

# Optimization of a Composite Based on Polyethylene Blends and Sepiolite. Effect of Surface Treatment of the Filler and Morphology of the Composite on Mechanical Properties

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## Synopsis

The optimization of a composite based on polyethylene blend matrices with unmodified and titanate coupling agent-modified sepiolite has been studied. The analysis of the tensile, flexural, and impact behavior shows that the tensile and flexural properties, mainly the moduli, improve with increasing content of both filler and high-density polyethylene (HDPE) in the composite. The surface-modified sepiolite has a behavior similar to the unmodified one and no improvement of the mechanical properties is noticeable. In order to explain these effects a morphological study on fracture surfaces of the composites was performed using scanning electron microscopy.

## INTRODUCTION

The shortage of raw materials has led to a higher consumption and a more efficient use of fillers and reinforcements as a way of extending the supply of resins and reducing the price of moulding compounds.

On the other hand, and more importantly, polymer composites or compounds improve many mechanical and physical properties of plastic materials.

These are some of the most important justifications for the great tendency to fill plastic materials with products of low cost and low energy consumption such as minerals and glasses, with the twofold aim of improving their properties and widening their fields of application. The results obtained to date suggest that sepiolite is a suitable filler for thermoset<sup>1</sup> and thermoplastic<sup>2</sup> materials.

The use of coupling agents has been, fundamentally, directed to increase the mechanical and chemical resistance of the composites as well as to improve their rheological behavior. Among the coupling agents used in this field are the titanium organic compounds whose application has increased in recent years.<sup>3-5</sup> The study of the reaction and characterization of titanate-modified sepiolite showed that organophylization takes place in a monolayer way and the decrease of the specific surface value of the sepiolite, as a function of the percentage of modification, reaches a minimum which corresponds to the optimum titanate percentage obtained from viscometric measures of filler/mineral oil dispersions.<sup>6</sup>

Finally, bearing in mind that municipal wastes contain a high proportion

of low- and high-density polyethylenes,<sup>7</sup> it is of great interest to study their recycling possibilities, in order not only to obtain an economic benefit, but also to diminish the ecological problems they can create. With this aim, a series of polymeric compounds based on polyethylene blends with sepiolite have been prepared. Natural as well as previously titanate-modified sepiolites have been used to study the influence of the organophylization on the mechanical and physical properties of the composite. In this way the ability of the sepiolite as a filler for polyethylene blends and its possible effect of compatibilization is investigated.

An additional study on the mechanical properties and the morphology of the composites is carried out in order to relate both characteristics.

## EXPERIMENTAL

### Materials

Low- and high-density commercial-grade polyethylenes, whose molecular characteristics are described in Table I, were used.

Sepiolite, hydrated magnesium silicate, whose chemical composition corresponds to  $2 \text{MgO}$ ,  $3 \text{SiO}_2$ ,  $2 \text{H}_2\text{O}$ , delivered by Tolsa (Spain), was used as a filler to prepare the composites. This sepiolite with isopropyl triisostearoyl titanate (KR-TTS, a titanate coupling agent manufactured by Kenrich Petrochemicals Inc.) -modified surface, whose chemical treatment and characterization were described elsewhere<sup>6</sup> was also used.

The physical and chemical properties of both natural and modified sepiolites are compiled in Table II.

### PREPARATION OF COMPOSITES

The composites were obtained by means of hot rolls, at a temperature of  $170^\circ\text{C}$  and for intervals of about 15 minutes. First, both homopolymers were blended and then the filler was incorporated to the polymer matrix. Plaques of nominal dimensions of  $120 \times 120 \times 4$  or 3 mm thickness were obtained at  $180^\circ\text{C}$  by compression moulding of these products in an electrically heated press and further quenching at room temperature under pressure. Test specimens were cut from the compression-moulded plaques with dimensions according to the standard specifications.

TABLE I  
Molecular Characteristics of the Homopolymers Investigated

Polymer	Code	Manufacturer	Melt index g/10 min 190°C		$M_w$	Density g/cm <sup>3</sup>
			2.16 kg	5 kg		
HDPE	Marlex 6006 L	Phillips Calatrava	—	2.33	164,000	0.945
LDPE	PE 017	Alcudia SA	6.7	—	—	0.916

TABLE II  
Physical and Chemical Characteristics of the Sepiolites

Filler	Spec. surface BET (m <sup>2</sup> /g)	% Org. Mat.	%Mol. Ti × 10 <sup>4</sup>	OH/nm <sup>2</sup>
Sepiolite	205	—	—	0.77
Sepiolite + 3% KR-TTS	102	3.17	32	0.67

These data have been taken from ref. 6.

### MECHANICAL TESTING

Tensile tests were carried out on an Instron TT-CM model at  $23 \pm 1^\circ\text{C}$  and at a cross-head speed of 5 mm/min. The dimensions and size of the specimens correspond to the type A described in the Spanish Standard UNE 53023.

Flexural tests were performed on an Instron 1026 model at  $23 \pm 1^\circ\text{C}$  at a cross-speed of 2 mm/min. The span was of 60 mm and the nominal dimensions of the specimens  $80 \times 10 \times 4$  mm, according to UNE 53022-76.

Impact tests were made following the UNE 53021 Charpy method. Conventionally shaped impact specimens with sharp Vee notches were tested in a Ceast Fractoscope testing machine, recording the energy to fracture at  $23^\circ\text{C}$ .

### MATHEMATICAL TREATMENT AND OPTIMIZATION OF THE COMPOSITE

To obtain the optimum matrix composition and filler content of the composite, the Box-Hunter statistical method was applied to the experimental results of the mechanical properties in a wide range of both variables and with a small number of experiences.<sup>8-11</sup> In this special case the two-variables method was used.

A design of this type, with eight experiences on the circumference and five in the center is shown in Figure 1. This design is formed by 13 experimental combinations distributed as follows:

- Four combinations correspond to the factorial  $2^2$ .
- Four combinations more to obtain the central design rotability. These are called "star" combinations.
- Five experiences in the center in order to calculate the experimental error.

