Reinforcing Effect of a Magnesium Silicate Treated with a 4-Amino Methyl Pyridine in Epichlorhydrin Rubber (ECO) Vulcanizates

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SYNOPSIS

This paper reports on the chemical surface changes of sepiolite, a natural magnesium silicate, caused by adsorption of 4-amino methyl pyridine, and the application of this product as a reinforcing filler in epichlorhydrin rubbers. The amine group of the reagent used in the surface modification of the mineral reacts with elastomer upon vulcanization. This gives rise to stronger rubber-filler bonds with the consequential improvement of the technological properties of the vulcanizates.

INTRODUCTION

Among the highly diversified fillers which find application in the rubber industry, carbon black occupies a preponderant position, i.e., ca. 60% of total filler consumption. Kaolins rank second, followed at a considerable percentage interval by the rest of withe fillers, silica, carbonates, chalks, etc.

In the recent past, carbon black and synthetic silica have experienced remarkable price increases. Hence it has become interesting to replace them by other materials requiring less energy in their preparation, such as natural minerals.

This research proposes this line of approach. The mineral of choice is sepiolite, a hydrated magnesium silicate of fibrous but rarely macroscopic morphology, a material of which there exist abundant deposits in our country.

In our laboratory we have been working for several years with this mineral as a filler in elastomers or other polymers, preferably thermoplasts (PE, PP, etc.) obtaining significant results.[1-3] One of the most outstanding characteristics of this silicate is its high adsorption power. In rubber blends it can even inhibit the crosslinking reaction, a feature which is substantially reduced by means of the incorporation of "activators" (i.e., amines, glycol) into the formulation.

Sepiolite, like other silicates, has been used as a catalyst in the transformation of organic compounds.[4-7] This mineral is constructed of talklike ribbons arranged in such a way that the tetrahedral sheet is continuous but inverts apical directions in adjacent ribbons, generating channels along the c-axis of the fiber. The octahedral layer, fundamentally composed of Mg^{+2}, presents, on a small scale, Al^{+3} substitution. The catalytic activity of the sepiolite is to be attributed to the presence of acid surface centers of the Brönsted and the Lewis type. The former could have been generated by the two water molecules linked to each of the centers are attributed to the Al^{+3} incorporated onto the octahedral layer by means of isomorphic Mg^{+2} substitution.

Recently Corma et al.[8] have replaced octahedrical Mg^{+2} in sepiolite by trivalent cations of a high charge density, which produces an increase in acidity on the mineral surface and at the same time confers enhanced surface activity upon the mineral.

Natural sepiolite possesses Al^{+3} in the order of 3 $\times 10^4$ eq/g present on the "external" surface, which can be blocked by means of coordination with pyridine molecules. This distinctive property of sepiolite, i.e., the ability to coordinate the active surface

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centers with pyridine or its derivatives, is the feature on which this research is focusing. Adsorption can be achieved with certain pyridine derivatives in such a way that the pyridinic nitrogen is coordinated at the mineral surface and, in addition, has a reagent group available which, during the curing process, will react with the polymer, thus enhancing the reinforcing response of the filler.

In previous work,[9,10] this approach was put to the test, adsorbing 4-vinyl pyridine onto sepiolite, which resulted in enhanced reinforcing power of the filler, when incorporated into ethylene–propylene copolymers.

In this paper adsorption onto the sepiolite is achieved with 4-amino methyl pyridine (4AMP). The pyridinic nitrogen blocks the Al^{+3} centers located on the edges of the microcrystal and in the Brönsted acid centers. Thus the amine group remains free to react during rubber vulcanization. The polymer selected for this study is an epichlorhydrine and ethylen oxide copolymer which contains two lateral chlorometyl groups able to react with diamines for crosslinking.

