JOURNAL OF MATERIALS SCIENCE 21 (1986) 725–728

The effect of interfacial adhesion and morphology on the mechanical properties of polypropylene composites containing different acid surface treated sepiolites

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

The study of the microstructure of polymeric composites and its relationship to mechanical properties, are of great importance. In the present study we have carried out a study of the microstructure of polymeric composites of polypropylene and different sepiolites treated with organic acids, in order to determine the mesophase produced around the filler particles and its relationship with the mechanical properties of the composites. This study was made using scanning electron microscopy, differential scanning calorimetry and mechanical tests.

1. Introduction

The properties of composite materials are determined by the properties of the components: by the shape of the filler, by the morphology of the system and by the nature of the interface between the phases. Thus, a great variety of properties can be obtained with composites just by alteration of the morphological properties of the interface.

One property which can affect mechanical behaviour is strength of the adhesive bond between the phases. Adhesion parameters and silane coupling agents [1–3] have been used to change the adhesive nature of the filler–polymer interface and the so-treated fillers often give composites with increased mechanical properties compared with the same composites with untreated fillers.

For us the most important property which can greatly affect mechanical behaviour is the morphology of the interface surrounding the particle. Nowadays it is accepted that it is the activity of the filler itself which induces the arrangement of the chain at the polymeric matrix next to the surface of the particle. This effect on the macroscopic properties of the composites is a function of the microscopic properties of this interface or mesophase [4, 5].

Taking into account the arguments put forward above, this paper pursues the following aims: (a) to determine the existence of a complex mesophase in polypropylene composites containing sepiolite or sepiolites surface treated with different organic acids; (b) to study the effects produced by sepiolites with different surface activities i.e. sepiolites treated with different organic acids – in the nature of this interface regarding adhesion and morphological properties; and (c) to determine the influence of the interfacial features on the mechanical properties of the composites obtained.

For this purpose the composites obtained were examined under the scanning electron microscope (SEM), non-isothermic crystallization kinetics were determined, as well as their mechanical properties.

2. Experimental details

The materials used were sepiolite (SEP) which is a magnesium silicate having the following ideal formula: $Si_{12}Mg_8O_{30}(OH)_4(H_2O)_4 \cdot 8(H_2O)$ and polypropylene (PP) supplied by Alcudia (Spain). We also used different surface modified sepiolites treated with organic acids, such as: isobutyric (ISO), enantic (ENA), caprylic (CAP) and lauric (LAU), using a method described elsewhere [6].

These differently treated sepiolites were incorporated into the polypropylene matrix at different concentrations in a Brabender Plasticorder [7]. The samples for the measurements were obtained from compression moulded plaques. The tensile and flexural tests of the composites were conducted on an Instron testing machine. Impact testing and Vicat softening points were measured under standard conditions [8].

Crystallization was followed by means of differential scanning calorimetry (DSC) measurements on a Perkin Elmer DSC-2. Measurements were made on 11 mg samples in the temperature range of 100 to 200° C.

The samples were first heated to 200° C in the instrument and held there for 5 min so as to minimize the effect of any previous history on the crystallization. The samples were then cooled at a rate (β) of 2.5, 5 and 10° C min^{-1}. During the cooling cycle, the crystallization exotherms were recorded.

The fracture surfaces of the specimens, as obtained from the Instron testing machine, were examined on a scanning electron microscope.

3. Results and discussion

The evidence of the existence of a mesophase was obtained experimentally and its extent was evaluated

0022–2461/86 $03.00 + .12

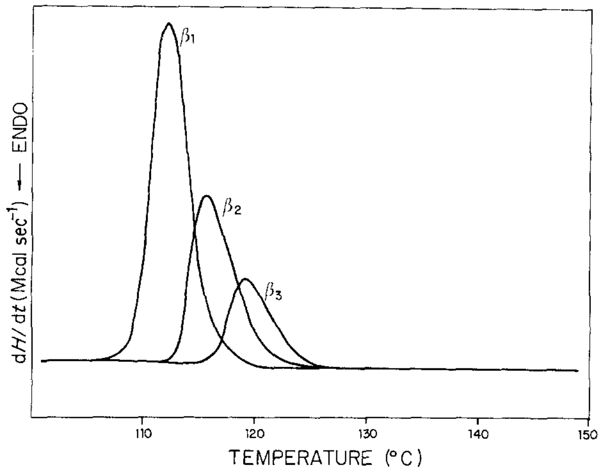

Figure 1 Differential scanning calorimetric thermograms of polypropylene for different cooling rates $\beta_1 > \beta_2 > \beta_3$.

