

# Effect of a Natural Magnesium Silicate Treated with a New Coupling Agent on the Properties of Ethylene–Propylene–Diene Rubber Compounds

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**ABSTRACT:** The behavior of sepiolite (magnesium silicate with a microfibrillar morphology) as a filler in ethylene–propylene–diene compounds was studied. A new coupling agent, *meta*-isopropenyl dimethyl benzyl isocyanate, was used. The effect of the filler modified by *meta*-isopropenyl dimethyl benzyl isocyanate on the physical properties was improved with respect to other fillers and commercial silane

coupling agents under the same conditions. In addition to a smoother surface, the flow behavior of compounds filled with sepiolite, on account of its fibrous morphology, was better than that obtained with other fillers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1489–1493, 2004

**Key words:** rubber; rheology; mechanical properties; fillers

## INTRODUCTION

Among the highly diversified fillers used in the rubber industry, carbon black occupies a dominant position, about 60% of total filler consumption. Kaolin ranks second, and it is followed after a considerable percentage interval by the rest of the white fillers, such as silica, carbonates, and chalks.

We propose replacing carbon black with other materials that require less energy in for preparation, such as natural minerals. The mineral of choice is sepiolite, a hydrated magnesium silicate of fibrous but rarely macroscopic morphology, of which there exist abundant deposits in Spain.

For many years, silane coupling agents have been used to improve the reinforcing response of mineral fillers incorporated into polymeric matrices. These substances can make available two functional groups, organofunctional and silicofunctional groups, the latter preferably being alkoxy groups, which react with the surface of a filler. In contrast, organofunctional groups, bonded via a short alkyl chain to the silicon atom, can be diverse in nature, reacting with rubber during the curing process.<sup>1–3</sup>

In this study, we examined a new type of coupling agent presenting new possibilities: *meta*-isopropenyl

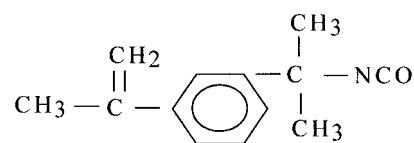
dimethyl benzyl isocyanate (TMI). This substance is a bifunctional monomer containing a reactive double bond and a tertiary aliphatic isocyanate group. This last group is capable of reacting with the silanol groups at the filler surface.

This article reports the behavior of the new coupling agent (TMI) in compounds of ethylene–propylene–diene monomer (EPDM). This new product was studied with three filler types: a clay, a sepiolite, and a precipitated silica. Also, a commercial silane was used as the reference point throughout the study: vinyl silane A-172.

## EXPERIMENTAL

### Materials

The rubber used was Dutral TER 054 [Enichem-Polimeri Europa, Milan, Italy; ethylene/propylene ratio (%) = 46/50.5, 5-ethylid-2-norbornene content = 3.5%]. Silane A-172 [vinyl-tris(2-methoxyethoxy)silane] was procured from Union Carbide Inter-America, Inc. (New York, NY). The chemical structure of TMI was supplied by Cytec Industries, Inc. (West Paterson, NJ):



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Sepiolite, commercialized as Pangel, was supplied by Tolsa SA (Madrid, Spain) and was extracted from

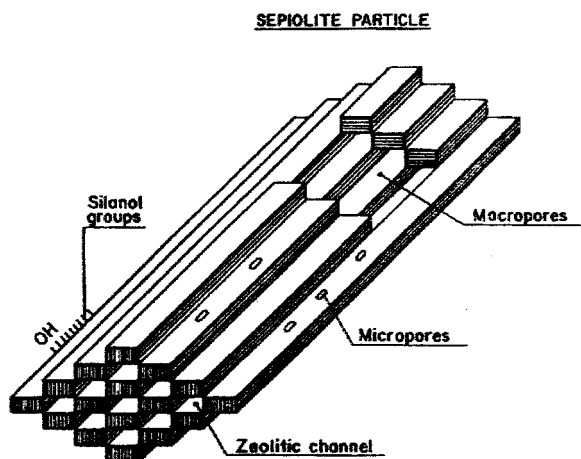


Figure 1 Schematic structure of a sepiolite crystal.

deposits near the Madrid area (which has the largest and purest deposits of this mineral in the world). The precipitated silica, Ultrasil V/N 3, was supplied by Degussa Hüls AG (Frankfurt, Germany).

