Morphological, Structural, and Interfacial Changes Produced in Composites on the Basis of Polypropylene and Surface-Treated Sepiolite with Organic Acids I. Surface Treatment and Characterization of the Sepiolites

J. L. ACOSTA, M. C. OJEDA, E. MORALES and A. LINARES, *Instituto de Plásticos y Caucho C.S.I.C. Juan de la Cierva 3, 28006, Madrid Spain*

Synopsis

This research was conducted in order to gain a better knowledge of the possibilities deriving from sepiolite as a polypropylene filler. Special stress has been laid on the study of morphological, structural, and interfacial changes produced by the simple incorporation of sepiolite in the polymeric matrix, as well as on the effects of these changes on all the properties of the resulting composites. In the light of the relevance of filler surface activity with regard to the physical behavior of these materials, we modified this activity through chemical reaction of the superficial silanol groups in the sepiolite with different aliphatic organic acids. This paper includes a description of the esterification procedures and a characterization of the different sepiolites obtained.

INTRODUCTION

Knowledge of polymeric composites goes back to antiquity. Yet their most spectacular boom, from a scientific point of view, began during the 1960s, when their microstructure was studied as it relates to their properties. The important role played by the interface in the overall behavioral pattern of the composite was immediately inferred. Since then such studies have enjoyed considerable popularity and have yielded an enormous amount of data, all of which coincided in highlighting the complexity of the interfacial zone and the consequential difficulties for research, as it is the field of interaction of many processes, which in different orders of magnitude have a bearing on the properties.

Among these processes the following deserve special mention.

1. The interfacial region is a space where there exist a great number of tensions generated by the different degrees of thermal expansion in the components.

2. As a general rule, fillers constitute the preferential sites of adsorption or desorption of certain molecular segments.

3. The interface may occasionally constitute a reaction site, because of the effect of the surface activity of the filler.

4. The interface activates adhesion phenomena, which are closely related to the phenomenon of compatibility.

CCC 0021-8995/86/072351-09$04.00

5. In crystalline polymers the interface constitutes a preferential environment for crystallization phenomena to take place around the filler particles, producing ordered microstructures different from those of the matrix proper.

6. The filler also affects the environmental microviscosity conditions, among others.

Progress in the design and application of these materials is dependent on adequate knowledge and control of all of these processes.

Initially the concept of interface was based on the definition of Hashin and Rosen,[1] according to which the interface was confined to the contact area between the polymer and the filler. It supported the view that the distinctive features of this zone had a special effect on the technological properties of the resulting composite, on the lines that good adhesion and/or compatibility would entail an improvement of the mechanical properties and, inversely, bad adhesion and/or compatibility would have a negative effect on them. As a consequence, compatibilizing organic compounds began to be used under the name of coupling agents, with good results in many cases.[2]

More recent theories[3,4] point towards the fact that adhesion and compatibility between the polymer and the filler–with or without coupling agents—were not the sole factors responsible for the improvements achieved in the properties. Moreover, in certain cases a decisive role was played in this respect by an intermediate zone, eventually called mesophase. As a function of the filler type, the polymer used, and the degree of interaction between the polymer and the surface of the solid particle, a superficial layer (mesophase) of variable thickness is built up on the particle periphery whose morphological and structural properties differ from those of the underlying polymer, even if the chemical composition remains the same.

Taking into account that the concepts of interfacial adhesion and compatibility, as well as that of the emergence of an ordered mesophase in polymeric composites, are constantly being revised, we undertook this research with the aim of producing argumentative evidence for discussion. We selected for our study a composite based on polypropylene and sepiolite (a clay found in abundance with excellent possibilities in the field of polymer reinforcement), which led us to center our interest on (1) the study of the influence of the different organic traces chemically bonded to the sepiolite surface vis à vis interfacial adhesion and compatibility, as well as a comparison between the technological properties of polypropylene composites containing surface-treated sepiolite and those of untreated sepiolite-polypropylene composites; and (2) a study to demonstrate that an ordered mesophase is actually built up around the sepiolite particles, when they are incorporated into a polypropylene matrix, and that their specific nature will influence the whole spectrum of composite properties.

In order to achieve these two objectives it was necessary to conduct a study of the thermal, mechanical, dynamic, morphological, and kinetic properties, the results of which will be forthcoming. This paper will deal with the synthesis and the distinctive features of sepiolites esterified with different aliphatic organic acids.

EXPERIMENTAL

Material

The raw materials were sepiolite (Sep) supplied by TOLSA (Spain) in micronized form and different sepiolites surface treated (esterified) with aliphatic organic acids.