To establish the experimental levels it is necessary to code both variables in order to obtain the five levels of  $-2^{1/2}$ ,  $-1$ ,  $0$ ,  $+1$ , and  $+2^{1/2}$ . The levels or values of the coded variables  $X_1$  and  $X_2$  were obtained from the equation:

$$X_i = \frac{X'_i - X_0}{\Delta}$$

where  $X_i$  is the value or level to code,  $X'_i$  is the uncoded variable,  $X_0$  is the

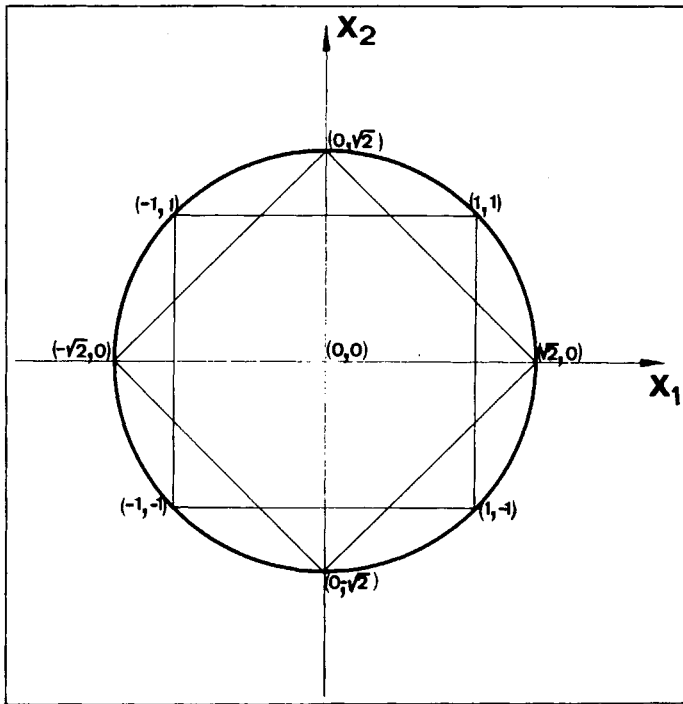


Fig. 1. Scheme of a compound design made up of a central and a rotative design for the case of two variables as Box-Hunter method.

central value (mean value of the matrix composition or percentage of sepiolite in the composite), and  $\Delta$  is the distance between the central value and the +1 and -1 levels.

The corresponding values of both variables, compiled in Table III, were calculated considering that the percentages of high- and low-density polyethylenes vary from 0 to 100% of the matrix composition and the filler content may vary from 0 to 30% in the composite.

Finally, the composition of the samples utilized in this study are shown in Table IV where  $X_1$  is the percentage of HDPE in the polymer matrix and  $X_2$  is the percentage of sepiolite (modified or not) in the composite.

TABLE III

Levels	$X_1$ (% HDPE in the polymeric matrix)	$X_2$ (% Sepiolite in the composite)
$-2^{1/2}$	0.0	0.0
-1	14.64	4.39
0	50.00	15.00
+1	85.36	25.61
$+2^{1/2}$	100.00	30.00

TABLE IV  
Experimental Combinations

Exp. no.	Codified variables		Uncodified variables	
	$X_1$	$X_2$	$X_1(\%)$	$X_2(\%)$
1	-1	-1	14.64	4.39
2	+1	-1	85.36	4.39
3	-1	+1	14.64	25.61
4	+1	+1	85.36	25.61
5	$-2^{1/2}$	0	0	15.00
6	$+2^{1/2}$	0	100.00	15.00
7	0	$-2^{1/2}$	50.00	0
8	0	$+2^{1/2}$	50.00	30.00
9	0	0	50.00	15.00
10	0	0	50.00	15.00
11	0	0	50.00	15.00
12	0	0	50.00	15.00
13	0	0	50.00	15.00

$X_1$  = % HDPE in the polymeric matrix.

$X_2$  = % Sepiolite in the composite.

## RESULTS AND DISCUSSION

### Mechanical Properties

The mechanical properties or responses of the composites in impact, tensile, and flexural testing are shown in Table V.

Series I corresponds to the composites prepared with unmodified sepiolite and series II to the titanate coupling agent-modified sepiolite.

### OPTIMIZATION OF THE COMPOSITE

In order to optimize the composition of the polymeric matrix and the percentage of filler, the Box-Hunter method was applied. From the results, treated in an Olivetti M-20 computer, the equations of the response surfaces were obtained. These equations are shown in Table VI.

The graphics obtained in the plotter are shown in Figures 2 to 11, and in each curve the level or value of the corresponding property is indicated. From these graphics, pairs of values of the experimental variables can be selected to obtain a composite with specific mechanical properties and also to compare the relative behavior of different materials.

The impact strength (Figs. 2 and 3) decreases as the filler content increases because the filler acts as a stress concentrator. For the same filler content, the impact strength remains practically constant until a 50% content of HDPE in the matrix is reached, then it increases as the HDPE percentage in the matrix increases. Both unmodified and organophylized sepiolites have a similar impact behavior.