EXPERIMENTAL

Materials

A natural magnesium silicate, sepiolite, with a microfibrous morphology was used in this study (Fig. 1). It was supplied by Tolsa S.A. under the trade
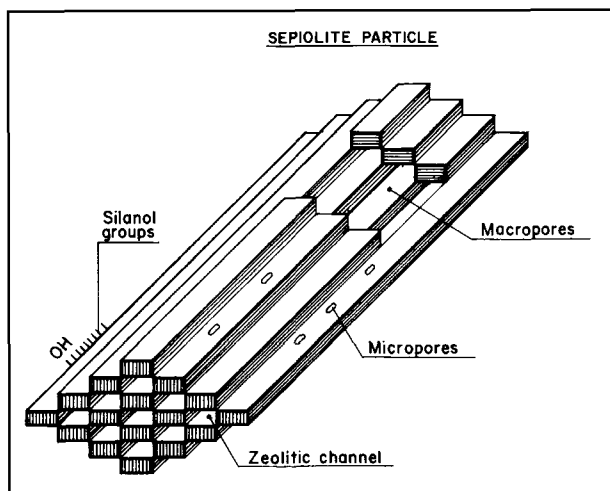

Figure 1 Schematic structure of a sepiolite crystal.

name Pansil, obtained from the Yunclillos deposit in Toledo, Spain. The mineral has the following physical properties: no residue in a ASTM 325 sieve; more than 75% of particles between 2 and 10 μm; specific gravity, 2; apparent density, 100–200 g/L; pH 8 in 10% suspension; dibutyl phthalate absorption (DBPA), 200 cc/100 g; specific surface area determination by BET; nitrogen adsorption, 288 m^2/g.

The rubber used was Hydrin 200 from B. F. Goodrich, epichlorhydrin and ethylene oxide copolymer, molar ratio 1:1, supplied by Quimidroga S.A.

Textural Analysis

The nitrogen adsorption isotherm at 77 K was determined in a volumetric apparatus (physical adsorption analyzer, Micromeritics, Model 2100 E). Specific surface was calculated through the BET method.

Thermogravimetric Analysis

For thermogravimetric determinations a Perkin Elmer apparatus was used, equipped with a TGS microscale. The heating rate was 10°C/min.

Infrared Analysis

The IR spectra were obtained in a Perkin Elmer apparatus, Model 475, in the region ranging over 250–4000 cm^{-1}. The KBr tablet system was used.

Chemical Modification of Sepiolite

4AMP adsorption onto the sepiolite was accomplished by bringing the mineral into contact with the reagent dissolved in different chloroform solutions of known concentration, maintaining the temperature of the suspension constant at 30±0.1°C for 72 h. The concentration in the solutions were measured using a Perkin Elmer UV spectrometer, Model 554. The selected wavelength was 256 nm, where there occurs an absorption peak. The nonadsorbed reagent portions in the solutions were calculated in the filtrate by means of calibration curve.[11]

The sepiolite have been previously dried at 115°C and 0.001 vacuum Torr to eliminate adsorption water prior to contact with the 4AMP solution.

Mixing and Curing

The rubber sample were prepared in Brabender apparatus at ambient temperature and 30 rpm. The vulcanization parameters were measured using a Monsanto rheometer, Model 750. The physical properties were determined in specimens cured at 165°C attending to their respective curing times and in conformity with national standards (Shore A: UNE 53 130; tensile strength test: UNE 53 510-85; tear strength on Delft-type specimens: UNE 53 516, part 2).

Dynamic Properties

The dynamic properties were determined with a Metravib Viscoanalyzer. The apparatus is based on the forced nonresonance technique, which is particularly suitable for the study of low modulus, high loss factor materials, such as filled rubbers.

