

Morphological, Structural, and Interfacial Changes Produced in Composites on the Basis of Polypropylene and Surface-Treated Sepiolite with Organic Acids II. Thermal Properties

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Synopsis

Heat capacity and thermal expansion measurements in composites have been relatively little used as research procedures. In recent times, however, they are beginning to be increasingly utilized in morphological studies. This motivated the application of both techniques to composites on the basis of polypropylene and sepiolite that had been surface treated with linear organic acids. Assessment of our results allows for the inference that the incorporation of these sepiolites produces important structural changes in the polypropylene containing them. These changes can be explained by the complex interface (mesophase) theory.

INTRODUCTION

Although the mechanical properties are at present the focus of attention in studies on plastics in general and composites in particular, there is growing interest in the research of other properties.

To date, the practical consequences of adding a filler to a polymer are not well known in the context of properties in general, although there do exist some semiempirical theories intending to predict property-induced effects, yet in a very limited way. With regard to the case of thermal properties as such, there is a line of thought in composite research pursuing two fundamental objectives:

1. The study of the influence of the physical filler features on the thermal properties of the composite, with the aim that the respective findings would make available objective criteria, in order to be able to modify selectively the relevant properties.

2. The study of the microstructure, adhesion, depth of the borderline phase(s), and so on, based on the study of the thermal properties of the composite and how they relate to the macroscopic properties of the material.

In compliance with the second objective, we conducted a study on the thermal properties of the composites (thermal expansion coefficient and heat capacity) on the basis of polypropylene and the different sepiolites used, as described below.

EXPERIMENTAL

The test materials utilized were polypropylene manufactured by Isplen (Spain), original sepiolite from Tolsa (Spain), and surface-treated sepiolite with different acids according to the procedure described elsewhere.^{1,2} The

sepiolites used in this study were esterified with the following acids: isobutyric acid (Sep ISO), heptanoic acid (Sep ENA), caprylic acid (Sep CAP), and lauric acid (Sep LAU).

The original sepiolite as well as the surface-treated products were incorporated with the polypropylene in a Brabender Plasticorder and a thermoplastics mixing chamber, type W 60, preheated to a temperature of 200°C. Rotor speed was set at 60 rpm, and the mixture remained in the chamber for 15 min, that is, a sufficiently long time to achieve a homogeneous dispersion at all filler concentrations. By this procedure composites at three different filler concentrations were obtained: 10, 25, and 40% in weight.

The samples for the thermomechanical tests were obtained by compression molding at 185°C. The sheets obtained were machined to produce cylindrical samples of 6-mm diameter and 2-mm wall thickness, the walls and edges being perfectly parallel. These samples were then tempered during 24 h at 90°C and held by fixation plates to maintain wall parallelism.

The test method used was a Perkin-Elmer Model TMS-2 system for thermomechanic analysis, which measures all dimensional changes in a sample as a function of temperature.

The samples were recorded in the same temperature range and at the same heating rate. Their linear thermal expansion coefficients were determined on the straight section of the expansion graphs by means of the equation

$$\alpha = \frac{\Delta L}{L_o \Delta T}$$

where α is the thermal expansion coefficient in linear expansion, ΔL the change in length, ΔT the temperature change, and L_o the original length of the sample.

The material used for heat capacity analysis and the mixing technique applied have been described above. Capacity heat analysis was performed on a Mettler system TA 3000.

RESULTS AND DISCUSSION

Thermal Expansion Coefficients

For the sake of oversimplification, when a material is heated, its atoms gain energy, vibration rates as well as interatomic distances increase, and as a consequence, the material expands. This expansion depends on the bonding energy between the atoms and has a ceiling determined by the potential energy barrier inherent in each compound.