Sepiolite is a hydrated magnesium silicate of fibrous morphology and superficial silanol groups (Si-OH), with the following ideal formula: $Si_{12}Mg_8O_{30}(OH)_4(H_2O)_48H_2O$.[5] Surface-treated sepiolites are obtained by means of condensation reaction of the superficial hydroxyl groups with the acid clusters of the reagent. The following acids were used for surface treatment: isobutyric (ISO), heptanoic (ENA), caprylic (CAP), and lauric (LAU) acid.

Procedures

Surface Treatment

The chemical surface treatment reaction was produced in a double-walled reactor filled with benzene (1500 ml) and sepiolite (200 g). The dispersion was heated to boiling temperature, at which point the water retained in the mineral began to separate azeotropically. Once the water was eliminated, the catalyst was added which was, p-toluene sulfonic acid (0.2 g). The acid reagent was gradually added (25 g). Azeotropic reagent water separation set in immediately. The water-free sepiolite was then filtered and cleared of impurities in several washouts with benzene, ethanol, and acetone and finally dried in a vacuum oven at 90°C and 10^{-1} mm Hg over 24–48 h until the sample weight remained constant. The samples obtained by this procedure were micronized and dried again under the same conditions.

Procedure Used to Determine Superficial Hydroxyl Groups

The number of superficial hydroxyls in the different sepiolite samples was determined by means of the method of Armistead and Hockey,[6] in which trichloromethylsilane is used as a specific reagent for the superficial silanol groups present on the sepiolite surface.

Procedure Used to Determine Specific Surface

The method used for specific surface calculations was BET[7] in all samples. Prior to application of this technique the samples were degasified (10^{-4} mm Hg) during 16 h and at 130°C.

Micropore volume was calculated by means of Dubinin's method.[8]

Elementary Carbon Microanalysis

Prior to the analysis, the original sepiolite was treated with hydrogen peroxide in order to prevent any remaining organic matter from interfering with the results of elemental microanalysis.

Analytic Techniques

For the surface treatment reaction a double-walled reactor was used with a silicone circuit between the inner and outer wall, which was maintained at a constant temperature of 86°C by means of a thermostatic Haake N3 bath.

Micronization of the surface-treated samples was done in a cyclone T-X Laboratory Jet Mill manufactured by Trost Equipment Co.

The spectroscopic techniques used were IR spectrophotometry on a 457 Perkin-Elmer. X-ray difractograms were obtained on a Philips PW-1050/TW-1051 with $K\alpha_1$ copper radiation $\lambda = 1.54501$; Ni filter and goniometer speed were $2°\theta/\text{min}$.

Elementary carbon microanalysis was done on a Perkin-Elmer CHNO microanalyzer, model 240.

Specific surfaces and micropore distribution were studied on a Micromeritics (Accusorb 2100E).

Differential scanning calorimetry (DSC) was performed by means of a Mettler system TA 3000; particle size was determined on a ZM Coulder Counter.

RESULTS AND DISCUSSION

All surface-treated sepiolites, as well as the original sepiolite, were analyzed by means of chemical, physical, and spectroscopic techniques in order to verify (1) from a chemical point of view, if a genuine chemical esterification had taken place; (2) from a physical point of view, if the surface treatment reaction had produced changes in the intrinsic properties of the sepiolite (such as particle size or specific surface), and (3) from a structural point of view, with regard to modifications in the crystalline network of the sepiolite.

Table I compiles the results obtained from elementary carbon analysis, the number of superficial hydroxyl groups, DSC, and particle size for the original sepiolite as well as for the surface-treated samples.

As was mentioned above, BET was the method of choice for specific surface determination. The respective data are shown in Table II. Specific surface and micropore distribution are reflected in Figs. 1 and 2 for untreated and surface-treated sepiolite, respectively.

TABLE I
Elementary Analysis, Superficial Hydroxyl Groups, Granulometric Analysis,
and Differential Scanning Calorimetry (DSC) for All Samples

Samples	Elem. analysis of carbon	Superficial hydroxyl groups (OH per 100 Å^2)	Diameters (50%) (μm)	Exothermic transformations (°C)
Sep	0.29	0.92	10.87	—
Sep ISO	4.51	0.00	9.61	373
Sep ENA	5.18	0.00	9.46	384
Sep CAP	5.23	0.00	8.95	393
Sep LAU	5.38	0.00	10.87	422

TABLE II
Isothermic Analysis (BET) for All Samples

Samples	Specific surface (m^2/g)	C (BET)	E (cal/g)	Vol. micropores (ml/g)
Sep	182	96	1988	0.09
Sep ISO	157	43	1865	0.06
Sep ENA	138	86	1972	0.05
Sep CAP	152	40	1855	0.06
Sep LAU	139	77	1955	0.05

The use of differential scanning calorimetry supplied evidence supporting the existence of exothermic transformations for the surface-treated samples, transformations that are not present in untreated sepiolite. Figure 3, by way of illustration, shows the thermograms of a sepiolite sample surface treated with caprylic acid. The remaining samples likewise present transformations at the temperatures indicated in Table I.