RESULTS AND DISCUSSION

The maximum adsorbate adhering to the adsorbent was determined by means of the adsorption isotherm of 4AMP onto sepiolite, which is calculated from the volume in the monolayer. Figure 2 shows the adsorption isotherm at 30°C (graph A), which adjusts to Langmuir's isotherm equation,[12] as the plot
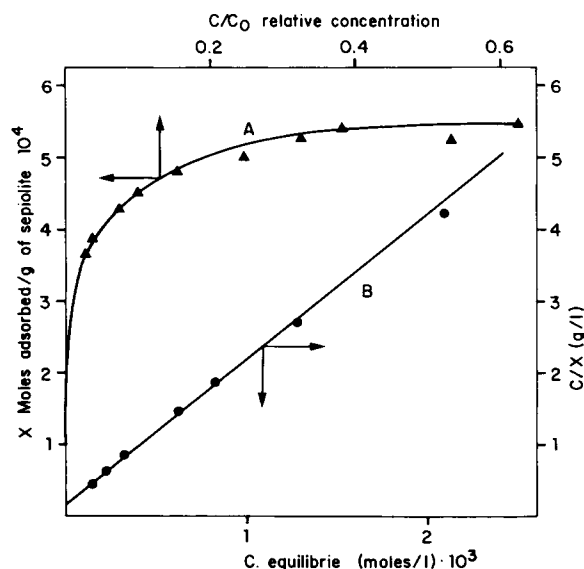
Figure 2 (A) Adsorption isotherm of 4AMP on sepiolite; (B) Langmuir equation.
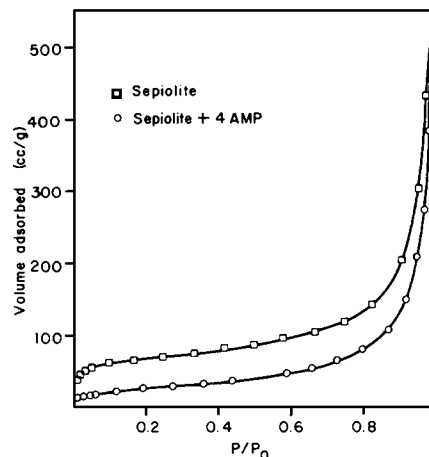
Figure 3 Adsorption isotherms of N_2 on unmodified and 4AMP-modified sepiolite.

of C/X against C results in a straight line (graph B); hence,

$$C/X = 1/bX_m + C/X_m$$

where X_m is the amount of adsorbate per gram of support, b stands for Langmuir's constant, the X_m are the moles adsorbed into the monolayer per gram of solid, and C expresses the adsorbate in moles in equilibrium with the solid. The gradient of the straight line allows for calculation of the monolayer volume X_m. The value obtained is the 5.25×10^{-4} mol 4AMP/g mineral. This X_m value permits one to estimate the number of active acid centers (Brönsted and Lewis) which can be accessed by 4AMP, yielding a value of 3.16×10^{20} acid centers per gram.

Figure 3 represents the nitrogen adsorption isotherms at 77 K of natural and modified sepiolite.

Table I Textural Characteristics of Sepiolite, Original and Modified with 4AMP

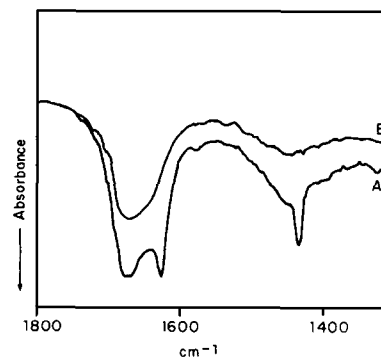|	Sepiolite	Sepiolite + 4AMP
Specific surface (m²/g)	240.3	93.7
Volume layer (cm³/g)	55.2	21.5
Micropores volume (cm³/g)[a]	0.0943	0.0358

[a] Micropore volume was determined by the Dubinin method.[13]
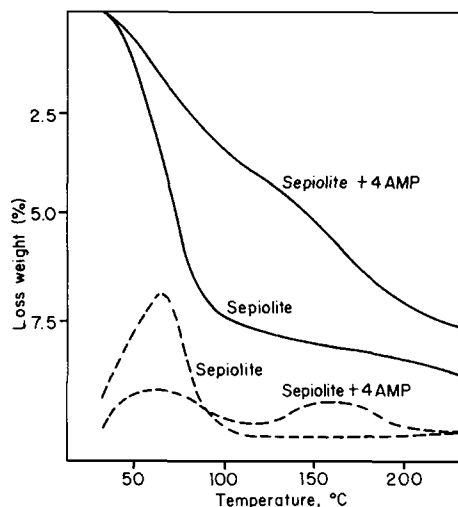
Figure 4   Thermogravimetric curves of unmodified and modified sepiolite.