Polymers possess a high degree of thermal expansion, in contrast to fillers, which show remarkably lower values. By the same token, they present two different types of thermal expansion coefficients, one below the glass transition temperature (α_1) and another above this point (α_2). The study underlying these concepts, however, is not that simple when these polymers are added as filler. In this case, the resulting isotropic composite has two phases, each with a different thermal expansion coefficient: the filler α_f

and the polymeric matrix α_m , the composite having again a different thermal expansion coefficient from the former two (α_c). This composite is generally manufactured from the melt (if thermoplastic). During the cooling process each phase contracts. Yet the polymeric structure, being larger in proportion than that of the filler, is obstructed by the disperse phase, which establishes compression stresses through the interface, which may increase or decrease over time as a function of the viscoelastic nature of the polymer. If this composite is reheated, the polymeric matrix expands more than the particles; yet if the interface is able to transmit the stresses activated, matrix expansion is reduced, or it is compensated. The ability of an interface to transmit stresses depends fundamentally on the nature of the interface and, above all, on interfacial adhesion.³

Experience⁴ has shown that there are several borderline cases, which we represent in Fig. 1. The case of nonadhesion ($\alpha_c = \alpha_m$) is shown in section *AB*. The ideal case, where the linear mixture equation is fulfilled ($\alpha_c = v_m\alpha_m + v_f\alpha_f$) occurs in section *AC*, as well as two types of actual behavior: the more common one (section *AD*) is where the values determined for the thermal expansion coefficients fall below the figures predicted by means of the linear mixture equation and are explained by the existence of a complex interface (mesophase) formed on the particle periphery as a consequence of the filler activity proper.^{5,6} The other pattern exclusively occurs

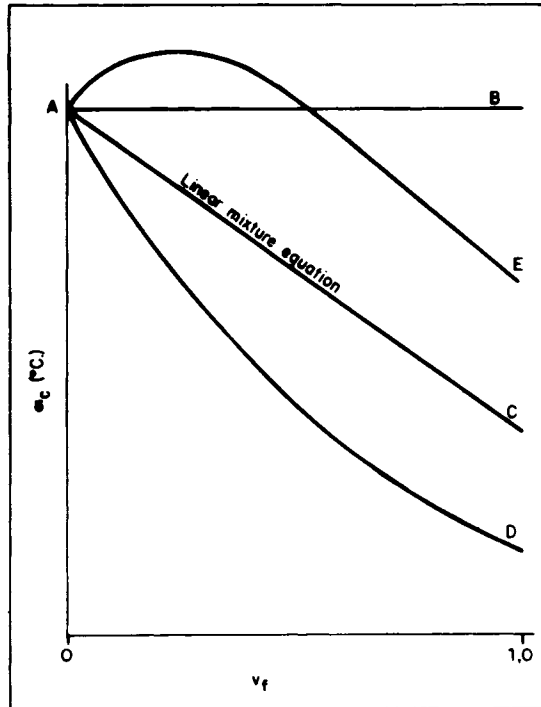


Fig. 1. Variation of thermal expansion coefficient α_c versus volume fraction in composites for the real and ideal following cases: *AB*, nonadhesion; *AC*, linear mixture equation; *AD*, normal behavior; *AE*, Teflon composites.

in polytetrafluorethylene composites, whose graph is described in section *AE*.

The results obtained from thermal expansion coefficient measurements in all the composites under study are compiled in Table I. The assessment of these results furnishes arguments in favor of the existence of a complex interface (mesophase), as discussed above; at the same time it substantiates the fact that the nature of this mesophase varies as a function of the different filler activities achieved by means of the chemical esterification reaction of the superficial silanol groups of the sepiolite vis à vis organic acids of different chain lengths.

Figures 2 through 4 represent linear thermal expansion variation in three samples: polypropylene and two composites, one on the basis of the original and untreated sepiolite and the other with caprylic acid surface-treated sepiolite, which is representative of all other surface-treated sepiolites as they show a similar behavioral pattern.