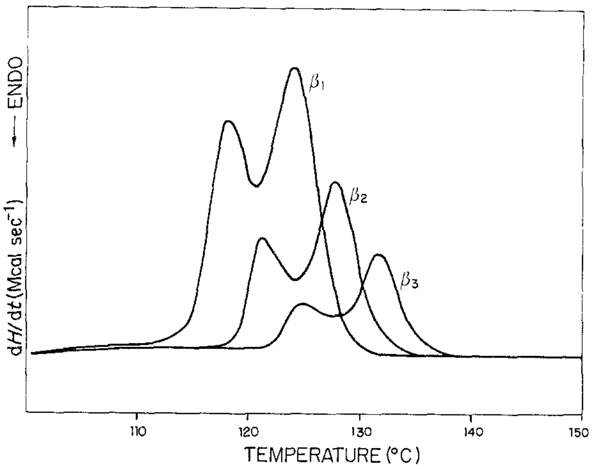

Figure 2 Differential scanning calorimetric thermograms of polypropylene–sepiolite (10 wt %) for different cooling rates $\beta_1 > \beta_2 > \beta_3$.

by Lipatov [4]. It may be determined in amorphous polymers by dynamic measurements of the storage moduli and the loss factors, calculated in the vicinity of the glass transition temperatures, T_g, of the matrix and the composites [9], and in crystalline polymers by thermal analysis [10].

It has been proved, however, that the existence of this mesophase was due to the surface activity of the filler itself. Varying this activity with different treatments, may vary the nature of the mesophase and all the properties.

We demonstrated the existence of the mesophase by means of the kinetic study of non-isothermic crystallization in all the samples using the method developed by Harnisch and Muschik [11]. In essence the method constitutes a tool to determine the exponent n in the Avrami equation on the basis of the corresponding crystallization exotherms recorded at different cooling rates. The magnitude of n supplies information about the growth geometry of any ordered structure which may emerge in the sample under study during the crystallization process, hence its enormous relevance. In Figs. 1 and 2 we indicate the crystallization exotherms of two samples which proved to be representative of the rest, recorded at three predetermined cooling rates. The first sample is an unfilled polypropylene, and the second a polypropylene filled with natural sepiolite at a concentration of 10%. Most of the remaining filled samples present an exothermic graph similar in shape to the one shown in Fig. 2. Table I shows the temperatures at which exothermic peaks were present for all samples at all experimental cooling rates. It also indicates the different values of n in the Avrami equation calculated according to the method mentioned above.

Fig. 2 allows for the inference that there exist two ordered species, each of which is assigned to one of the two exothermic peaks, which appear in the thermograms of all the tested composite samples and which are not present in the unfilled polypropylene samples tested under the same conditions. The higher temperature peak refers to the crystalline structure of the polypropylene matrix, and the lower one to the lower (secondary) temperature of the ordered particle mesophase.

TABLE I Experimental kinetics data determined by non-isothermal (n–DSC) technique for all the samples at different cooling rates: $\beta_1 = 10°\mathrm{C\,min^{-1}}$, $\beta_2 = 5°\mathrm{C\,min^{-1}}$ and $\beta_3 = 2.5°\mathrm{C\,min^{-1}}$

Samples	Filler (wt %)	Temperature main peak (°C)			Temperature secondary peak (°C)			Avrami's exponent*	
		β_1	β_2	β_3	β_1	β_2	β_3	n	n'
PP	–	112.2	115.7	118.8	–	–	–	4.3	–
PP–Sep	10	124.3	128.2	131.9	118.2	121.6	124.7	4.4	1.8
PP–Sep	25	129.8	133.8	137.2	–	–	–	4.5	2.3
PP–Sep	40	120.9	124.8	138.2	–	–	–	4.6	2.2
PP–Sep ISO	10	123.7	127.3	130.7	118.9	122.1	124.1	4.4	2.0
PP–Sep ISO	25	127.3	131.1	134.6	119.4	123.6	126.6	5.4	2.1
PP–Sep ISO	40	126.1	129.3	132.3	–	–	–	4.0	2.7
PP–Sep ENA	10	118.5	121.9	124.9	–	–	–	4.1	–
PP–Sep ENA	25	125.6	129.3	133.0	120.0	123.4	126.3	4.7	2.2
PP–Sep ENA	40	129.1	133.0	136.5	121.0	124.3	–	5.7	2.1
PP–Sep LAU	10	120.1	124.0	127.8	–	–	–	3.0	–
PP–Sep LAU	25	126.7	130.8	134.3	120.5	124.3	127.8	4.5	2.6
PP–Sep LAU	40	128.9	133.0	136.5	120.3	124.5	127.6	4.4	2.5
PP–Sep CAP	10	120.0	123.8	127.4	–	–	–	3.4	–
PP–Sep CAP	25	125.4	129.2	132.7	–	–	–	3.8	2.4
PP–Sep CAP	40	128.6	132.6	133.7	121.0	124.5	129.8	4.2	2.1