Figure 5   Infrared spectra of adsorbed 4AMP on sepiolite (A) and natural sepiolite (B).

The treated mineral shows a considerable diminishment of nitrogen adsorption. In Table I some textural parameters are indicated for both samples. Specific surface is reduced from 240 to 94 m²/g, due to the effect of chemical surface modification in the form of a diminution of microporosity. The 4AMP molecules cover part of the external surface inhibiting access of the nitrogen molecules.

Figure 4 shows the variation of weight loss and the respective rate (derive curve) as a function of temperature, for natural and modified sepiolite, respectively. The natural silicate presents a single weight loss event in the thermal range under study, with maximum loss rate at 70°C, corresponding to the release of the physical adsorbed water. In contrast, the modified mineral shows two loss phases: one attributable to adsorbed water with a content in the order of 5%, i.e., lower than in the original sepiolite, and a second phase whose loss peak occurs at 177°C and corresponds to the loss of 4AMP, in

the order of some 5%, a similar value as the one obtained with the adsorption isotherm in solution, X_m, which amounted to 5.5%.

Figure 5 shows the IR spectrum for 4AMP adsorbed onto the sepiolite (a) and for natural sepiolite (b) in the 1800–1300 cm^{-1} region. Modified sepiolite shows the 4AMP IR bands as coordinated to the Lewis centers. The band characteristic of the pyridinic ion, which appears at 1550 cm^{-1}, does not become manifest. The bending band on the N—H plane (1605 cm^{-1}) and the CH₂ bending band (1420 cm^{-1}) of the 4AMP, when adsorbed to the sepiolite, appear at higher frequencies. These bands remain detectable even after heat-treating the product at 130°C under high vacuum conditions (0.0001 Torr), which is indicative of the stability and resistance of the molecules adsorbed onto the active surface centers of the sepiolite.

Effect of 4AMP-Modified Sepiolite on ECO Vulcanizates

In order to determine the reinforcing capacity of this surface-modified mineral, its technological be-

Table II   Rubber Vulcanizate Formulations (phr)[a]

Sample	1	2	3	4	5	6	7	8
Sepiolite	30			50				30
Sepiolite + 4AMP		30			50		30	
Carbon black N550			30			50		
Ethylene thiurea	1.5	1.5	1.5	1.5	1.5	1.5		

[a] Formulations: Hydrin 200, 100; stearic acid, 1; red lead, 5; nickel dibutyl–dithiocarbamate (NBC), 1.
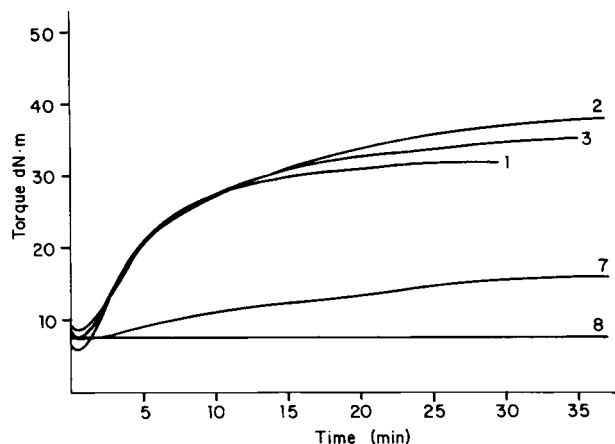
Figure 6 Vulcanization rheograms of different blends. Numbers on curves represent the number blend according to Table II.

havior was studied in ECO vulcanizates. This rubber type was selected because it allows for vulcanization with diamines. The filler, which has several coordinated 4AMP molecules available, acts like a polyamine in the crosslinking reaction. The formulation employed is indicated in Table II. Carbon black, type N 550 (FEF), is included as a reinforcing filler for the purpose of comparing the results obtained with the original and the modified sepiolite, as this particular filler is known for its favorable technological behavior.

