Epoxy resins as surface treatments for mica flakes in propylene/ethylene copolymer composites

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Abstract—The use of epoxy resins as surface treatments for mica flakes in polyolefine composites was studied in comparison with a commonly used silane coupling agent. Improvements in mechanical properties should be expected for both treatments but, in addition, epoxy systems involved economic advantages. An experimental procedure for epoxy resin deposition was developed; various parameters, such as the nature of the curing agent used to harden the epoxy prepolymer, the deposition process, the amount of coating, the ratio between the epoxy prepolymer and the curing agent and the curing temperature were investigated. Data show that only the three first parameters had a significant influence on the mechanical properties. In all cases, an improvement in tensile properties was obtained for epoxy-coated composites but in lower proportions compared to silane-treated composites. However, the impact characteristics worsened.

Keywords: Mica; propylene/ethylene copolymer; composite; epoxy resin; silane; surface treatment; curing agent; mechanical properties.

1. INTRODUCTION

Fillers are often used for the improvement of certain properties of polymers (stiffness, compressive strenght, dimensional stability, high temperature properties, and others) in order to meet the requirements of specific applications. Among these fillers, mica is a well known and abundantly found mineral having great potential as a mineral filler for polymers. Nevertheless, these fillers are chemically inert towards a polyolefine matrix. Thus, to reach optimum performance the interactions between the polymer matrix and the filler must be adjusted. Several types of coupling agents and adhesion promoters are usually used. Among these coupling agents, the silanes and other silicon-containing compounds are the most commonly used because they seem to perform best [1–9]. Indeed,

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surface treatment with silicon-containing coupling agents appears to change the free energy of a mica surface by interacting physically and/or chemically, thereby improving the wettability with the polyolefine matrix and the deagglomeration of the fine mica particles. Many investigations have been carried out which suggest that silane compounds of different functionality (amine [7–9], vinyl [5, 6], epoxy [7], etc.) create both (i) strong chemical bonds and a monolayer which results in stiff and brittle materials and (ii) a diffuse interlayer which offers more advantageous properties such as a relatively high impact resistance. These authors also tried to evaluate the influence of different parameters (i.e. the hydrophobic character of the silane, the crosslinking of the siloxane structure, the thermal stability of the silane, etc.) on the mechanical performance.

Another class of coupling agent often used to treat mica particles includes zirconate- [7] and titanate- [2, 8, 9] based agents. These yield lower modulus and ultimate strength than those treated with silane but much higher than untreated ones. Malik [8] assumed that the titanate agent should behave as a lubricating agent. Titanate appears to cause a breakdown of the aggregates in response to the applied stress resulting in an increase in elongation whereas the silane agent should increase the adhesion between the mica and the polymer matrix resulting in an increase in modulus as well as strength. Moreover, through fracture observations, Xavier et al. [9] speculated that the interfacial adhesion between titanate-treated mica and polypropylene is poor although the former had developed a transcrystalline interphase with polypropylene. An altering of the plastic zone in front of the crack was also observed by these authors.

Carboxy-terminated butadiene (CTB) and carboxy-terminated butadiene–acrylonitrile copolymer (CTBN) have also been used as coupling agents for mica–polypropylene composites [10]. According to the authors, these lead to composites which give the highest yield strengths and elastic moduli compared to a chlorosilane agent. Moreover, Trotignon et al. [11] have shown that coating mica with silane and chloroparaffin gave similar tensile properties. But the use of the later treatment may involve changes in the material colour. Finally, Chun and Woodhams [12] suggested that chlorinated waxes may tend to decompose at processing temperature and to evolve corrosive gas. Therefore, they proposed to modify polypropylene with the addition of 1 to 5% carboxylated polypropylene. This material may substitute for silane coupling agents.

Nevertheless, silane agents seem to give the best mechanical properties (tensile and impact) according to previous studies. But their disadvantage is their relatively high price which has an unfavourable impact on commercial applications. Therefore, this study describes attempts to find another coupling agent for mica reinforced composites that will be more commercially viable.