#### Filler

Sepiolite is a magnesium silicate with a microfibrillar morphology. It is structured in discontinuous octahedral layers, which form open channels extended in the fiber direction.<sup>4</sup> The sepiolite structure, with its channels aligned in the fiber direction, is illustrated in Figure 1. An important structural characteristic of this mineral that explains some of its properties is that its surface is covered with silanol groups spaced 5 Å apart along the edges of the fibers. This disposition makes the silanols very accessible for coupling reactions. Some characteristic and properties of sepiolite are listed in Table I.<sup>5</sup>

The clay was supplied by Caobar (Guadalajara, Spain), and its reference was Caosil SP-SE. In Table II, some properties of this clay are listed. Finally, the

TABLE I  
Properties of Sepiolite

Ideal formula	$\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_2(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$
Fiber size	
Length ( $\mu\text{m}$ )	0.2–2.0
Width (Å)	100–200
Thickness (Å)	50–100
Braunauer, Emmett, Teller (BET) surface area ( $\text{m}^2/\text{g}$ )	320
Porosity ( $\text{cm}^3/\text{g}$ )	0.70
Specific gravity ( $\text{g}/\text{cm}^3$ )	2.0–2.2
Cation exchange capacity (CEC) (mequiv/100 g)	10–15
Refraction index	1.51–1.52

TABLE II  
Properties of Clay

Particle size	
<4.5 $\mu\text{m}$	90%
<1.0 $\mu\text{m}$	50%
<0.6 $\mu\text{m}$	25%
Moisture (maximum %)	1
BET surface area ( $\text{m}^2/\text{g}$ )	15.5
pH	5
Specific gravity ( $\text{g}/\text{cm}^3$ )	2.6
$\text{SiO}_2$	47.5
$\text{Al}_2\text{O}_3$	37.5

precipitated silica was UltrasilV/N3, and its properties are listed in Table III.

#### Rheological measurements

The apparent rheological measurements were carried out in a Göttfer 2002 capillary rheometer manufactured by Göttfer Werkstoff-Prümaschinen (Karlsruhe, Germany); it had a 30/1 length/diameter ratio and a 180° angle of entry. The measurements were performed at 120°C. The shear rate was varied from 36 to 722  $\text{s}^{-1}$ .

#### Mixing and curing

The rubber compounds were prepared in a Rheomix 600 instrument (Haake, Karlsruhe, Germany). First, the rubber was mixed at 80°C at a rotor speed of 60 rpm for 2 min. Then, the filler was incorporated, and the mixing was continued for another 3 min so that a homogeneous distribution would be ensured. The coupling agent was also incorporated, and after another 5 min of mixing, the curative was finally added. The hot mix was taken out and passed through a tight-nip two-roll mill to form a sheet. The cure characteristics of the compounds were determined in a Monsanto MDR 2000E rheometer (Alpha Technologies, Wiltshire, United Kingdom). The vulcanizates were molded at 160°C at their respective optimum cure times in a thermofluid press at a pressure of 5 MPa. The physical properties were determined according to International Organization for Standardization (ISO) and national standards.

TABLE III  
Properties of Ultrasil V/N 3

$\text{SiO}_2$	86–87%
Loss at 105°C	5%
Specific gravity ( $\text{g}/\text{cm}^3$ )	1.9–2.0
pH	6
Particle size ( $\mu\text{m}$ )	16
BET surface ( $\text{m}^2/\text{g}$ )	234