The vulcanization rheograms of the different blends are shown in Figure 6. Table III compiles the kinetic parameters of blends containing 30% filler portion. Natural sepiolite proves to have a catalytic effect in the crosslinking reaction, higher rate constants, and a lower activation energy, as compared

Table III   Kinetic Parameters from Crosslinking Reaction of ECO Compounds

Temp (°C)	Sample Unfilled	1	2	3	7
		Rate constants k, min^{-1}			
165	0.1534	0.2033	0.1099/0.0526	0.1509	0.0327
175	0.2689	0.2971	0.1515/0.0926	0.2599	0.0559
185	0.379	0.3377	0.1990/0.1277	0.3767	0.0797
		Activation Energy (kJ/mol)			
	74.8	53.9	50.2/74.2	76.0	74.0

Table IV   Physical Properties of the Compounds

Sample	1	2	3	4	5	6
Unvulcanized properties						
t_c 90 (min), 165°C	17	25	21.5	15	38	24
T_{min} (dN m)	8.5	9	5	14.5	11	7
T_{max} (dN m)	32.5	49	36	43.5	57	48
t_{s2} (min)	2	1.8	1.5	1.8	2.5	1.3
Wallace plasticity	68	67	55	88	85	74
Vulcanized properties						
Stress at 100% (MPa)	2.5	3.6	2.2	3.5	7.8	4.1
Stress at 300% (MPa)	4.1	6.2	6.8	5.1	9.5	10.6
Tensile strength (MPa)	11.6	10.5	10.9	9.6	10.6	11.8
Elongation at break, (%)	935	455	510	865	305	405
Tear strength (N) (die Delft)	35.6	38.5	31.2	48.3	62.2	46
Hardness, Shore A	56	65	55	67	81	68
Compression set (%) (method B, 22 h/150°C)	77	78	69	61	79	58
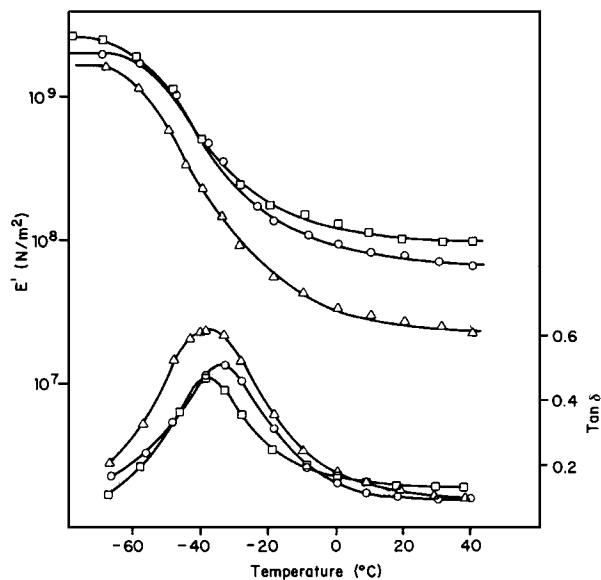
Figure 7 Variation of storage modulus, E', and loss factor, tan δ, versus temperature for mixes based on ECO with 30 phr of filler: ($\square$) sepiolite; ($\bigcirc$) sepiolite + 4AMP; ($\triangle$) carbon black N-550.

to the filler-free blend. In contrast, carbon black presents a similar response to that of the filler-free sample. Regarding the blend prepared with 4AMP-modified sepiolite, an increase in crosslinking density is observed, as well as an increment in stalled torque which even surpasses that of the carbon black attributable to the higher crosslinking density, which, in turn, is triggered by the 4AMP chemically adsorbed to the filler surface and bonded to it by means of reaction with the polymer. In the blends with modified sepiolite there appear two rate constants, as a consequence of two first-order reactions: a first one up to 40% conversion with a high reaction rate, and then another, slower one up to 95% conversion. This latter reaction presents an activation energy comparable to the one in blend no. 7 which does not contain ethylen thiourea as a crosslinking agent, so that the degree of crosslinking obtained in the sample is exclusively due to the action of the modified sepiolite.

