Reinforcing Effect and Electrical Properties of Ethylene-Propylene Rubber Filled with Calcined Sepiolite

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ABSTRACT: A mineral sepiolite (magnesium silicate with microfibrilar morphology) was calcined at 325°C and its behavior as filler for ethylene-propylene (EPM) compounds designed for electrical cable coating was studied. This calcined sepiolite is a material with good dielectric and physical properties and provides a reinforcing effect, increased when is treated with a coupling agent. The performance of this filler was compared to a commercial clay calcined at 1000°C. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 714–718, 2001

Key words: rubber; electrical and mechanical properties; sepiolite calcined; reinforcement

INTRODUCTION

In compounding rubber for electrical insulation, it is of prime importance which mineral fillers are employed. Although normally any mineral filler is acceptable for achieving good initial electrical properties, certain ones are rejected because of their high water adsorption. In addition to electrical properties, the requirements for reinforcing properties must be taken into account.

One of the most suitable types of filler for insulation on rubber compounding are calcined clays, due to their low water adsorption and good extrusion properties. Despite calcined clays' reported low physical properties in rubber compound, it is at present the most recommended filler for cable applications.

The amount of filler used in insulation formulations is usually a compromise between meeting the requirements of electrical properties and compound cost. The best electrical properties are obtained with low (or zero) filler addition. However, the best processing behavior is obtained when the proportion of filler is elevated more. With respect to physical properties, there is always an optimum at a certain proportion for each filler type.

EPM rubber, with its nil molecular unsaturation and its absence of dipoles (existing on polychloroprenes, PVC, etc.), is the most promising rubber of formulating compounds for high-voltage insulation, with excellent ozone resistance, weather resistance, heat resistance, and outstanding corona resistance. For this rubber, the curing agent chosen is organic peroxides.

In this work we studied the behavior of a calcined sepiolite (magnesium silicate with a microfibrilar morphology) as a rubber filler for compounds designed for electrical cable coating where insulation performance must be as high as possible. A commercial clay calcined at 1000°C, the most convenient filler for this type of application, was taken as the reference point throughout.

To improve the physical properties, both sepiolite and clay were treated with a coupling agent, vinyl silane, which was very appropriate for EPM

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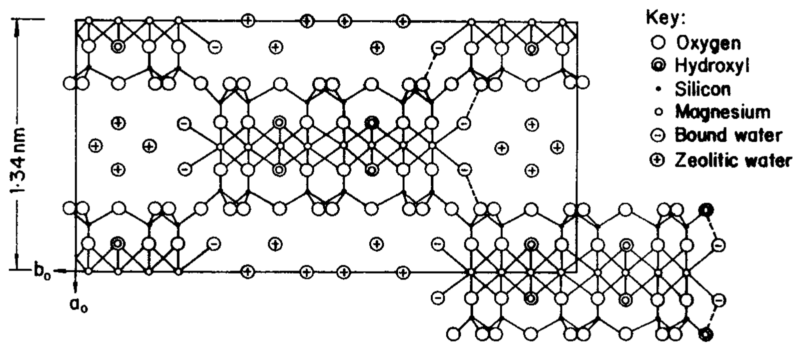

Figure 1 Projection of the atoms in the sepiolite structure onto the (001) plane.

rubber, which has to be crosslinked with peroxides.

EXPERIMENTAL

Materials

The rubber used was EPM Dutral Co 054 from Enichem Elastomeri (E/P in %, 58/42). The curing agent was Perkadox 14/40 (dicumyl peroxide 40%) from Flexsys. Sepiolite, commercialized as Pangel^{TM}, was supplied by Tolsa SA and extracted from deposits localized close to the Madrid area of Spain (a location of larger and purer deposits of this mineral in the world). The reference calcined clay was Polestar 200 R from Cromogenia-Units, SA. Silane treatment was done with Silane A-172 [vinyl tris(2-methoxy ethoxy silane)] from Union Carbide.

Fillers

Sepiolite is a magnesium silicate with a microfibrilar morphology. It is structured in discontinuous octaedric layers, which form open channels extended in the fiber direction.[1] In Figure 1, the projection of the atoms in the structure onto the (001) plane is shown.[2] The layer of silica tetrahedrons extends as a continuous layer but with an inversion of the apical ends every six units, which originates channels known as zeolitic channels. A picture of sepiolite structure, with the channels aligned in the fiber direction, can be seen in Figure 2. The cross section of these channels is 3.6 $\times$ 10.6 Å^2, enough to allow the penetration of water and other fluids.

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^2 along the edge of the fibers. This disposition makes the silanols very accessible for coupling reactions.