TABLE IV  
Formulation Recipes (phr) and Physical Properties of EPDM Compounds

Compound	1	2	3	4	5	6	7	8	9
Caosil SP-SE	60	60	60						
Sepiolite				45	45	45			
Ultrasil V/N 3							45	45	45
TMI	—	2	—	—	2	—	—	2	—
Silane A-172	—	—	2	—	—	2	—	—	2
Rheometer cure at 160°C									
Maximum torque, $M_H$ (dNm)	23.2	23.5	22.9	26.5	29.8	25.6	53.3	53.6	49.0
Minimum torque, $M_L$ (dNm)	1.09	0.86	0.97	3.35	2.65	1.80	10.4	6.9	7.2
Scorch time, $t_{s2}$ (min)	0.96	1.15	0.84	1.1	1.0	1.23	0.90	1.0	0.66
Optimum cure time, $t_{97}$ (min)	27	30	16	52	45	53	52	49	53
Vulcanizate properties									
Tensile strength (MPa)	5.5	4.6	7.9	5.8	12.4	7.5	14.9	12.6	16.8
100% Modulus (MPa)	3.4	3.0	4.1	3.0	4.4	2.3	2.3	2.7	2.2
300% Modulus (MPa)	—	—	—	—	10.1	4.6	4.3	6.4	3.9
Elongation at break (%)	234	232	334	274	325	557	807	525	919
Hardness (shore A)	67	67	67	68	70	60	78	77	77
Tear (die delft; N)	23	20	27	36	58	32	46	40	47
Loss abrasion (mm <sup>3</sup> )	148	169	195	116	81	158	96	93	125

Dutral TER 054, 100; zinc oxide, 5; stearic acid, 1; 2-mercaptobenzothiazole (MBT), 2; tetramethylthiuram disulfide (TMTD), 1.5; sulfur, 2.

## RESULT AND DISCUSSION

### Physical properties

The formulations for EPDM compounds with different fillers and coupling agents and the physical properties of the cured compounds are shown in Table IV.

In compounds filled with clay, the reinforcing effects of coupling agents are not very important. This is expected because the surface of this mineral is poor in hydroxyl groups. Nevertheless, the sepiolite filler provides an important reinforcing effect. The presence of numerous silanol groups along the edge of the sepiolite fiber makes easy the reaction with silane A-172 and with TMI. This last product leads to a significant improvement in the modulus, tensile strength, and tear strength and to a significant increase in the abrasion resistance, and good elongation values are maintained. Surface-modified sepiolite clearly shows better technological behavior than the same filler without chemical surface treatment. The enhanced values can only be explained in terms of increased polymer–filler interactions, that is, a greater number of direct bonds between the filler and the polymer achieved through the reaction of the double-bond group with the rubber.

The physical properties of the precipitated silica compounds modified with TMI or silane A-172 appear to present only a slightly reinforcing effect.

### Flow behavior

The effect of the shear rate on the viscosity of the compounds at 120°C is shown in Figure 2. At a high

shear rate, the viscosity is independent of the filler type and the presence of a coupling agent. At a low shear rate, Ultrasil V/N3 presents a higher viscosity, probably because of its strong tendency to agglomerate and form a developed filler network in the compounds.

The chemical modification of the filler surface with coupling agents does not affect the flow behavior. Shear-viscosity/shear-rate plots for sepiolite compounds, without and with TMI and silane A-172, are shown in Figure 3. The viscosity, in the range of the shear-rate study, is not affected by the filler surface organofunctionalization.

A decrease in the shear viscosity ( $\eta$ ) with the deformation rate ( $\dot{\gamma}$ ) can be calculated from the following power-law equation:

$$\eta = k\dot{\gamma}^{n-1}$$

where  $n$  is the index for non-Newtonian rheological behavior and  $k$  is the consistency parameter (the viscosity at the unit shear rate). Table V shows the power-law constants,  $n$  and  $k$ , calculated with regression analysis. The  $n$  values of the clay compounds are higher than those of the compounds with sepiolite and silica, whereas the  $k$  parameters are lower. This result for the clay compounds shows that a minor energy of flow is required. The sepiolite compounds present an intermediate behavior. In general, the  $n$  values of sepiolite and silica compounds suggest an increase in filler surface and rubber interactions, and this increases the rigidity of the compounds.

