2.84

Table 3. Influence of the monomer on the catalytic and MWD ac-
tivity of the system $VOCl_3/Al_2Et_3Cl_3$.

lytic activity is presented in Table 3. As it can be seen, the
the catalytic activity in the presence of indene remained un-
changed showing that there is no interaction of the monomer
with the active sites. 5-Ethylidene-2-norbornene also does not
influence, but styrene and dicyclopentadiene show a clear reduc
tion of the catalytic activity. From the literature (1) this de
crease of activity with DCP may be attributed to the interac-
tion of the secondary unsaturation of the termonomer with the
active sites of the catalyst. This assumption receives some sup
port looking at the values of $\bar{M}_w$ and $\bar{M}_n$. It is evident the high
er values of $\bar{M}_w$ for dienic termonomers, but the same is not ob-
served for $\bar{M}_n$; only the EPDM based on ENB achieved a higher $\bar{M}_n$.
This can mean differences on termonomer reactivity; besides
branching, it is also known that the presence of termonomers as
ENB enhances ethylene reactivity, whereas the reactivity of pro
pylene is slightly reduced (1). Table 1 shows this effect; the
ethylene content decreased with ENB incorporation.

Molecular Weight Distribution
        The MWD profiles of the four polymers are presented in
Figure 3. Besides the larger MWD it can be observed multimodal
GPC curves for DCP and ENB terpolymers and monomodal MWD when
aromatic monomers were used. It is also evident a larger height
of the high molecular weight side of the DCP curve which, as ex
pected, is smaller for ENB terpolymer, because his secondary un
saturation is less reactive than that of DCP. GPC results can
be considered similar to the reported by Cesca (1), from which
MWD profiles were bimodal for DCP rubbers prepared using simi-
lar reaction conditions. However, it is pointed out the impor-
tance of the type of monomer, all the reaction factors such cat
alyst preparation, solvents, temperature, etc. and the complex-
ity of the polymerization kinetic scheme (1).
        As reported by Cozewith and ver Strate (10) the catalyt
ic system $VOCl_3/Al_2Et_3Cl_3$ present one active species in EPM po-
lymerization, but there is the possibility of the third monomer
besides inserting into EPDM chains promote side reactions as
branching, termination, transfer, etc., due to the presence of
two centers of reactivity in the diene, which can affect MWD
profiles. This, and changes on olefins reactivities could be an
explanation for the results obtained in this work once all reac
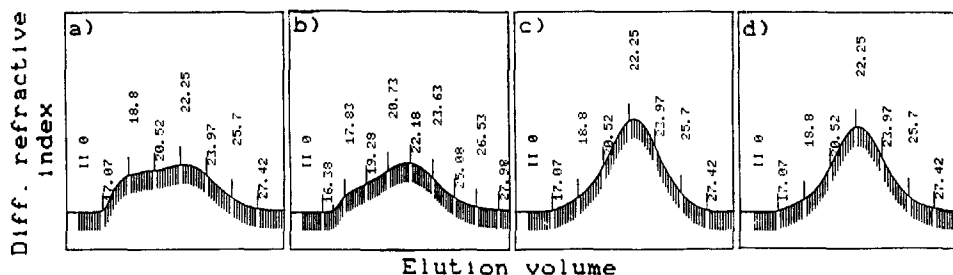tions were carried out under similar conditions.

Figure 3. MWD profiles: (a)DCP, (b)ENB, (c)IND, (d)ST. Column
porosities $500,10^4,10^5$Å, using 1,2,4-trichlorobenzene at $135°C$,
a flow rate of 1ml/min and PS as standard.