Graph evaluation allows us to draw first conclusions, that is, the typical case of isostatic polypropylene (fig. 2) with a clear-cut differentiation between the slopes above and below the glass transition temperature over the whole range measured. This standard behavior has nothing to do with the atypical pattern observed when testing composite samples consisting of untreated sepiolite and samples that had been surface treated with different acids. In the case of untreated sepiolite and caprylic acid surface-treated sepiolite (Figs. 3 and 4), slope inflection in the glass transition zone is hardly perceptible, the less the greater the filler portion in the composite. Furthermore, the linearity of thermal expansion coefficients is not maintained with regard to temperature, which evidences significant changes in the polypropylene structure because of the effect of filler addition. These

TABLE I
Values Obtained from Thermal Expansion Test

Samples	Filler (wt. %)	L_o (mm)	V_m	V_f	$\alpha_2 \times 10^5$ (K)	
					LM ^a	EXP ^b
PP	—	1.82	1.000	0.000	—	9.04
PP-Sep	10	1.77	0.954	0.046	8.65	12.34
PP-Sep	25	1.70	0.842	0.158	7.71	9.92
PP-Sep	40	1.61	0.774	0.226	7.13	9.90
PP-Sep ISO	10	1.64	0.954	0.046	8.65	11.18
PP-Sep ISO	25	1.67	0.842	0.158	7.71	9.41
PP-Sep ISO	40	1.64	0.774	0.226	7.13	11.53
PP-Sep ENA	10	1.69	0.954	0.046	8.65	10.08
PP-Sep ENA	25	1.68	0.842	0.158	7.71	10.14
PP-Sep ENA	40	1.78	0.774	0.226	7.13	10.14
PP-Sep CAP	10	1.65	0.954	0.046	8.65	7.05
PP-Sep CAP	25	1.74	0.842	0.158	7.71	6.69
PP-Sep CAP	40	1.73	0.774	0.226	7.13	8.75
PP-Sep LAU	10	1.62	0.954	0.046	8.65	10.96
PP-Sep LAU	25	1.69	0.842	0.158	7.71	9.47
PP-Sep LAU	40	1.76	0.774	0.226	7.13	9.42

^a Linear mixture equation.

^b Experimental data.

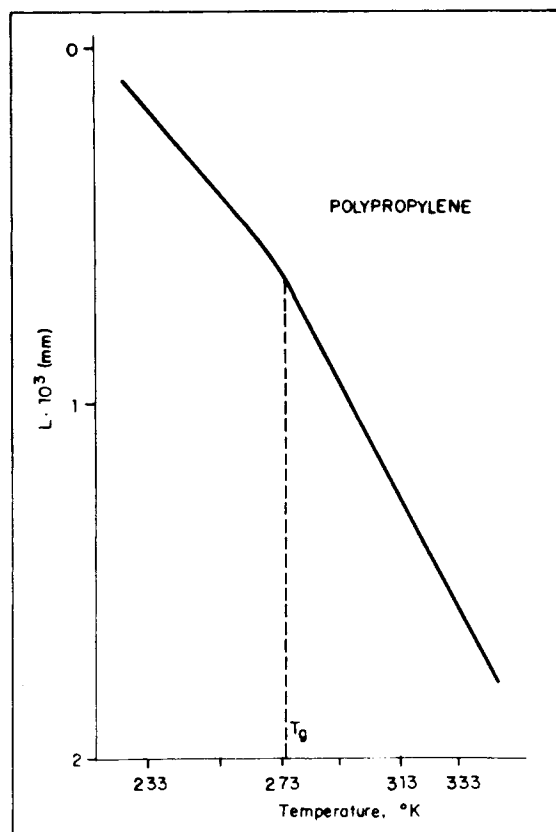


Fig. 2. Variation of linear thermal expansion versus temperature for polypropylene.

changes become more overt when testing caprylic acid surface-treated sepiolite. Here, especially at low sepiolite concentrations, significant variations can be observed in composite transitions. There appear transformations involving most probably different structures as a consequence of interactions, such as filler/matrix and matrix/matrix with different structures.