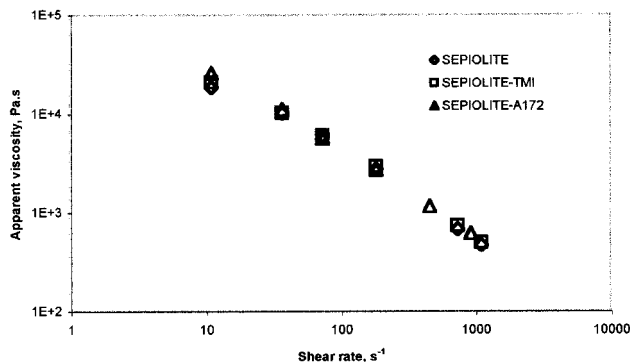
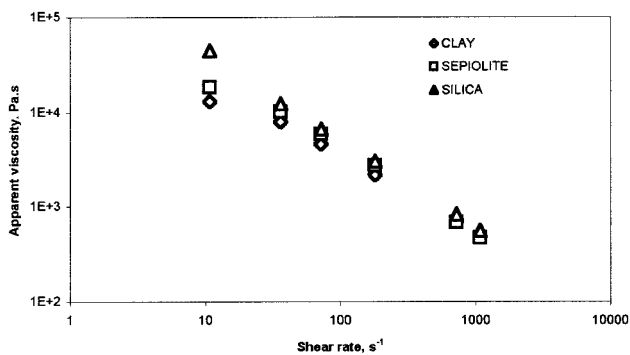


Figure 3 Variation of the apparent viscosity of sepiolite compounds with the shear rate at 120°C.

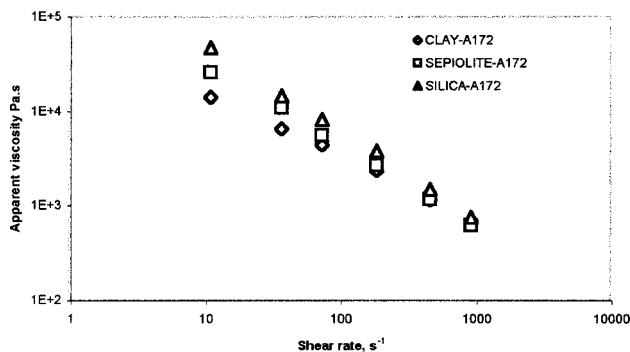
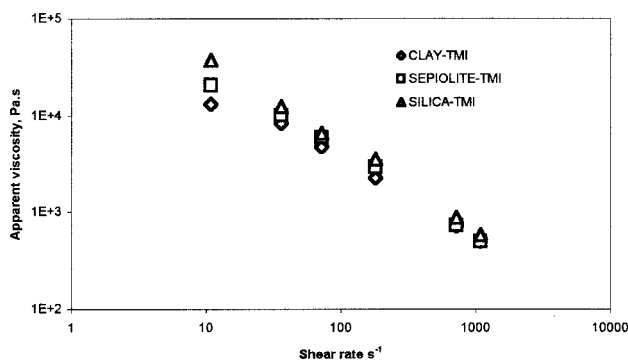


Figure 2 Variation of the apparent viscosity with the shear rate at 120°C.

The extrudate deformation characteristics of different compounds at 120°C and at shear rates of 36 and 722 s<sup>-1</sup> are shown in Figure 4. At the low shear rate, the extrudates present a smooth and uninterrupted surface. On the contrary, at the high shear rate, the extrudates present a different texture. The compounds with clay show a rough surface and a nonuniform diameter attributed to melt fracture when the shear stress employed on the melt during extrusion exceeds the strength of the melt.<sup>6</sup>

The compounds with silica present extrudates with larger distortion surfaces when the filler is modified with TMI. On the contrary, the samples prepared with sepiolite present a smooth surface. This smooth characteristic of the extrudates that contain sepiolite, superior to that of compounds with clay or silica, can be attributed to the fiber morphology. The particles are oriented in the flow direction and give a smooth surface and reduced die swell.