*n = Avrami's exponent first stage; and n' = Avrami's exponent secondary stage.

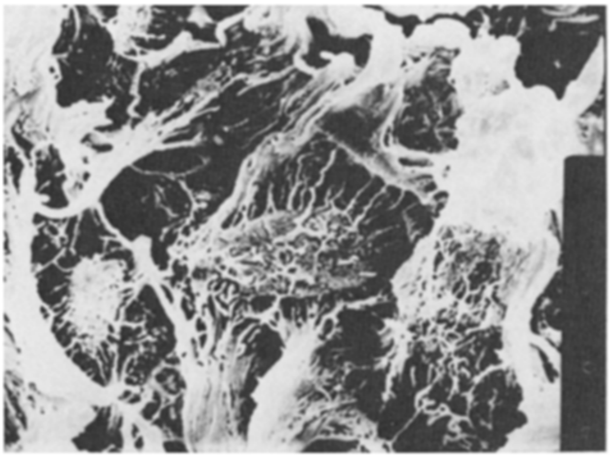

Figure 3 Scanning electron micrograph of the fractured surface of the PP–Sep. LAU specimen (×3500).

Whenever there exists a single ordered structure in the sample, the value of the Avrami *n* exponent is unique (e.g. in the case of unfilled polypropylene). In the case of two coexisting structures in the same sample, however, *n* acquires two values, as shown in Table I, neither of which, for all the samples, corresponds to the value of *n* found for unfilled polypropylene. This can be taken as conclusive evidence for the existence of an ordered structure surrounding the particles. The different nature of the mesophase as a function of the treatment applied to the filler becomes manifest through the variation in the secondary temperature peak when comparing samples with the same filler ratio and cooling rate (Table I). By the same token, when assessing the differences found for the value of *n* calculated for each sample and each cooling rate, the results indicate that the sample has undergone two types of growth of different geometry.

The good interfacial adhesion between the different sepiolites and the polypropylene have been observed through scanning electron microscopy in all the samples. Fig. 3 shows adhesion properties between polypropylene and lauric acid treated sepiolite. The interface formed between a sepiolite particle treated with lauric acid and the polypropylene matrix can be clearly seen, the particle being held (bonded) to the plastic matrix by a considerable number of polypropylene filaments, which confirms the existing excellent adhesion.

All the samples were subjected to mechanical property analysis, according to ASTM standards. The results are shown in Table II. It can be seen that sepiolite treatment did not improve the properties measured in absolute figures, in spite of the good adhesion. Tensile and flexural moduli, however, were affected.

It is well known [12] that moduli in general, and in particular tensile and flexural moduli, are sensitive to the changes produced by the incorporation of fillers to both amorphous and crystalline polymer matrices.

Young's modulus, which was measured in tensile and flexural tests for all the composites as a function of the filler concentration, shows a behavioural pattern related to the varying interfacial structure in each sample.

If for all the composites studied surface treatment produced a similar effect in the polypropylene matrix, the graphs of the moduli against filler concentration would overlap. On the other hand, if for each surface-treated sepiolite a mesophase of a different nature were generated, it would entail variations in magnitude that are sensitive to this kind of structural change, such as Young's modulus.

In our particular case, it has been proved that Young's modulus for polypropylene composites showed variations, due to the incorporation of different types of sepiolite (Fig. 4). Further analysis showed that the higher values were reached by lauric acid surface-treated sepiolite in the composite samples. Hence the structural stiffness achieved by this filler in its mesophase is greater, in contrast to the PP–Sep ISO and PP–Sep CAP samples with a lesser degree of stiffness and consequently lower performance levels with regard to the mechanical properties.