A new surface treatment based on an epoxy resin was used because of its low price compared to a silane coating. A previous study [13] using a combination of an epoxy prepolymer and various aminimide curing agents had already been carried out. The results give evidence for (i) the same increase in tensile strength with these

epoxy systems compared to unfilled matrix as when silane coupling treatments are used, and for (ii) the importance of the choice of the curing agent used to harden the epoxy resin. That is the reason why the present work will attempt to use different curing agents which are well known and commercially used compared to aminimide curing agents which require a particular chemical synthesis [14]. Previous studies [15, 16] have already reported preliminary results with curing agents of different flexibility levels. In this paper, the influence of the nature of the curing agent will also be studied and moreover the influence of various parameters will be investigated: (i) the deposition process (dry or wet process) used to modify the mica surface; (ii) the ratio between the epoxy prepolymer and the curing agent; (iii) the amount of coating added to mica particles; and (iv) the curing temperature of the epoxy resin.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

The polymer used was a propylene/ethylene copolymer (called PP/PE) supplied by Appryl Co., France under the trade mark 3150MN5.

Muscovite mica flakes (Micarvor 80, Kaolins d'Arvor Co., France) with an average particle size of 48 μm were used in this study. It is a layered aluminosilicate mineral with silicon–oxygen tetrahedral layers linked to gibbsite $Al(OH)_3$ octahedral layers. Each sheet is strongly negatively charged due to the substitution of some aluminium atoms by silicon ones in the tetrahedral layer. These charges are balanced by cations (mostly potassium) located between the sheets. Unlike silica, there are no surface silanol groups on mica.

Mica flakes were coated by a combination of an epoxy prepolymer (Epikote 828, Shell Co., France) and different curing agents. A triethylenetetramine (Prolabo Co., France) called TETA and two polyetheramines (Texaco Chemical Co., France) with two (called PEA2) or three (called PEA3) amine groups were used as curing agents. A silane coupling agent (PC1A/PC1B in the ratio 3/1) supplied by Osi Co., France, was also used as a surface modifier for the mica flakes.

2.2. Surface treatment of mica flakes

The mica flakes were coated with Epikote 828 and the curing agents using either a dry process or a wet process (parameter 1).

In the dry process, the epoxy prepolymer and the curing agent were dissolved in 900 ml of ethanol in a fixed epoxy prepolymer/curing agent ratio (parameter 2). This ethanol solution was then introduced in a mixer apparatus (Drais) which already contained 3 kg of mica flakes. After continuous stirring, mica flakes were dried in an oven at 60°C over 12 h. Two different amounts of surface modifier (Epikote 828 + curing agent) added to the mica flakes were chosen (parameter 3).

Table 1.
Parameters which influence the performance of the epoxy based surface treatments

Parameter number	Description	Parameters
1	coating process	dry or wet
2	epoxy resin/curing agent ratio	9/1 or 9.5/0.5
3	coating amount	1 or 3%
4	curing temperature	80 or 210°C

In the wet process, a fixed ratio of epoxy prepolymer and of each curing agent were also dissolved in ethanol but in a greater quantity (5 l). The mica flakes (3 kg) were then immersed in the ethanol solution with continuous stirring and first partially dried under vacuum at room temperature during 2 h. Finally, ethanol was totally evaporated under a ventilated hood over 12 h.

In both processes, surface-modified mica flakes encapsulated by epoxy prepolymer with the curing agent were obtained. Then these surface-modified mica flakes were subjected to different curing profiles (parameter 4). A coating layer adhering tightly to the mica surface was thus obtained.

The mica flakes were also dry-coated by a combination of two silane coupling agents called PC1A/PC1B. The same experimental procedure described above was used. But after the ethanol evaporation, no curing step was applied, so as to give a surface-coated mica with the silane-based coupling agent.

2.3. Composite specimens elaboration

These differently modified fillers were incorporated with the PP/PE copolymer through an extrusion process (twin screw extruder Clextral BC21). Filler content was about 40 wt%. Then compounds were molded through an injection process (Sandretto trademark) using a damping force of 90 tons. A composite reinforced by untreated mica flakes was also extruded and molded.

3. TECHNIQUES

3.1. Tensile and impact measurements

Young's modulus, yield stress and strain, ultimate stress and strain measurements were performed in tensile mode on an Adamel Lhomargy DY26 testing machine. The experimental procedure as well as the sample dimensions were defined according to the International Norm ISO 527 standard method. Afterwards, ultimate stress values were not reported because they follow the same evolution as yield stress values.

Charpy impact resilience was measured on unnotched samples by means of a Zwick 5102 apparatus according to the International Norm ISO 75 standard method.

Impact direction was parallel to the thickness of the sample and the initial energy was 4 J.

In all cases, ten specimens per sample were tested and the measured values were averaged.