Some characteristics and properties of sepiolite are listed in Table I.[3]

Natural sepiolite has a high content of different water types (up to 16% of the total weight): physically adsorbed water, zeolitic water, and coordination or crystallization water. These different water types differ on the strength of the link with the mineral. When sepiolite is heated, important changes are produced not only in weight but also in morphology.

Adsorbed and zeolitic water is eliminated at temperatures below 200°C, being a reversible loss. Coordinated water[4–5] is lost in two stages: one half at the temperature range of 200–300°C, and the other half at 350–550°C. Coordination water loss involves structural changes resulting in a new phase where channel cross section is

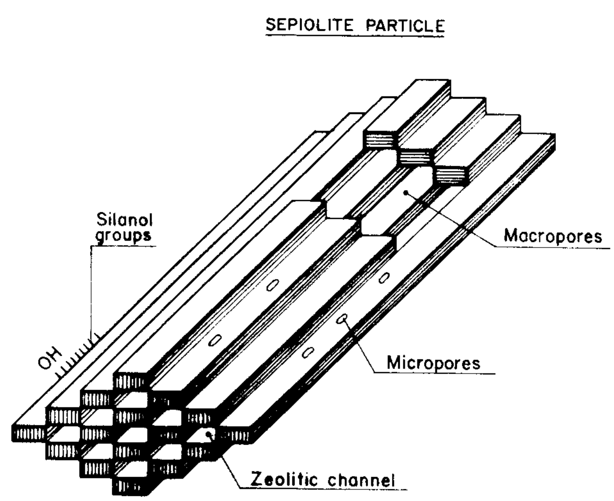

Figure 2 Channels on the sepiolite structure.

Table I Properties of Sepiolite

Ideal formula	$Si_{12}Mg_8O_{30}(OH)_2(H_2O)_4 \cdot 8H_2O$
Fiber size:	
Length (μm)	0.2–2.0
Width (Å)	100–200
Thickness (Å)	50–100
BET surface area (m^2/g)	320
Porosity (cm^3/g)	0.70
Specific gravity (g/cm^3)	2.0–2.2
Melting point (°C)	1550
Hardness (MΩ)	2.0–2.5
C.E.C. (meq/100 g)	10–15
Refraction index	1.51–1.52

Table II Calcined Clay Properties

Brightness (ISO)	88.0 ± 1.5
Particle size	
+300 mesh (%max)	0.05
+10 micron (%max)	12
−2 micron (%)	50–55
Moisture (%max)	0.5
BET surface area (m^2/g)	8.5
pH	6.5 ± 0.5
Specific gravity (g/cm^3)	2.6
SiO_2	55
Al_2O_3	41

reduced and water loss is irreversible. The mineral with this new structure $[Si_{12}O_{30}Mg_8(OH)_4]$ is called anhydrous sepiolite. At this stage, the material has no water but it keeps silanols at the edge of the channels, being necessary to go to temperatures of 1100°C to destroy them.[5] In Figure 3, the changes produced with the treatment are shown.

For this work, Pangel™ (sepiolite) was calcined at 325°C for 1 h. At this temperature, adsorption zeolitic and half of the coordination water is lost with structural changes and channel cross section reduction. Specific surface of the calcined mineral, measured from the curve of isothermal adsorption of nitrogen (BET method), is now 161 m^2/g (original value in Table I).

With respect to the reference clay, there are two types of calcined clays commercially available: a first type calcined at temperatures not lower than 750°C, which results in a material denominated metakaolinite and a second type calcined at 950-1000°C in which dehydroxylation inside the particle has been completed. During this calcination, chemical, morphological, and mineralogical changes occur, producing a unique filler with special applications in the rubber industry. In Table II, some properties of the calcined clay used in this work are shown.[6]

Mixing and Vulcanization

The rubber compound was prepared in an open two-roll mill (friction, 1 : 1.4) by using conventional mixing procedures. Curing was done in a thermofluid heated press. Measurements of the degree of cure were conducted by using a Monsanto Moving Die Rheomether MDR 2000 E.

Physical Testing

The physical properties were determined on the specimens cured at their respective optimum curing times (t_{97} of the rheometer) as follows: tensile properties according to ISO 37, tear strength to ISO 816, and the other physical properties to national standards. The formulation compounds can be seen in Table III.

The silane treatment of both fillers was done by adding the silane during the compounding stage on the mill.