The representation of the thermal expansion coefficient as it relates to the filler volume fraction in each of the tested composites evidences even further the atypical behavior of polypropylene composites with different percentages of surface-treated and original sepiolite. As can be observed in Fig. 5, the thermal expansion coefficients in all cases are above linear mixture equation predictions, except the caprylic acid surface-treated samples, this deviation from the equation being even more patent in the case of untreated sepiolite composites. This behavior has been observed exclusively in polytetrafluorethylene composites³ on the basis of pulverulent fillers. The underlying reasons, however, have not been described to date, although reference has been made to relevant morphological changes in the polymeric Teflon matrix.

In our case it has been confirmed that the possible structural changes produced are not exclusively due to the addition of a certain amount of

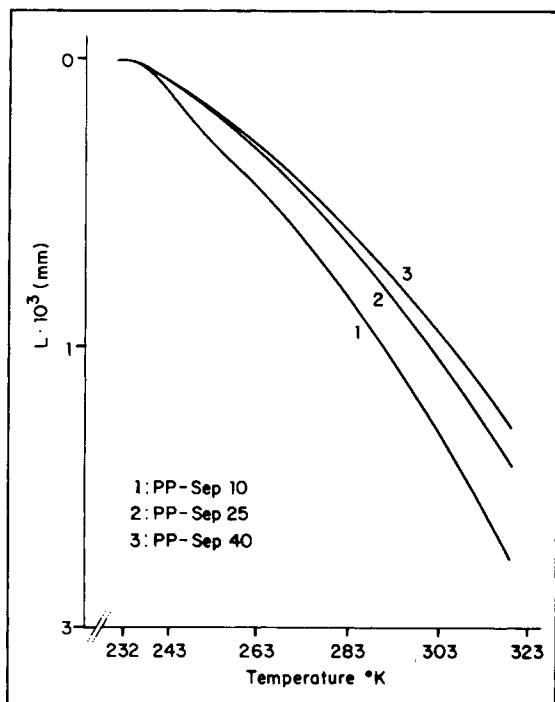


Fig. 3. Variation of linear thermal expansion versus temperature for composites with untreated sepiolite.

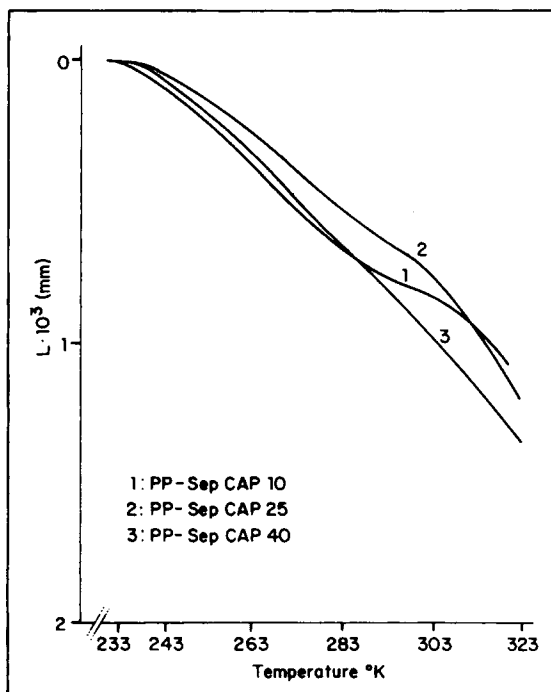


Fig. 4. Variation of linear thermal expansion versus temperature for composites with caprylic acid surface-treated sepiolite.