3.2. HDT (heat deflection temperature) measurements

The HDT measurements were carried out using a MIE-JPS apparatus according to the International Norm ISO 75 standard method with a loading of 3.27 N and with a heating rate of 2°C/min.

3.3. Wettability measurements

The wettability index of mineral powders was measured according to Stevens' method [17]. The experimental procedure consisted in the preparation of isopropanol/water mixtures of different surface tensions. The surface tension (E_S, mJ/m^2) is correlated to the isopropanol content ($V_{isopropanol}$, ml) used to prepare 100 ml solution through the following equation:

$$E_S = -11.34 \ln V_{isopropanol} + 68.97. \tag{1}$$

Wettability of powders is measured by sieving the powder upon the isopropanol/water mixtures of various surface tensions. Then the wettability index is the surface tension value of the solution which wets this powder. It is easier to see whether a powder is wetted or not when some methylene blue is added to the solution.

4. RESULTS AND DISCUSSION

4.1. Influence of the amount of coating

4.1.1. Wettability measurements. The influence of the amount of coating was studied through wettability measurements, only in the case of the TETA curing agent and according to the experimental procedure described above. These tests allowed the quality of the encapsulation of the mica flakes by the epoxy resin to be estimated. Indeed, the more efficient the mica encapsulation, the more hydrophobic the mica surface and the lower the wettability index.

Before any wettability tests, the curing profile of the epoxy prepolymer by the TETA curing agent has been optimized by using a Differential Scanning Calorimeter (DSC92, Setaram Co.. France). The TETA curing agent was mixed with the epoxy prepolymer at an epoxy prepolymer/curing agent ratio of 9/1. Then the thermogram was recorded over the temperature range 30–250°C at a heating rate of 10°C/min (Fig. 1). Three heating treatments corresponding to different temperatures and times in the curing process were chosen. These treatments were: 2 h at 50°C, 30 min at 110°C and 30 min at 180°C.

The curing times were selected through isothermal measurements in order to obtain a complete crosslinking of the resin. The amounts of surface modifier (epoxy prepolymer + curing agent) added to mica flakes varied from 0.5 to 3%. The wettability index variations are plotted in Fig. 2 and show that the hydrophobicity of the mica surface increased as both the curing temperature and the amount of coating increased.

For this study, two amounts of surface modifier added to particles were chosen: 1% corresponding to a partial encapsulation and 3% corresponding to a total
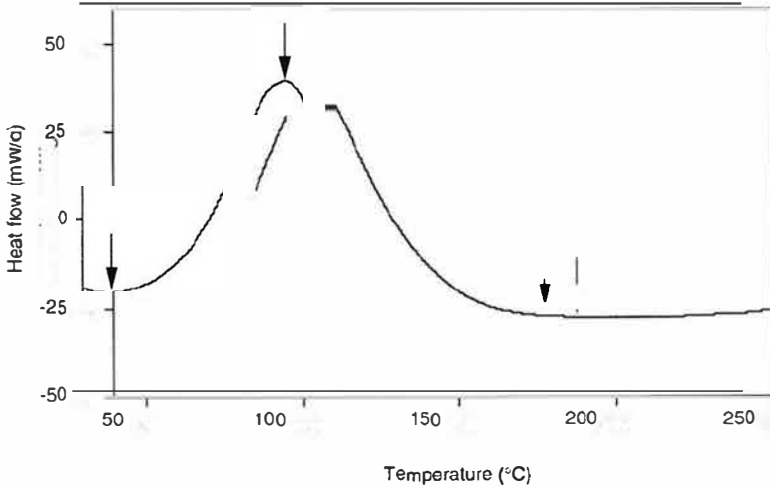

Figure 1. DSC plot of the crosslinking of the epoxy prepolymer (Epikote 828) by the curing agent TETA for an epoxy prepolymer/curing agent ratio of 9/1 (heating rate: 10°C/min).
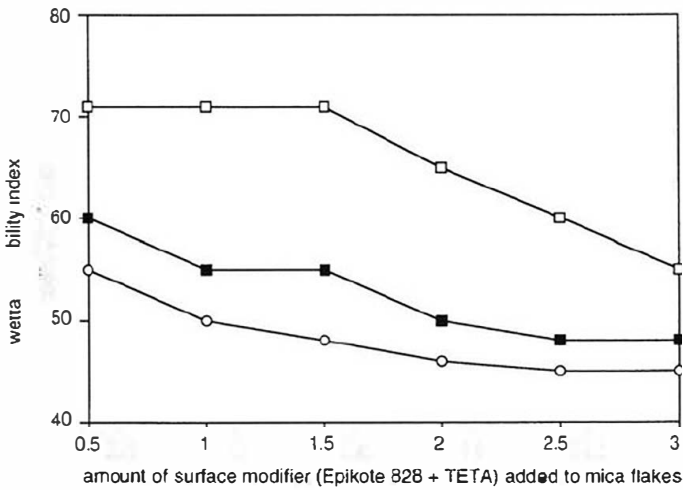