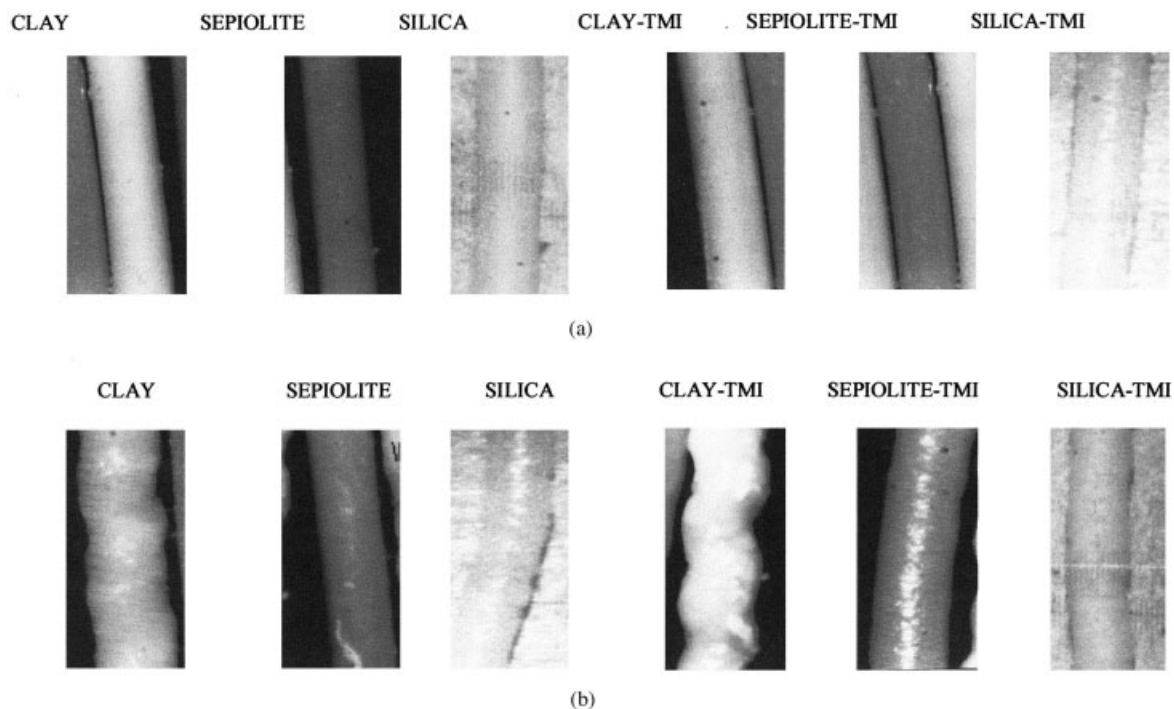
CONCLUSIONS

A natural magnesium silicate, sepiolite, of which there exist abundant deposits in Spain, is improved with respect to its reinforcing properties in EPDM rubber when its external surface is modified with TMI.

The increases in the modulus, tensile strength, tear strength, abrasion resistance, and Shore hardness can be legitimately attributed to the increase in the interactions between the filler and the polymer, which is caused by the participation of isopropenyl groups. These groups react with the polymeric matrix during the curing phase. The isocyanate groups react with the silanols, which are very accessible and are extended on the sepiolite surface, during the mixing process.

TABLE V  
Flow Parameters of Compounds at 120°C

Sample	<i>n</i>	<i>k</i> × 10 <sup>-4</sup> (Pa s)	Correlation coefficient (R <sup>2</sup> )
1	0.258	9.5	0.986
2	0.258	9.8	0.984
3	0.315	7.7	0.998
4	0.173	17.1	0.986
5	0.101	31.0	0.996
6	0.145	21.1	0.998
7	0.093	37.7	0.998
8	0.101	31.0	0.997
9	0.075	42.3	0.999



**Figure 4** Optical photographs of extrudates of different compounds at 120°C and at two shear rates: (A) 36 and (B) 722 s<sup>-1</sup>.

The physical properties are clearly improved when sepiolite is modified with TMI, which is quite superior to vinyl silane A-172; in general, its results are comparable to those of silica-filler compounds.

Moreover, the flow behavior of the filler sepiolite, on account of its fibrous morphology, is better than that of clay and silica compounds.

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