X-ray spectroscopy (Fig. 4) and IR spectroscopy (Fig. 5) were the techniques used for spectroscopic characterization.

Primary evidence that proves that the esterification reaction has in fact taken place is supplied by the azeotropically eliminated water, that is, the output from the condensation of the acid groups in the reagent with the superficial silanol groups of the sepiolite. As the sepiolite samples, prior to the onset of the surface treatment reaction, had been carefully dried, eliminating all water adsorbed by the mineral, the only way to explain why further azeotropic elimination of water occurs when adding the respective reagent in the presence of the catalyst is to assume that a true condensation reaction has actually been produced.

In order to confirm the presence of organic matter chemically bonded to the mineral surface and in the attempt to verify the stuctural transformations produced in the original sepiolite under the effect of surface treatment, we applied the chemical, physical, and spectroscopic methods described. Prior to the use of any of the characterization techniques, as indicated above, the samples were carefully purified and repeatedly washed in several organic solvents (benzene, ethanol, and acetone) and subsequently dried at 90°C and 10^{-1} mm Hg over 24–48 h until constant sample weight
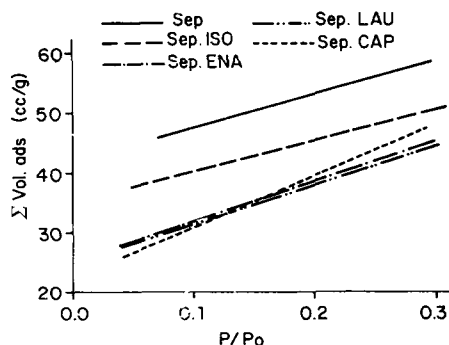

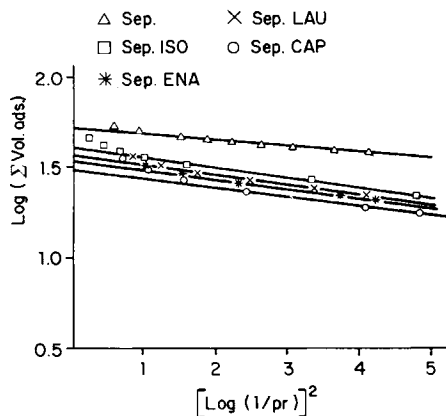Fig. 1. Specific surface by isothermic analysis for all the samples.

Fig. 2.   Distribution of micropores by Dubinin's method for all the samples.

was reached. These conditions ensure that the sample is free of any residue of reagent acid that could have been potentially adsorbed by the mineral surface and that, in some way or other, could falsify the results obtained.

With regard to the chemical characterization methods, elementary carbon analysis was performed and the number of superficial hydroxyl groups was
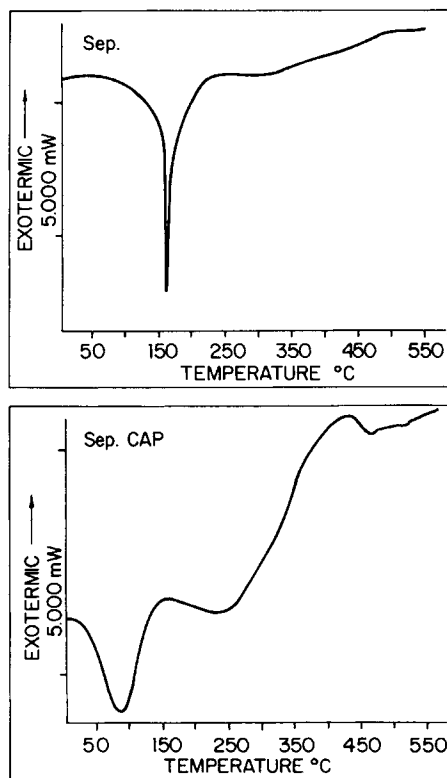