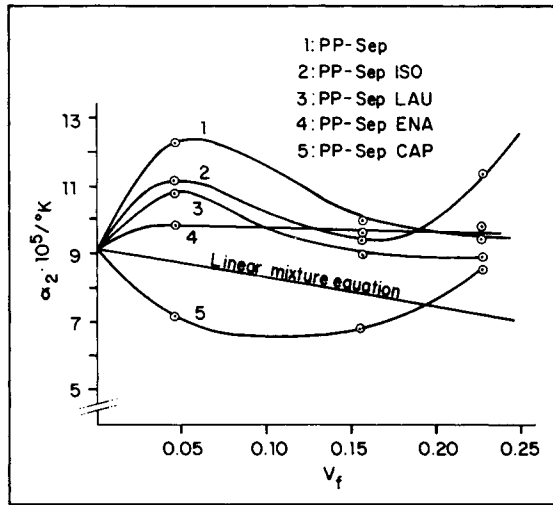


Fig. 5. Variation of linear expansion coefficient α_2 versus volume fraction of the filler for the composites studied.

filler to the polypropylene; moreover, they are attributable to the surface activity of this filler, which is easy to verify and logically reasonable. Hence the addition of untreated sepiolite to polypropylene yields an atypical response with regard to the general rule in the linear expansion coefficient (Fig. 5), and the addition of the same sepiolite, surface treated with different acids, produces a different response, atypical as well, with regard to standard behavior.

All this is clearly indicative of the fact that filler surface activity, as a consequence of its chemical nature, plays a decisive role in the structure of the polymeric matrix, as demonstrated in the thermal expansion tests performed. Sepiolites with a different chemical surface configuration, and hence different surface activity, generate different morphological structures in the polypropylene composites containing them.

Heat Capacity

Heat capacity has traditionally been considered as data without further interest in the study of composites, with the exception of certain applications in the field of engineering.

At present, heat capacity measurements in macromolecular composites is in the focus of fundamental research, in the sense that these measurements allow us to accumulate data about the interface, based on the study of the sudden changes to which heat capacity is subject in the case of polymeric material and in the glass transition temperature zone, as has been demonstrated by several authors,⁷ taking into account that heat capacity variation in this zone is closely linked to the number of macromolecules involved in the cooperative process of T_g .

Capacity heat was measured in all samples. We have, however, selected two cases that we consider representative of the rest, that is, the composites containing untreated sepiolite and sepiolite surface treated with caprylic acid, respectively. Figures 6 and 7 show the graphs for capacity heat vis à

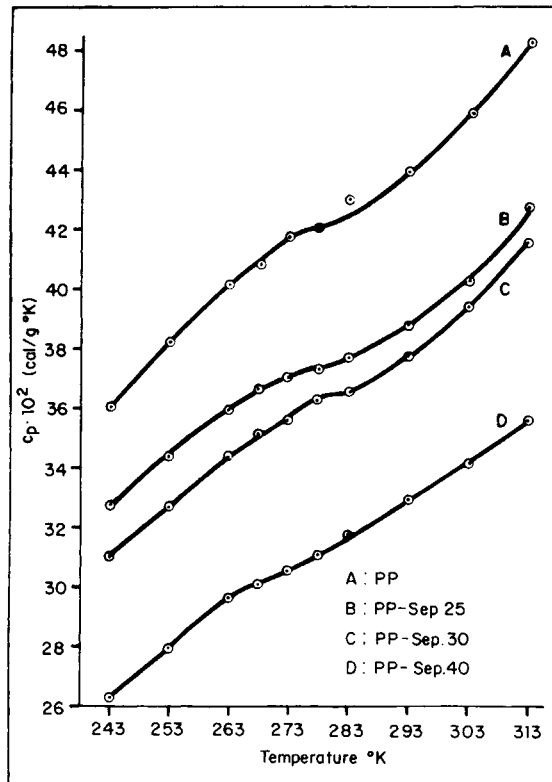


Fig. 6. Variation of heat capacity versus temperature for polypropylene and composites with untreated sepiolite.

vis temperature in the samples mentioned at three different percentages in weight, together with that of polypropylene without a filler.

In all cases it must be highlighted that the curves present a sudden change corresponding to glass transition temperatures in the samples. The change is well defined and straightforward in the case of polypropylene and any of the composites with lower filler portions, yet it loses clarity for higher filler concentrations and, in addition, moves toward lower temperature ranges.