Mechanical Properties
        The results of hardness, tensile strength, and elonga-
tion at break are presented in Table 4. As the compositions and
vulcanization conditions were the same for the various elasto-
mers the hardness may reflect vulcanization efficiency.
        The copolymer, composed of essentially saturated chains,
must require the highest energy for abstraction of H atoms by
the vulcanization agent. In fact, its composition has shown the
lowest hardness which is similar to styrene-based rubber. Di-
ene, as well as indene polymers presented better hardness which
is slight enough to attribute any special effect on vulcanizing
properties.
        Although the dienic termonomers have shown the largest
tensile strength, as can be expected from the hardness results,
the tensile strength of the aromatic monomers compositions have
been lower than that of the copolymer composition. However, the
value of the elongation at break of the copolymer , composition
have also been greater than the values correspondent to the aro
matic monomers compositions.
        These results can be explained by the extreme nature of
the crosslink density influence on the tensile strength, i.e.,
the fraction of elastically effective network chains increases
with the crosslink density, whereas the extensibility decreases
with increasing crosslink density (2). On the other hand, the
copolymer chains could reach a larger extension before the
occurrence of the breakdown of the polymeric framework bonds
which would cause the specimens failure. Also, it would be pos-
sible to establish some correlation between the mechanical pro-
perties and the GPC results of these rubbers, even without co-
polymer data, which for diene elastomers were larger than the
aromatic rubbers showing the influence of branching on these
results.

Monomer	Hardness (Shore A)	Tensile Strength (MPa)	Elongation at Break (%)
---	54 ± 0.5	4.99 ± 0.22	720 ± 21
DCP	63 ± 0.5	8.72 ± 0.22	315 ± 21
ENB	58 ± 0.5	·6.47 ± 0.22	433 ± 21
Indene	57 ± 0.5	3.61 ± 0.22	640 ± 21
Styrene	54 ± 0.5	3.38 ± 0.22	645 ± 21

Table 4. Influence of the monomer on the mechanical properties
of the vulcanized compositions. Mean values from six measure-
ments.

Electrical Properties
        The results of dielectric strength follow approximately
the same order shown in the hardness results (Figure 4). This
observation suggests that the dielectric strength of the vul-
canized compositions is influenced by the crosslink density,
i.e., the dielectric breakdown is associated with discharges
inside the specimens.
        The effect of the temperature on the relative permit-
tivity is twofold: as the temperature is increased, the dipoles

embeded in the bulk can be oriented more rapidly by the exter-
nal electric field, but the thermal movement disturbs that ori-
entation further and further. So, the internal electric field
caused by the oriented dipoles is established in a faster way
by increasing temperature, but it is progressively weaker. As a
result, the relative permittivity becomes smaller.

That was the general behaviour observed for all the dif_
ferent compositions studied (Figure 5). Besides, the harder a
composition, the greater its relative permittivity was for al-
most all temperature range studied. This is a reasonable re-
sult, for as the crosslink density increases, the action of the
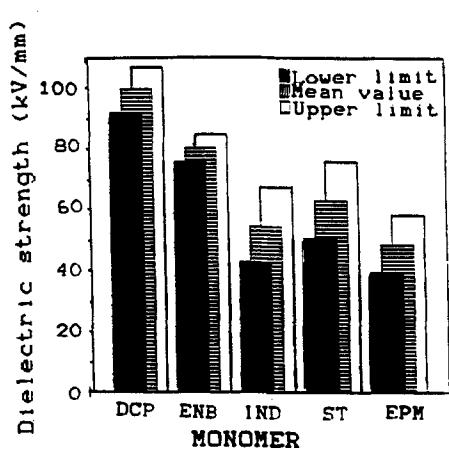thermal movement on the dipole orientation is less effective.

Figure 4. Dielectric strength
of vulcanized compositions.
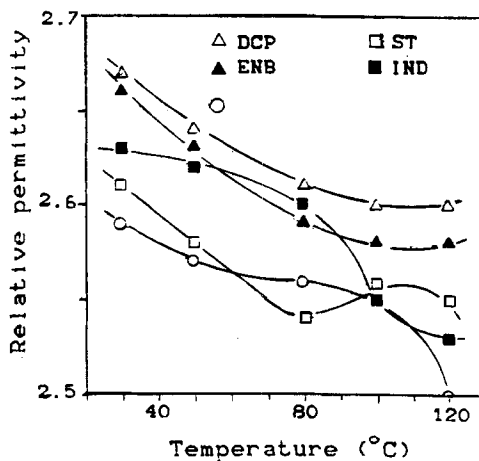Probable values from Weibull
distribution statistical anal_
ysis.

Figure 5. Relative permittivity
vs temperature of vulcanized
compositions. DC (60 Hz). Pro-
bable values from Weibull dis-
tribution statistical analysis.

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