It can be seen in Figures 4 and 5 that the moduli increase as the filler content increases, following the normal behavior of composite materials

TABLE V  
Mechanicals Properties of the Composites

Sample	Impact energy		Tensile behavior				Flexural behavior					
	(KJ/m <sup>2</sup> ), -30°C		Moduli, MPa		Strength, MPa		Moduli, MPa		Elong. max. strength <sup>a</sup>		Strength 2 mm <sup>b</sup>	
	I	II	I	II	I	II	I	II	I	II	I	II
1	3.77	3.33	380	364	9.8	9.7	315	311	13.58	12.72	3.4	3.4
2	3.24	3.44	1107	1333	21.3	20.9	843	829	12.51	11.43	9.5	8.9
3	1.95	1.55	579	579	11.4	11.4	493	502	13.73	12.67	4.9	5.5
4	2.10	2.14	1608	2054	23.1	22.8	1283	1283	10.51	9.86	14.2	14.3
5	2.43	2.81	326	406	9.7	9.8	224	205	12.47	13.44	2.6	3.0
6	3.37	2.82	2102	1767	26.2	23.7	1250	1354	10.96	10.21	13.5	14.0
7	5.57	5.57	698	698	14.7	14.7	533	533	13.36	13.36	9.3	9.3
8	1.57	1.26	1389	1411	17.3	17.3	1079	998	10.46	10.66	11.1	10.3
9	2.24	2.08	1140	961	16.4	16.3	753	667	11.56	11.98	8.4	7.4
10	2.40	2.07	1059	975	15.9	16.2	772	671	11.80	11.80	7.9	7.4
11	2.00	2.60	1087	1127	16.2	16.9	773	742	11.80	11.61	8.4	8.1
12	2.07	2.34	1075	1073	15.7	16.7	778	739	11.20	11.63	8.3	7.9
13	1.98	2.39	1023	1150	16.0	16.4	717	754	11.58	11.80	8.0	8.0

Series I: Composites filled with unmodified sepiolite. Series II: Organophylized sepiolite.

<sup>a</sup> Elongation corresponding to the maximum flexural strength, mm.

<sup>b</sup> Flexural strength corresponding to a deflection of 2 mm, MPa.

TABLE VI

Parameters	Response equations
Impact strength I	$Y = 2.138 + 0.118 X_1 - 1.077 X_2 + 0.263 X_1^2 + 0.598 X_2^2 + 0.170 X_1 X_2$
Impact strength II	$Y = 2.296 + 0.089 X_1 - 1.147 X_2 + 0.134 X_1^2 + 0.434 X_2^2 + 0.120 X_1 X_2$
Young's modulus I	$Y = 1076.8 + 533.408 X_1 + 209.634 X_2 + 16.037 X_1^2 - 69.212 X_2^2 + 75.5 X_1 X_2$
Young's modulus II	$Y = 1057.2 + 546.057 X_1 + 243.023 X_2 + 17.650 X_1^2 + 1.650 X_2^2 + 126.5 X_1 X_2$
Tensile strength I	$Y = 16.048 + 5.819 X_1 + 0.896 X_2 + 0.805 X_1^2 - 0.157 X_2^2 + 0.055 X_1 X_2$
Tensile strength II	$Y = 16.5 + 5.283 X_1 + 0.903 X_2 + 0.082 X_1^2 - 0.293 X_2^2 + 0.037 X_1 X_2$
Flexural modulus I	$Y = 758.5 + 346.226 X_1 + 173.715 X_2 - 20.094 X_1^2 + 14.406 X_2^2 + 65.475 X_1 X_2$
Flexural modulus II	$Y = 714.72 + 365.521 X_1 + 162.796 X_2 + 22.034 X_1^2 + 15.209 X_2^2 + 65.9 X_1 X_2$
Flexural strength 2 mm deflection I	$Y = 8.2 + 3.855 X_1 + 1.093 X_2 - 0.36 X_1^2 + 0.720 X_2^2 + 0.800 X_1 X_2$
Flexural strength 2 mm deflection II	$Y = 7.768 + 3.742 X_1 + 1.105 X_2 + 0.075 X_1^2 + 0.732 X_2^2 + 0.802 X_1 X_2$
Price of the composite (Ptas/kg) I	$Y = 149.95 + 3.005 X_1 - 15.592 X_2 - 0.001 X_1^2 - 0.001 X_2^2 - 0.375 X_1 X_2$

Series I: Unmodified sepiolite.

Series II: Organophylized sepiolite.

based on a polymeric matrix and a rigid particulate filler. However, the increase of the moduli seems to be higher in the case of the unmodified sepiolite than in the case of the organophylized one. The moduli also increase with the HDPE content in the matrix.

On the other hand, the maximum value of tensile strength obtained from the stress-strain curves slightly increases with filler content for the same polymeric matrix composition; however, there is no sensible difference in the behavior of the composites prepared with both fillers (Figs. 6 and 7).

The results obtained in flexural testing show an increase of the moduli with filler content and, in general, this increase is slightly higher in the case of the unmodified sepiolite (Figs. 8 and 9). The values of the elongation at maximum strength and the strength at a deflection of 2 mm are very similar and they behave in the same way (Table V and Figs. 10 and 11).

In all cases the mechanical properties improve as the HDPE content increases.

However, as indicated above, the filler treatment has little effect on these properties. This can be explained by considering that the organophylation tends on one side to increase the adhesion at the filler/polymer interface

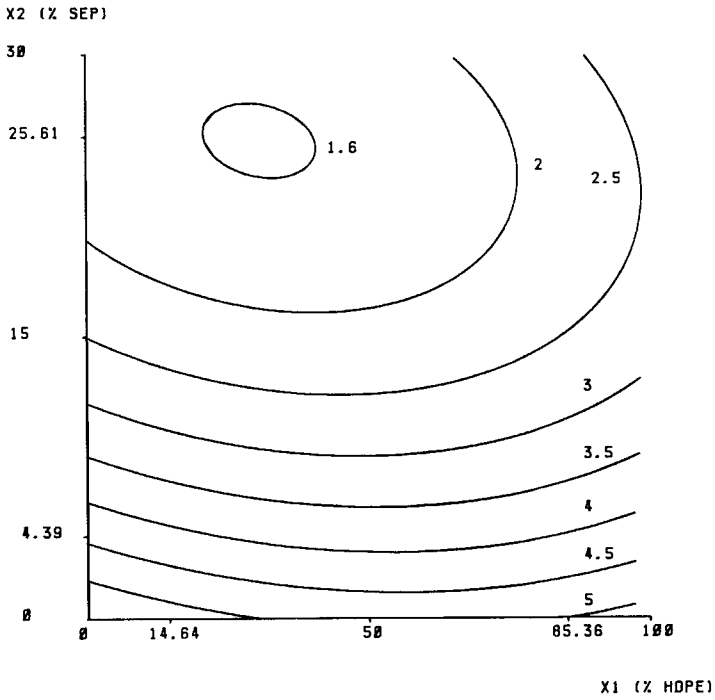


Fig. 2. Impact strength (KJ/m<sup>2</sup>) as a function of HDPE (X<sub>1</sub>) and unmodified sepiolite (X<sub>2</sub>) percentages.