Figure 2. Wettability index comparing the amount of surface modifier (Epikote 828 + TETA) added to mica flakes and the curing profiles (□) 2 h at 50°C (■) 30 min at 110°C (O) 30 min at 180°C of the epoxy-coated mica flakes.

encapsulation. Below the value of 1%, the surface treatment did not seem to be effective. Moreover, the highest curing temperature was selected, i.e. 30 min at 180°C.

4.1.2. *Mechanical properties.* According to previous results, the composites presented in Table 2 were studied.

Moreover, blends of PP/PE copolymer and epoxy resin were also elaborated through the same extrusion-injection process in the case of the TETA curing agent. The amount of epoxy resin was about 1 and 3%. Table 3 shows all the blends used for this study.

For all composites and blends presented respectively in Table 2 and in Table 3, the impact direction was perpendicular to the thickness of the sample. Charpy impact resilience was measured on notched samples for blends.

As shown on Fig. 3, the following results can be listed: (i) the presence of an epoxy resin did not significantly modify the Young's modulus, either for composites or for blends; (ii) the presence of an epoxy treatment on mica flakes seems to increase the yield stress but this increase is independent of the amount of coating; (iii) in the presence of an epoxy resin used either in composites or in blends, the impact strength was drastically decreased and this decrease in impact strength was proportional to the amount of coating; and (iv) no significant variations in HDT values were observed. Therefore, if an epoxy coating did not significantly modify tensile properties, it led to a fall in impact properties. Finally, it appeared more interesting to have a partial encapsulation of mica flakes (coating amount of 1%) for better mechanical performance.

Table 2.
Composites used to study the influence of the amount of epoxy coating added to particles

Curing agent	Coating process	Coating amount	Epoxy resin/ curing agent ratio	Curing profile	Composites
—	—	0%	—	—	A
TETA	wet	1%	9/1	180°C (30 min)	B
TETA	wet	3%	9/1	180°C (30 min)	C

Table 3.
Blends used to study the influence of the amount of epoxy coating added to particles

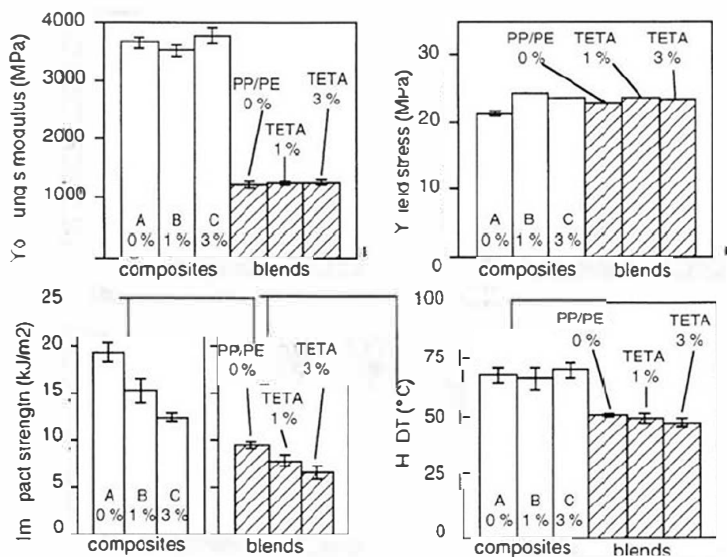| Curing agent	Coating amount	Epoxy resin/ curing agent ratio	Curing profile	Blends
TETA	1%	9/1	180°C (30 min)	TETA-1%
TETA	3%	9/1	180°C (30 min)	TETA-3%

Figure 3. Influence of the amount of surface modifier (Epikote 828 + TETA) added to the mica flakes on the mechanical characteristics of (□) composites (process: wet — curing: 180°C — epoxy resin/curing agent ratio: 9/1) and of (▨) blends.