The representation of heat capacity at a certain temperature (273 K) vis à vis the sepiolite portion in weight (Fig. 8) shows a normal yet dissimilar behavioral pattern for each composite, as a result (see our comments in the case of thermal expansion) of the deep structural changes produced in the polypropylene when adding sepiolites with different chemical surface activities.

CONCLUSIONS

In the light of the results obtained from the study of thermal properties, the atypical behavior observed is easily attributable to the presence of structural singularities deriving from the different surface activities of the sepiolite, which induce morphological structures of a different nature in the polymeric matrix. Otherwise, no reasonably logical explanation could be

THERMAL PROPERTIES OF SEPIOLITE INCORPORATION 1877

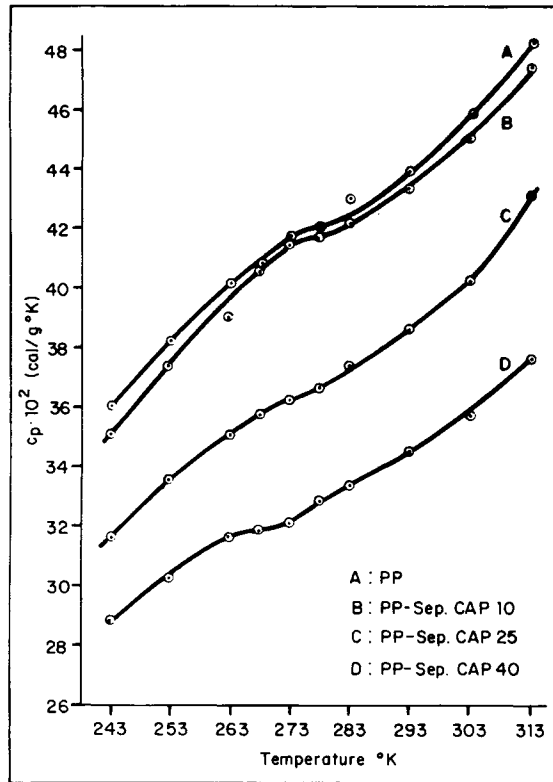


Fig. 7. Variation of heat capacity versus temperature for polypropylene and composites with caprylic acid surface-treated sepiolite.

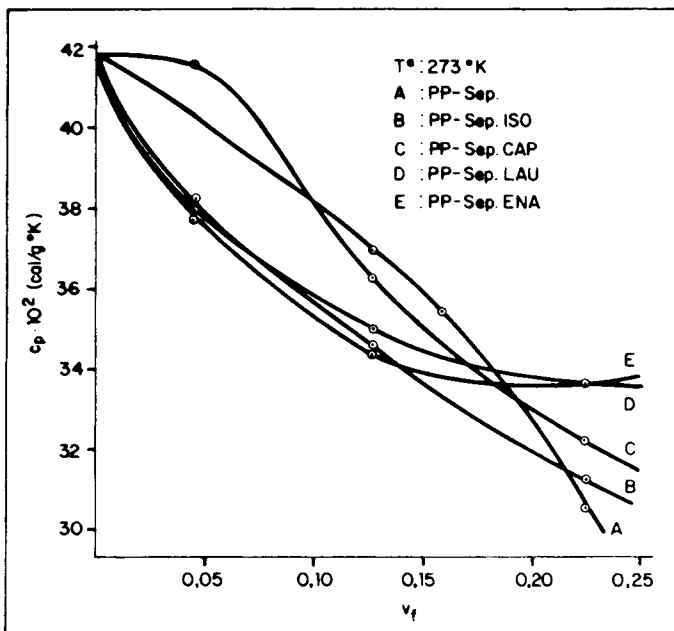


Fig. 8. Variation of heat capacity versus volume fraction of the filler at 273 K for the composites studied.

given for the singular behavior of these fillers in polypropylene matrices that comes to light when their thermal properties are studied.

In research pursuing different objectives we have been able to demonstrate the existence of such structures, especially supported by the argument of the presence of a complex interface (mesophase).

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