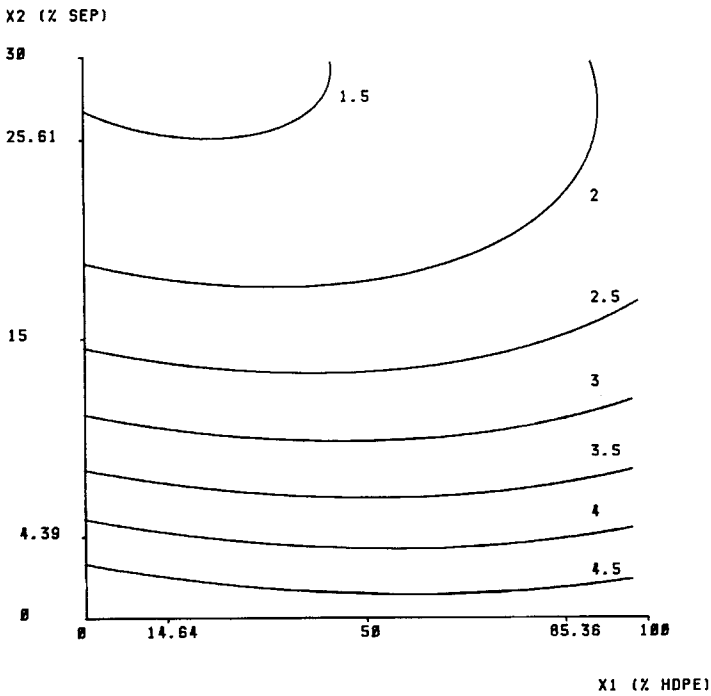


Fig. 3. Impact strength (KJ/m<sup>2</sup>) as a function of HDPE (X<sub>1</sub>) and organophylized sepiolite (X<sub>2</sub>) percentages.



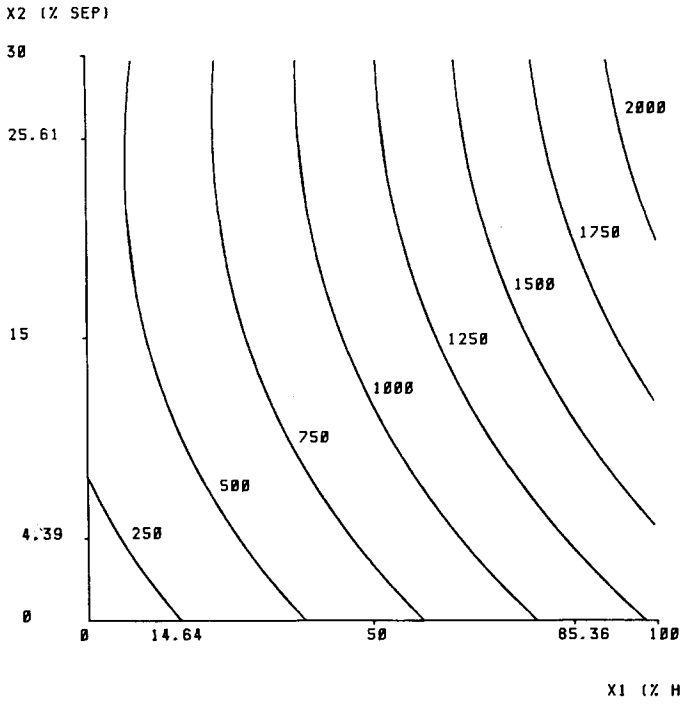


Fig. 4. Tensile modulus (MPa) as a function of HDPE ( $X_1$ ) and unmodified sepiolite ( $X_2$ ) percentages.

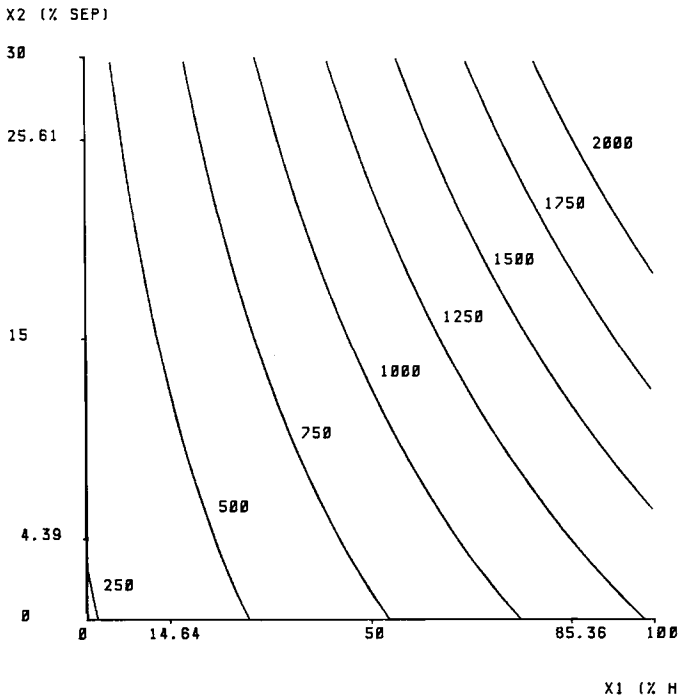


Fig. 5. Tensile modulus (MPa) as a function of HDPE ( $X_1$ ) and organophylized sepiolite ( $X_2$ ) percentages.