Table 4.
Onset temperatures (T_{onset}), temperatures corresponding to the maximum of the curing peak (T_{max}) and enthalpies of the curing reaction between Epikote 828 and each curing agent

Curing agent	T_{onset} (°C)	T_{max} (°C)	Enthalpy (J/g)
TETA	70	104	369
PEA2	76	124	106
PEA3	80	126	101

4.2. Influence of the curing temperature

4.2.1. Calorimetry measurements. The curing profiles of the epoxy prepolymer by the three curing agents were optimised through DSC measurements using the experimental procedure described above. The onset temperature as well as the temperature corresponding to the maximum of the curing peak and the curing enthalpy are given in Table 4.

From these results, the curing reaction induced by the TETA curing agent occurred at a lower temperature and involved a more energetic reaction than that from the two other curing agents (PEA2 and PEA3). According to the thermograms shown in Fig. 4, two curing profiles were chosen: 2 h at 80°C and 30 min at 210°C. The curing times were selected through isothermal measurements.
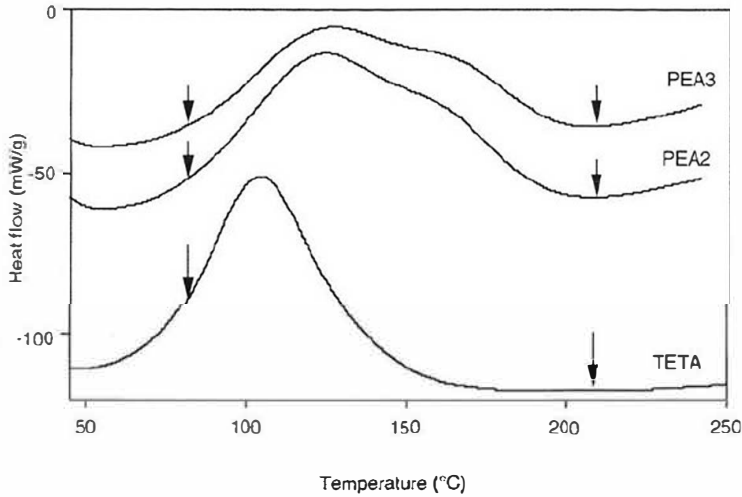
Figure 4. DSC plots of the crosslinking of the epoxy prepolymer (Epikote 828) by the three curing agents for an epoxy prepolymer/curing agent ratio of 9/1 (heating rate: 10°C/min).

Table 5.
Composites used to study the influence of the curing profile of each curing agent

Curing agent	Coating process	Coating amount	Epoxy resin/ curing agent ratio	Curing profile	Composites
TETA	wet	1%	9/1	80°C (2 h)	D
TETA	wet	1%	9/1	210°C (30 min)	E
PEA2	wet	1%	9/1	80°C (2 h)	F
PEA2	wet	1%	9/1	210°C (30 min)	G
PEA3	wet	1%	9/1	80°C (2 h)	H
PEA3	wet	1%	9/1	210°C (30 min)	I

4.2.2. Mechanical properties. According to these results, the composites described in Table 5 were studied.

As shown in Fig. 5, the following results can be listed: (i) for both TETA and PEA3 curing agents, no significant variations in the Young's modulus, the yield stress, the impact strength or the HDT values according to the curing temperature were obtained and (ii) in the case of the PEA2 curing agent, a high curing temperature seemed to decrease the composite strength (Young's modulus and HDT) whereas the impact strength increased. Finally, according to these results, it was a low temperature of 80°C which was preferred.

4.3. Influence of the epoxy resin/curing agent ratio

The influence of the epoxy resin/curing agent ratio was studied in the case of the PEA2 and the PEA3 curing agents and for two epoxy resin/curing agent ratios: 9/1
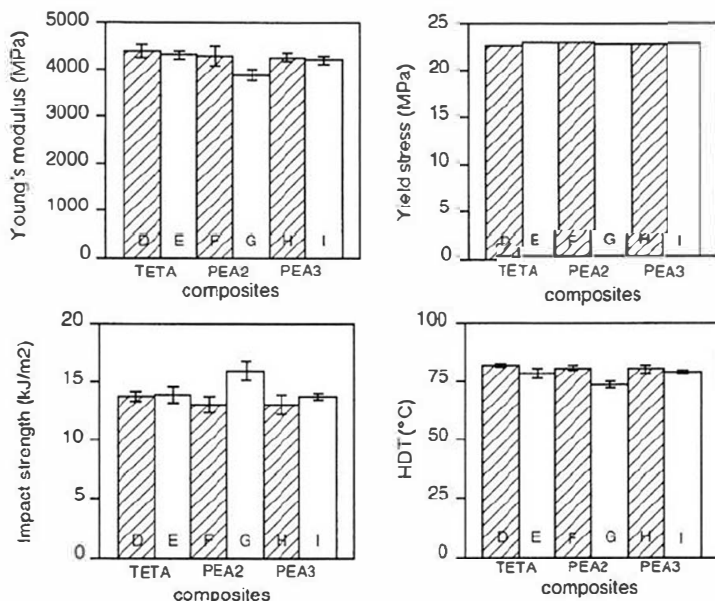
Figure 5. Influence of the curing profile of epoxy-coated mica flakes (□) 2 h at 80°C (▨) 30 min at 210°C on the mechanical characteristics of composites (process: wet — coating amount: 1% — epoxy resin/curing agent ratio: 9/1).