Fig. 3.   Differential scanning calorimetry of the sepiolite sample and sepiolite sample surface treated with caprylic acid.
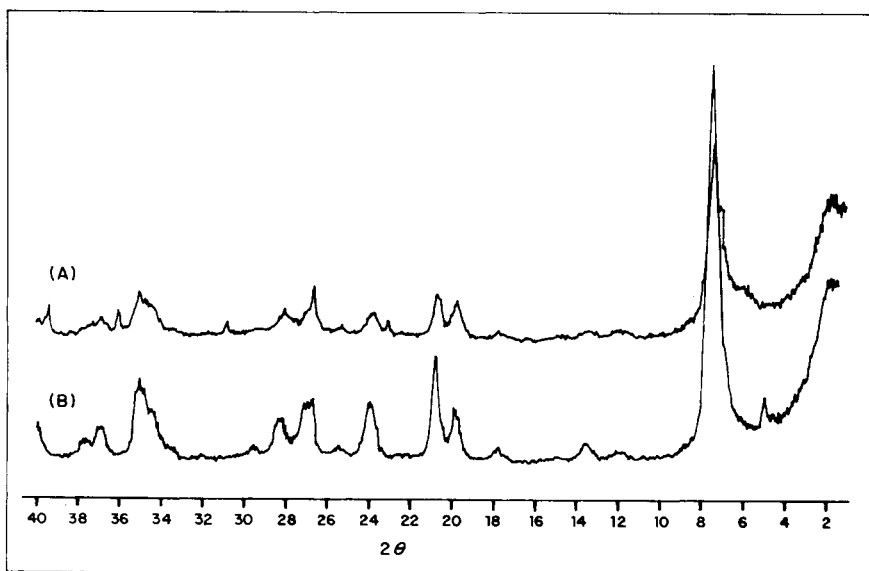
Fig. 4. X-ray spectroscopy: (A) untreated sepiolite; (B) surface-treated samples.

determined. The results obtained (Table I) allow for the conclusion that significant increases in the carbon content are produced in all surface-treated samples compared with the original sepiolite. Thus a practically nonexistent carbon content (0.29%) in the untreated sample contrasts with the surface-treated specimens, which vary between 4.51 and 5.38%.
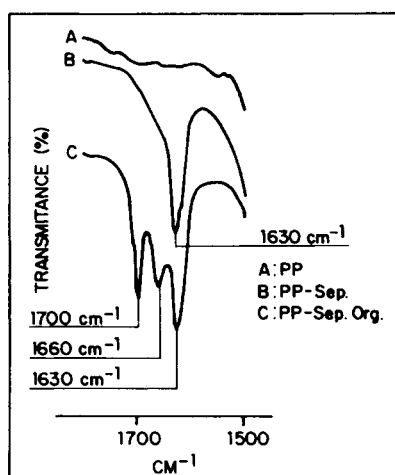

Fig. 5. IR spectroscopy: (A) polypropylene; (B) untreated sepiolite; (C) surface-treated samples.

The number of superficial hydroxyl groups was determined with the Armistead and Hockey method. It yielded a single positive result in the case of untreated sepiolite (0.92 OH per 100 Å^2) and nothing for the rest of the samples (or else the method proves to be insensitive to traces). These results constitute, to a great extent, conclusive evidence that the chemical esterification reaction has taken place on the surface silanol groups in question. Hence, they are no longer analytically detectable in the surface-treated sepiolite samples.

The physical characterization techniques refer to determination of specific surface and micropore distribution for all samples (Table II and Figs. 1 and 2). The results indicate that the surface-treated samples vis à vis the untreated sepiolite show a clear decrease in specific surface, which translates into a total micropore volume reduction, because some of them have been buffered by organic matter as a consequence of surface treatment. These results are in agreement with the references in the literature with regard to the effect of the chemical anchoring of organic matter to the surface structure of a mineral.[9-12]

The techniques of differential scanning calorimetry, together with thermogravimetric analysis (TG) and differential thermal analysis (DTA), have been widely used in the study of minerals, specifically in the case of sepiolite[13-16] with the principal aim of determining the temperature ranges at which the different types of water are lost (hygroscopic, zeolytic, and crystallization water) and in order to examine the structural changes that occur when the sepiolite progressively gets rid of these types of water.