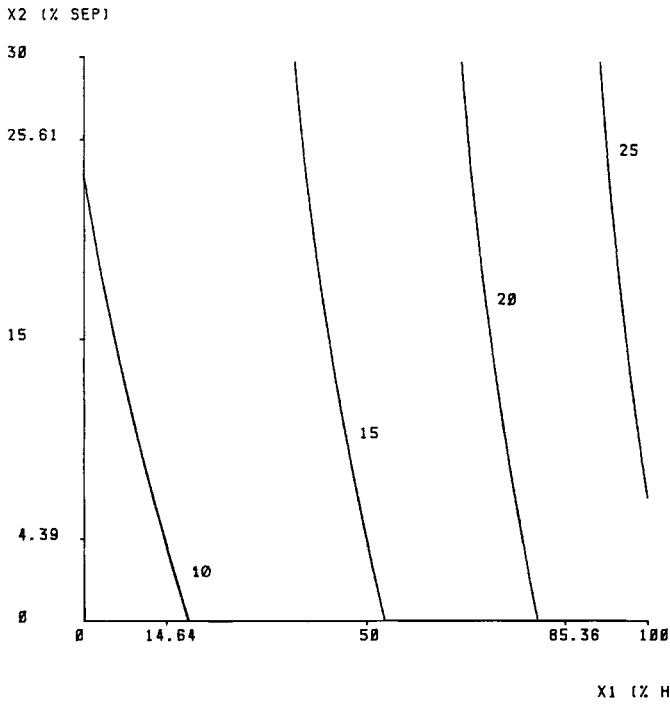


Fig. 6. Tensile strength (MPa) as a function of HDPE ( $X_1$ ) and unmodified sepiolite ( $X_2$ ) percentages.

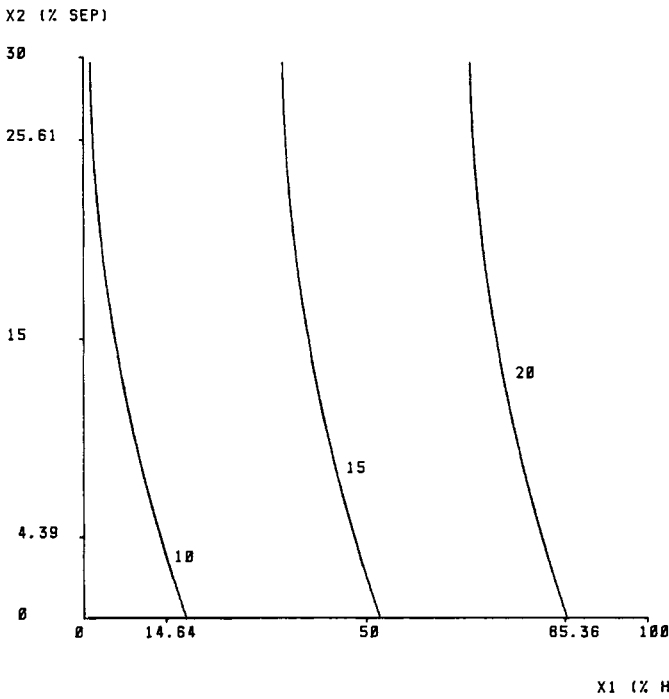


Fig. 7. Tensile strength (MPa) as a function of HDPE ( $X_1$ ) and organophylized sepiolite ( $X_2$ ) percentages.

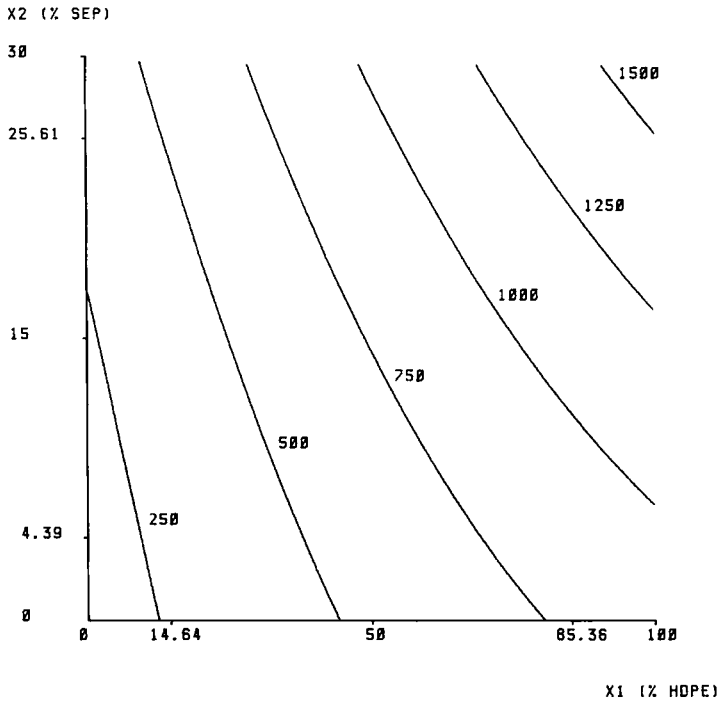


Fig. 8. Flexural modulus (MPa) as a function of HDPE ( $X_1$ ) and unmodified sepiolite ( $X_2$ ) percentages.

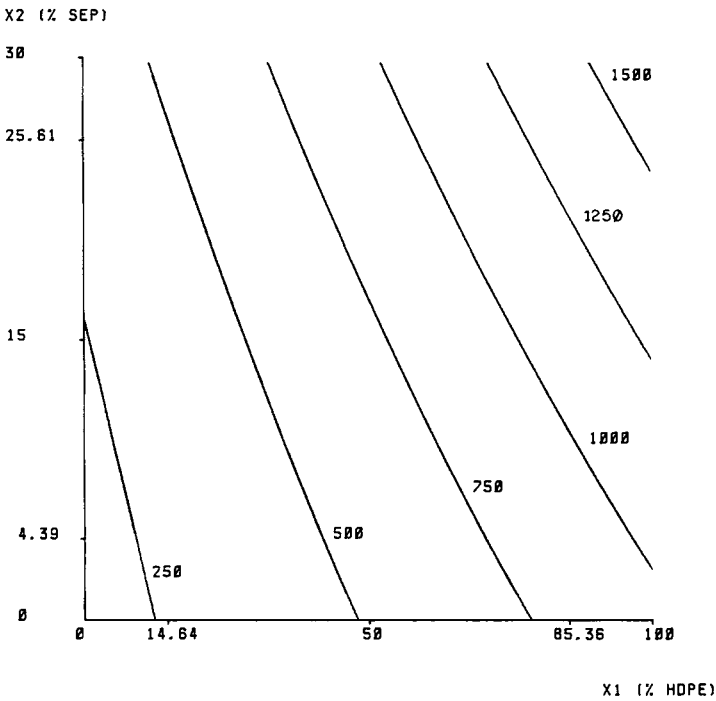


Fig. 9. Flexural modulus (MPa) as a function of HDPE ( $X_1$ ) and organophylized sepiolite ( $X_2$ ) percentages.