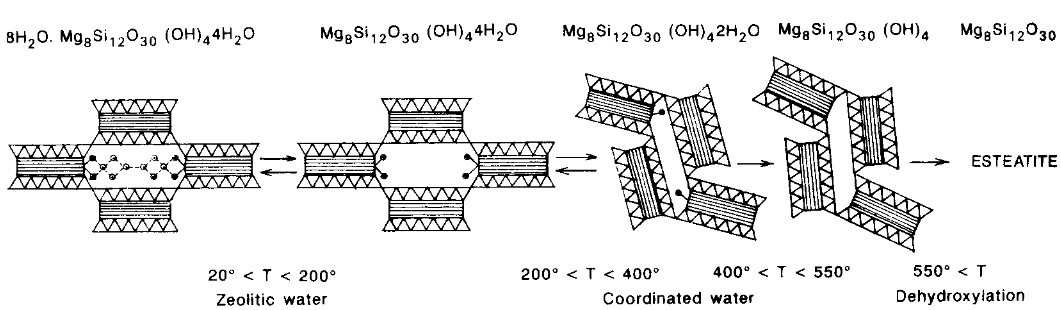

Figure 3 Changes on sepiolite structure with thermal treatment.

Table III Compound Recipes

	Compound Code							
	P40	PS40	P70	PS70	C40	CS40	C70	CS70
Pangel 235	40	40	70	70	—	—	—	—
Calcined clay	—	—	—	—	40	40	70	70
Silane A-172	—	1	—	1	—	1	—	1

EPM Dutral Co 054, 100; zinc oxide, 5; Perkadox 14/40, 5; Co-agent TAC, 1.

Electrical Testing

The resistivity of the samples was determined by using probes with typical dimensions of $100 \times 100 \times 2\ mm^3$. The specimen was inserted between two circular electrodes and a potential of 500 V was applied. The resulting current was measured by using a Keithley instrument. Resistance of the sample was calculated by using the equation $R = V/I$, where V is the applied voltage and I is the resulting current. The resistivity was calculated by using the equation $\rho = (RA/t)$, where A is the area and t is the thickness of the sample.

RESULTS AND DISCUSSION

The formulations of the compounds designed for electrical properties are shown in Table III and their corresponding physical properties of the cured compounds are shown in Table IV.

Calcined sepiolite provides a reinforcing effect far higher than calcined clay. The 100 and 300% moduli and tensile-strength values are in average double for sepiolite in respect to clay. As a consequence of this better reinforcing effect, hardness values are higher and tear strength and abrasion resistance are improved.

When the fillers are treated with the coupling agent silane A-172, physical properties are much increased. As expected, the presence of numerous silanol groups along the edge of the sepiolite fiber, that remain after calcination at 325°C, facilitates reaction with the silane, leading to a significant improvement of the modulus and the tear strength, while keeping good values of elongation.

In Table V, values of the volumetric resistivity for the prepared compounds are shown. It is clear that the values for calcined clay compounds are superior; however, a clear definition for insulating elastomers does not exist, and, if materials are considered insulators when resistivity values are equal or above $10^{14}\ \Omega$ cm, then sepiolite compound values fall within this range and can be considered insulators. When filler content increases, volumetric resistivity decreases.

To sum up briefly, we are in the presence of a mineral filler that, when incorporated to a rubber, does not decrease resistivity significantly, with values close to the values of a compound formulated with clay calcined at 1000°C, a well-known

Table IV Physical Properties of EPM Compounds Filled with Sepiolite and Clay Calcined and Treated or not with Vinyl Silane

	Compound							
Physical Properties	P40	PS40	P70	PS70	C40	CS40	C70	CS70
Hardness, Shore A	66	73	75	80	58	60	63	64
Modulus, 100% (MPa)	3.2	8.8	5.0	12.4	1.6	1.9	2.1	3.1
Modulus, 300% (MPa)	5.7	—	—	—	3.0	—	3.8	—
Tensile strength (MPa)	7.2	14.7	7.1	16.0	3.6	7.4	4.4	9.5
Elongation at break (%)	555	186	360	135	400	308	400	250
Tear, die Delft (N)	33	42	41	51	13	14	16	19
Abrasion loss (mm^3)	270	106	280	113	337	180	350	190

Table V Volume Resistivity of EPM Compounds Filled with Sepiolite and Clay Calcined and Treated or not with Vinyl-Silane

Compound	P40	PS40	P70	PS70	C40	CS40	C70	CS70
Volume resistivity Ω cm $\times 10^{-14}$	6	9	3	5	31	36	16	22

and widely used filler when good insulating properties are intended. Thus, with sepiolite calcined at 325°C, a material with good insulating properties is obtained at lower energetic cost for the calcination step. Furthermore, better physical properties for the vulcanizates are obtained as a premium, when compared to commercial calcined clays. This allows, for instance, for an increment on the content of paraffinic plastifiers in the formulation to improve processing and further reduce the production cost of the compound.

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