4. Conclusions

In the light of our findings and results the following

TABLE II Values of the mechanical tests for all the samples

Samples	Filler (wt %)	Tensile test		Flexural test		Impact test Strength (kg cm cm^{-2})	Vicat (degree)
		Strength (MPa)	Modulus (MPa)	Strength (MPa)	Modulus (MPa)		
PP	–	27..0	–	36.0	1255	71.4	89
PP–Sep	10	25.6	16383	43.8	1873	62.6	99
PP–Sep	25	27.8	19382	44.2	2408	40.8	103
PP–Sep	40	31.6	31066	49.8	4096	33.4	121
PP–Sep ISO	10	26.0	16631	43.4	1747	55.8	95
PP–Sep ISO	25	24.7	19716	46.4	2365	38.2	105
PP–Sep ISO	40	27.9	30160	45.1	3171	27.6	114
PP–Sep ENA	10	25.7	20178	42.5	1796	63.1	94
PP–Sep ENA	25	25.2	19972	43.3	2545	44.8	105
PP–Sep ENA	40	27.0	33099	47.0	4092	38.2	113
PP–Sep CAP	10	26.0	17155	40.0	1555	60.9	97
PP–Sep CAP	25	26.9	25870	45.3	2684	31.4	110
PP–Sep CAP	40	28.0	29407	47.4	3173	27.5	109
PP–Sep LAU	10	26.5	16686	45.3	1964	58.4	99
PP–Sep LAU	25	25.8	20971	46.1	4054	33.5	108
PP–Sep LAU	40	29.2	42483	47.6	4211	35.5	115

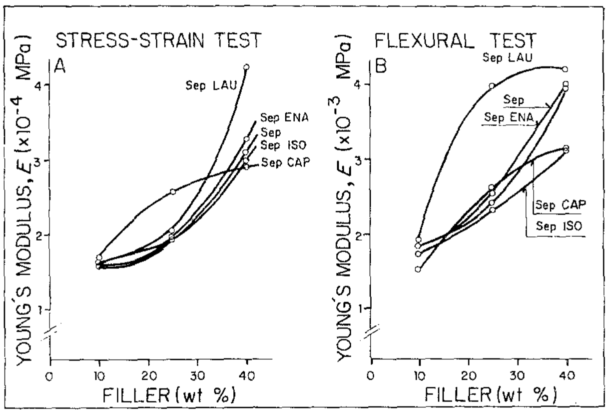

Figure 4 Variation Young's modulus against filler content.

conclusions can be reached with regard to the mechanical properties

1. The sepiolite builds up a mesophase in the polypropylene matrix, whose structure will vary as a function of the surface treatment applied to the sepiolite.

2. Untreated and treated sepiolites both present good adhesion properties and compatability with the polypropylene matrix.

3. The enhanced mechanical properties of the sepiolite–PP composites were not due to adhesion alone. Moreover the process is commanded by both adhesion and the structure of the mesophase.

4. Sepiolite substitutes advantageously for other clays traditionally incorporated into polypropylene, with regard to cost effectiveness and enhancement [7].

References

1. S. SAHU and L. J. BROUTMAN, *Polym. Eng. Sci.* **12** (1972) 91.
2. S. STERMAN and J. G. MARSDEN, *ibid.* **6** (1966) 97.
3. E. P. PLUEDLEMANN, H. A. CLARK, L. E. NELSON and K. R. HOFFMAN, *Modern Plast.* **39** (1962) 135.
4. Y. LIPATOV, *Adv. Polym. Sci.* **22** (1977) 1.
5. P. S. THEOCARIS, *J. Reinf. Plast.* **3** (1984) 204.
6. A. LINARES, M. C. OJEDA and J. L. ACOSTA, Spanish Patent 504 509 (1981).
7. J. L. ACOSTA, O. LAGUNA and M. ARROYO, *Rev. Plast. Modern.* **309** (1982) 283.
8. Impact Test, DYNSTAT Mod. CEMP; UNE 53.118.
9. P. S. THEOCARIS, B. KEFAR and G. SPATHIS, *J. Appl. Polym. Sci.* **28** (1983) 3641.
10. J. L. ACOSTA, A. LINARES, M. C. OJEDA and M. ROMERO, *J. Polym. Sci., Polym. Lett. Ed.*, in press.
11. K. HARNISCH and H. MUSCHIK, *Coll. Polym. Sci.* **261** (1983) 908.
12. L. E. NIELSEN, "Mechanical Properties of Polymers and Composites" (Marcel Dekker, New York, 1974) p. 379.

*Received 15 January
and accepted 13 February 1985*