In our concrete case, DSC, in addition, allowed us to furnish supportive evidence of the presence of organic matter chemically bonded to the sepiolite surface. In the case of all surface-treated samples there appear exothermal transformations attributable to the combustion of organic matter, vis à vis a single endothermal peak in the original sepiolite corresponding to the elimination of adsorbed water (Fig. 3). These exothermal transformations, which were present in all surface-treated samples, appear at different temperatures owing to the different nature of the organic rest bonded to the surface of the mineral. There furthermore seems to exist a correlation between maximum temperatures (Table I) at which exothermal peaks occur and the chain length of the acid reagent: the longer the aliphatic chain of the reagent, the higher the temperature at which the exothermal transformation occurs.

Another physical characterizatin method used was the determination of mean particle diameter in all samples. It can be observed from the data compiled in Table I that all the sepiolite samples analyzed possess a strongly similar particle size. Surface treatment with aliphatic organic acids did not significantly modify mean particle diameter, as has been confirmed in other cases.[17]

X-ray analysis enabled us to demonstrate, on the one hand, that the crystalline network of the sepiolite remain unaltered in the reaction conditions established: all the peaks at all angles are preserved in the different surface-treated samples (Fig. 4b) with regard to the untreated sepiolite (Fig. 4a). Figure 4 shows a clear peak enhancement (for the surface-treated samples) as a consequence of the fact that the particles are decemented by the reaction, which in turn translates into a better solution of the corresponding

diffractogram. Thus we are able to prove, although p-toluene sulfonic acid was used as a catalyst in the surface reaction, that if the crystalline network could be modified in some way through the extraction of metal elements, the structure would remain unaltered. Hence one of the objectives of this research has been achieved, that is, surface treating the sepiolite without changing its original structure.

On the other hand, the IR spectra of the untreated sepiolite as well as those of the surface-treated samples present the differences shown in Fig. 5. The bands indicated in spectrum C (which occur in all surface-treated samples in the $1800-1655$ cm^{-1} zone) can be attributed to the tension vibration of the C=O groups of the ester cluster produced in the reaction, although bandwidth is not very great because of the minimal portion ($\sim 5\%$) of organic matter bonded to the mineral surface. All sample spectra were done on hot-rolled extremely thin layers of the sepiolites incorporated in the polypropylene, the material used as a transparent support in the wavelength range studied.

In the light of the results obtained by means of the characterization techniques described, we may conclude that a genuine chemical esterification reaction has taken place on the surface of the mineral between the superficial silanol groups of the sepiolite and the acid groups of the respective reagent. Thus surface-treated sepiolites have been obtained with different organic groups bonded chemically to their surface, without producing any structural modification in the original crystalline network of the mineral, although their surface activity has been proved to be modified beyond any doubt. It will be the object of future work to study the effects of a changed surface activity on the physical and technological properties of a polypropylene composite containing them.

References

1. Z. Hashin and B. W. Rosen, *J. Appl. Mech.*, 223 (1964).
2. E. P. Plueddemann and G. L. Stark, 32nd Annual Technical Conference, Soc. Plast. Ind., 1977.
3. Y. S. Lipatov, *Int. Polym. Sci. Tech.*, 8(8), T/77 (1981).
4. P. S. Theocaris, *J. Reinf. Plast. Comp.*, 3, 204 (1984).
5. K. Brauner and A. Preisinger, *Mineralog. Petrogr.*, 6, 120 (1956).
6. C. G. Armistead and J. A. Hockey, *Trans. Faraday Soc.*, 63, 2549 (1967).
7. S. Brunhuer, R. H. Emmett, and E. Teller, *J. Amer. Chem. Soc.*, 60, 309 (1938).
8. M. M. Dubinin, *Quart. Rev. Chem. Soc.*, 9, 101 (1959).
9. S. Kitahara, K. Takada, and H. Muraishi, *Colloid Interf. Sci.*, 84, (2) 519 (1981).
10. C. C. Ballard, E. C. Broge, R. K. Iler, D. S. John, and J. R. McWhorter, *J. Phys. Chem.*, 65, 20 (1961).
11. A. U. Kiseley, *Quart. Rev. Chem. Soc.*, 15, 99 (1961).
12. K. K. Unger, Porous silica, *J. Chromat. Libr.*, 16, 104 (1979).
13. H. Logchambon, *C. R. Acad. Sci., Paris*, 204, 35 (1936).
14. G. Kuebicki, *Am. Miner.*, 44, 752 (1959).
15. A. Preisinger, Clays Clay Miner., Proc. 10th Natl. Conf., Pergamon Press, Oxford, 1963, p. 365.
16. M. Rautureau and A. Mifsud, *C. R. Acad. Sci., Paris*, 281, 1071 (1975).
17. A. Linares and J. L. Acosta, *Rev. Plast. Mod.*, 325, 43 (1983).