Table IV compiles the physical properties of the vulcanizates of the different blends with 30 and 50% filler.

Surface-modified sepiolite shows a clearly better technological behavior than the same filler without chemical surface treatment. Shore hardness A, the moduli, and the tear strength are considerably higher than the values obtained from natural sepiolite and

comparable to the response pattern shown by carbon black N 550. The enhanced values can only be explained in terms of increased crosslinking density, i.e., a greater number of direct bonds between the filler and the polymer achieved through reaction of the amine group with the rubber.

Dynamic Properties

Subsequently the effect of chemical filler surface modification on the dynamic properties of the blend was examined. Figure 7 shows the temperature variations of the elastic modulus E' and the loss factor, tan δ, for vulcanizates with 30% filler portion at a frequency of 7 Hz. As can be observed, the elastic modulus E' of the vulcanizates containing modified sepiolite is higher than the one obtained for original sepiolite and remarkably better than that of carbon black. Regarding loss factor variations, the maximum tan δ value in the sample containing modified sepiolite is displaced towards higher temperatures. It is a well-known fact that the adsorption of polymer chains onto the filler surface produces changes in chain mobility and flexibility, which translates into changes of the glass transition temperature T_g.[14] This phenomenon is enhanced with surface-treated fillers, as during vulcanization chemical bonds between the filler and the polymer are formed.

CONCLUSION

The natural magnesium silicate, sepiolite, of which there exist abundant deposits in our country, improves its reinforcing properties in ECO rubbers, when modified at its external surface with 4-amino-methyl-pyridine. The adsorption energy is high, and the chemical reagent is detected in the Lewis and Brönsted acid centers, which are located at the external surface of the mineral.

The increments in the moduli, tear strength and Shore hardness can be legitimately attributed to the increase in crosslinking density, which has been caused through the participation of the amine groups in the curing reaction of the rubber, thus remaining bonded to the latter.

Based on the above results, the adsorption mechanism of 4AMP on sepiolite (reaction 1), and its application as reinforcing filler in ECO vulcanizates (reaction 2) are summarized in the following scheme:

Reaction 1

Sepiolite

Reaction 2

ECO
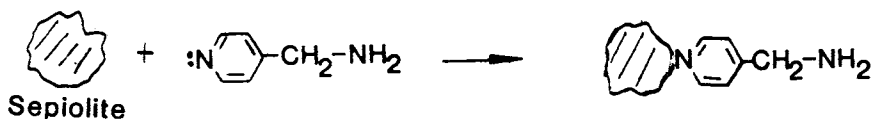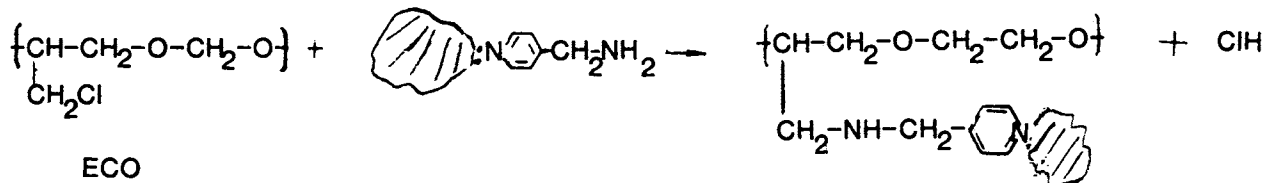
Scheme   Reinforcing mechanism of sepiolite + 4AMP in ECO vulcanizates

The field of application of this chemically modified sepiolite may be extended to other rubbers which allow for vulcanization with diamines, without prejudicing the interesting technological response of this filler shown upon ECO rubber incorporation. Candidates for such extended application would be, among others, polychloroprene, fluorinated and acrylic ethylen (Vamac), as well as polyacrilic rubbers.

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