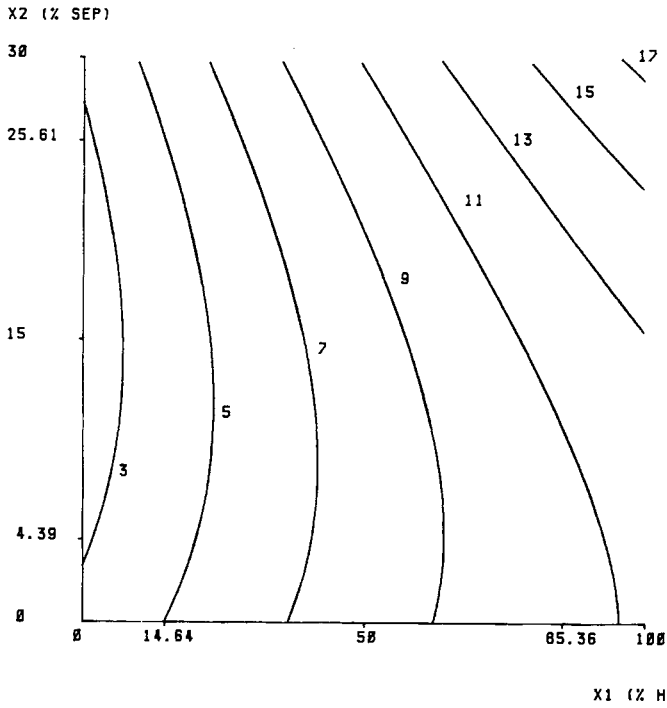


Fig. 10. Flexural strength (MPa) as a function of HDPE ( $X_1$ ) and unmodified sepiolite ( $X_2$ ) percentages.

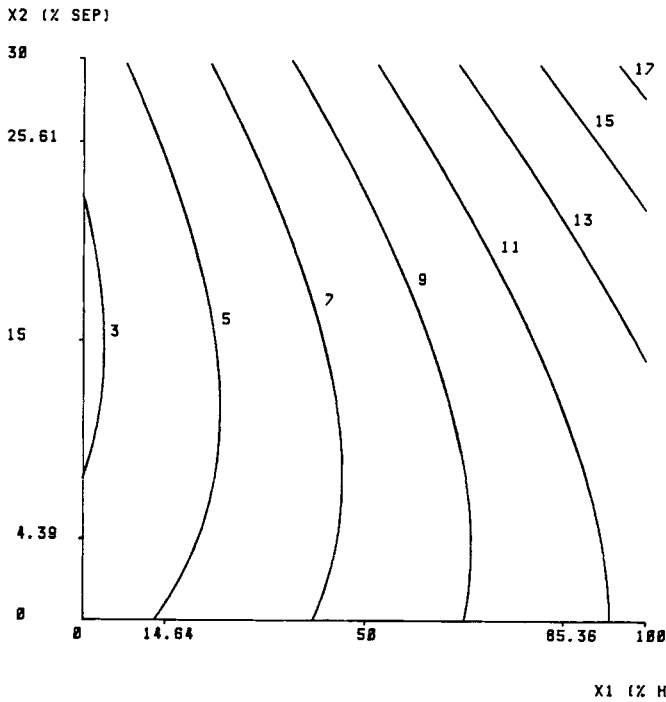


Fig. 11. Flexural strength (MPa) as a function of HDPE ( $X_1$ ) and organophylized sepiolite ( $X_2$ ) percentages.

and also to increase the particle size, as it can be deduced from the decrease of the filler specific surface value.<sup>6</sup> The effect of both phenomena on the mechanical properties are opposite and consequently cancel each other.

### ECONOMICAL STUDY OF THE COMPOSITES

Taking into account the prices of both polyethylene and the unmodified filler at December 1984, the Box-Hunter method has been applied to investigate the price of the composites. It has been found that the price of the composite increases as HDPE content does and decreases as the filler content increases.

If the mechanical properties and prices of the composites are compared, it can be seen that the incompatible blends of both polyethylenes have better properties, with a lower price, as the filler content increases. These results are shown in Figure 12.

### MORPHOLOGICAL STUDY

Fracture surfaces of the composites have been observed in a scanning electron microscope to study their morphology. The microphotographs obtained suggest that the unmodified sepiolite by itself infers a physical joint between its surface and the polymeric matrix due to its fibrous structure.

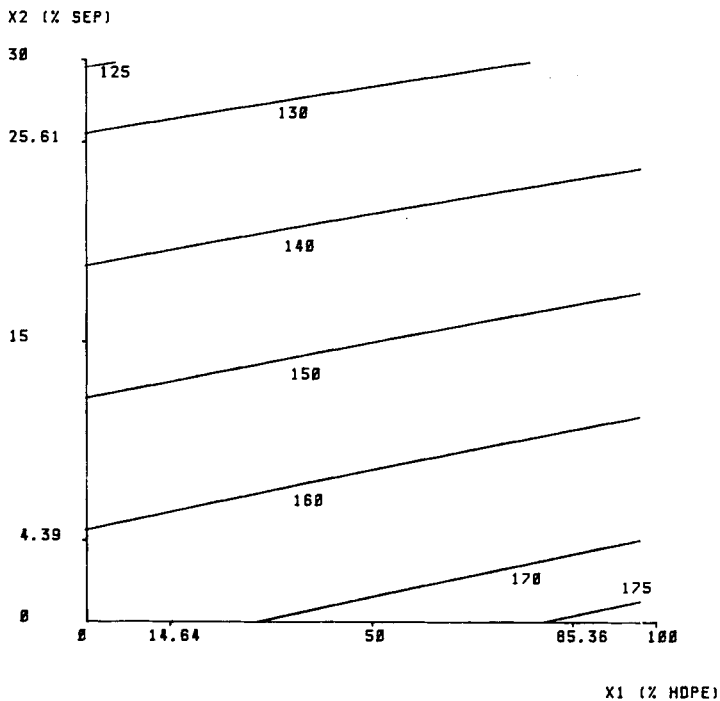


Fig. 12. Cost of the composite (Ptas/kg, December 1984) as a function of HDPE ( $X_1$ ) and unmodified sepiolite ( $X_2$ ) percentages. (U.S.\$ = 170 Ptas.)

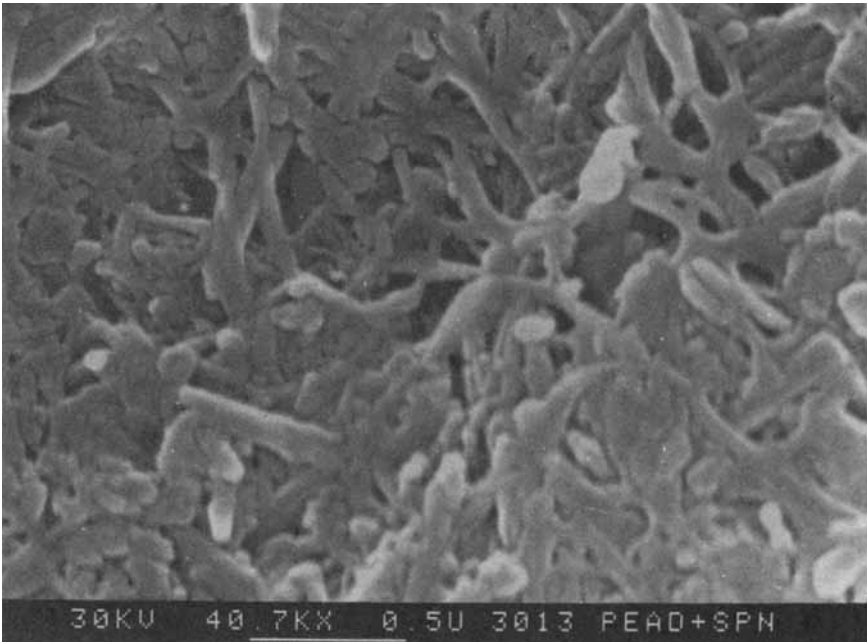


Fig. 13. Structure of the unmodified sepiolite.

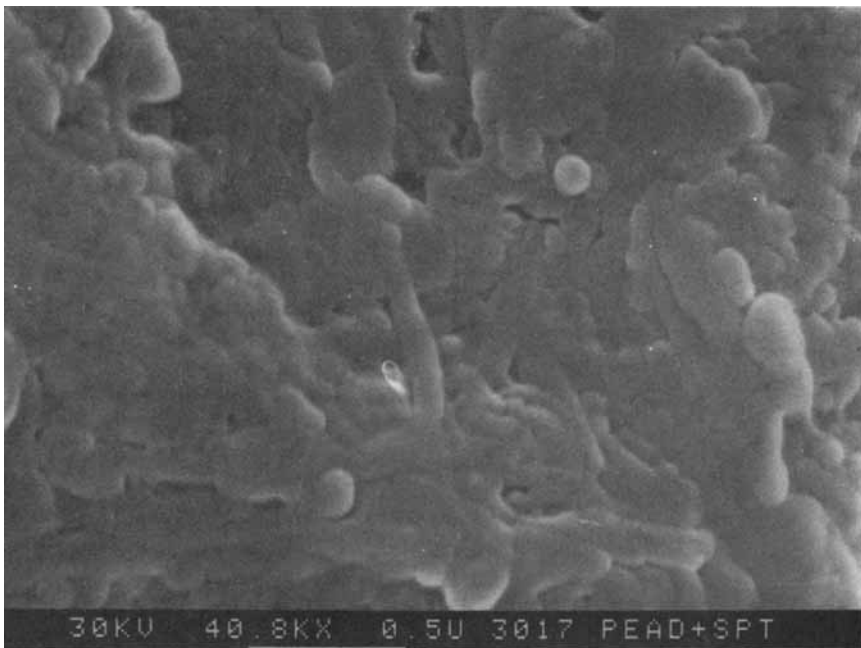


Fig. 14. Structure of the organophylized sepiolite.

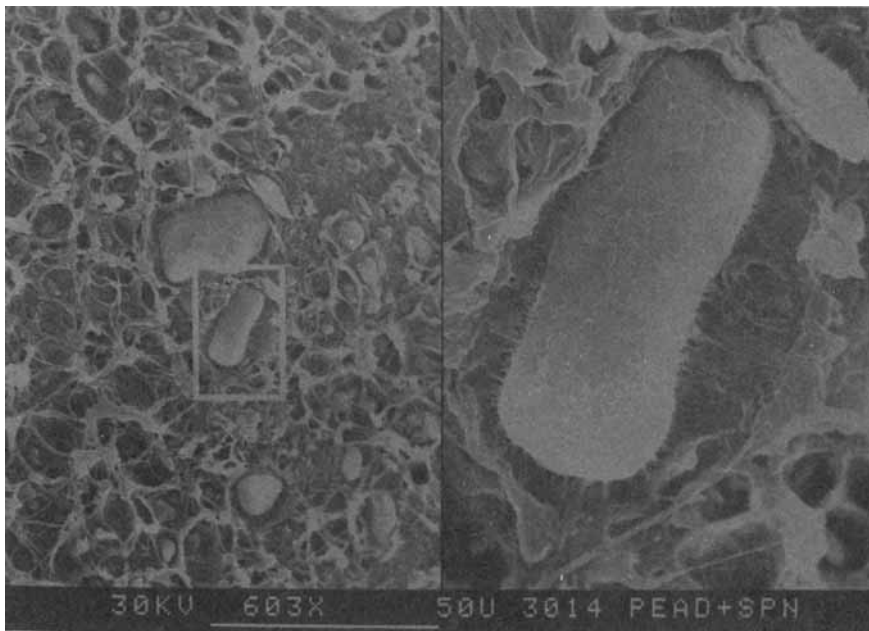


Fig. 15. Fracture surface of a composite based on a 50/50 HDPE and LDPE polymeric matrix and 15% of unmodified sepiolite. (603 and 3015 magnifications.)

This fact confirms the higher effectivity of the sepiolite as a filler for polymers in comparison with other traditional fillers.<sup>11</sup>

The organophylization of the sepiolite partially removes its fibrous structure (Figs. 13 and 14), but it promotes joint domains between the particle and the matrix as can be seen in Figures 15 to 17 where the filler/polymer interface of both the unmodified and the organophylized sepiolites can be compared.

## CONCLUSIONS

This study leads to the following conclusions:

Tensile and flexural mechanical properties of the composites, mainly the moduli, improve as the filler content increases. However, impact resistance decreases.

Tensile and flexural mechanical properties increase as HDPE content in the polymeric matrix does. Practically, the percentage of HDPE in the matrix has no effect on impact strength.

The organophylization hardly affects the mechanical properties of the composites. For this reason, the organophylization with KR-TTS titanate is uneconomical.

The economic study carried out on the composites with better mechanical properties suggests that the use of sepiolite as a filler for these polymer blends is not only advantageous but also advisable.

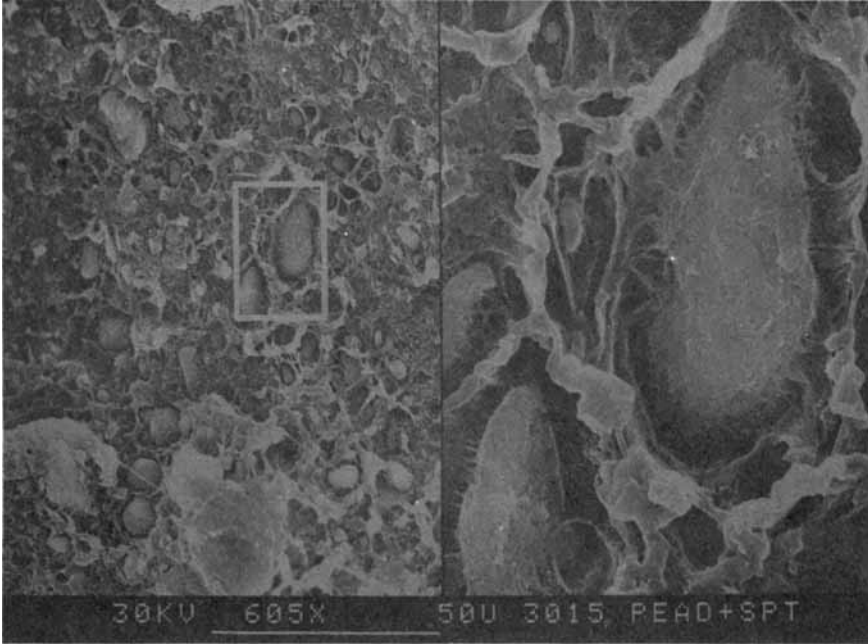


Fig. 16. Fracture surface of a composite based on a 50/50 HDPE and LDPE polymeric matrix and 15% of organophylized sepiolite. (605 and 3025 magnifications.)

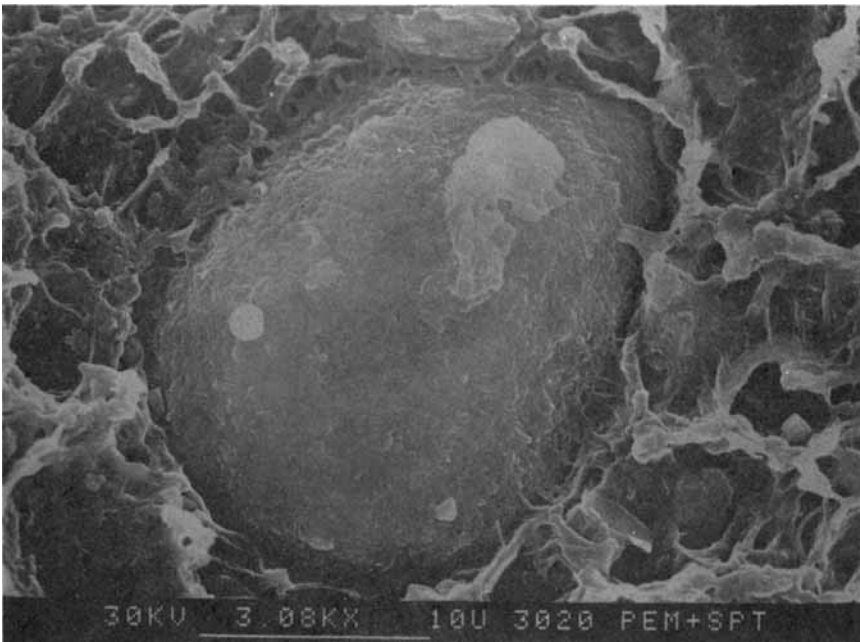


Fig. 17. Particle of organophylized sepiolite in a 50/50 HDPE and LDPE polymeric matrix. (3080 magnifications.)



Finally, it would be interesting to study the effect of other types of titanate coupling agents which would lead to obtaining not only a physical joint but a chemical linkage at the filler/polymer interface. At present, our studies are going in that direction and the results will be reported in the near future.

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