Table 6.

Composites used to study the influence of the epoxy resin/curing agent ratio

Curing agent	Coating process	Coating amount	Epoxy resin/ curing agent ratio	Curing profile	Composites
PEA2	dry	1%	9/1	80°C (2 h)	J
PEA2	dry	1%	9.5/0.5	80°C (2 h)	K
PEA3	dry	1%	9/1	80°C (2 h)	L
PEA3	dry	1%	9.5/0.5	80°C (2 h)	M

and 9.5/0.5. The mechanical properties of the corresponding composites listed in Table 6 were compared.

As shown in Fig. 6, no significant variations in the Young's modulus, the yield stress or the impact strength, nor in the HDT values were observed. Moreover, this behaviour was independent of the nature of the polyetheramine used as curing agent. This result seems to justify the previous choice of a ratio of 9/1 to optimize the amount of coating and the curing temperature.

4.4. Influence of the coating process and of the nature of the surface modifier

All composites used for the study of the influence of both the coating process and the nature of the surface modifier are given in Table 7.
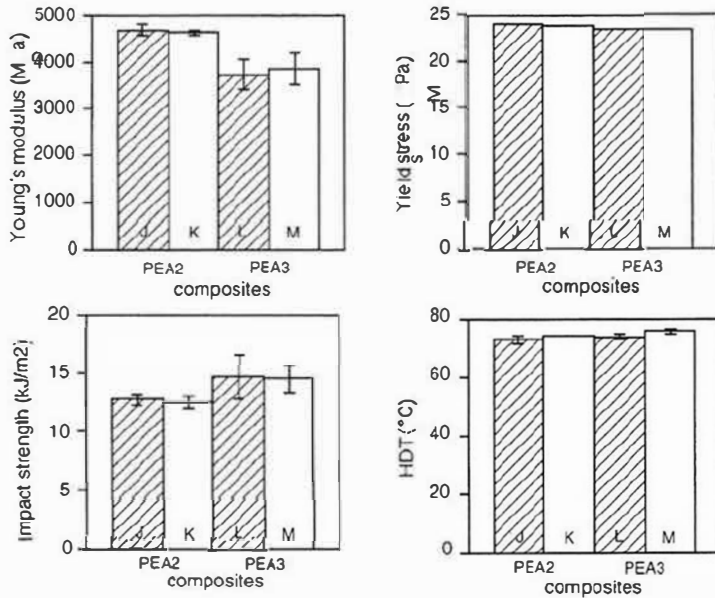
Figure 6. Influence of the epoxy resin/curing agent ratio (□) 9/1 (▨) 9.5/0.5 on the mechanical characteristics of composites (process: dry — coating amount: 1% — curing: 80°C).

Table 7.
Composites used to study the influence of both the coating process and the nature of the surface modifier

Curing agent	Coating process	Coating amount	Epoxy resin/ curing agent ratio	Curing profile	Composites
—	—	0%	—	—	A
TETA	wet	1%	9/1	80°C (2 h)	D
PEA2	wet	1%	9/1	80°C (2 h)	F
PEA2	dry	1%	9/1	80°C (2 h)	J
PEA3	wet	1%	9/1	80°C (2 h)	H
PEA3	dry	1%	9/1	80°C (2 h)	L
silane	dry	1.5%	—	—	N

Figure 7 compares the mechanical properties depending on (i) the nature of the curing agent for all composites and (ii) the coating process for composites reinforced by epoxy coated mica flakes when PEA2 and PEA3 curing agent are used.

Concerning the tensile properties, data show that: (i) the Young's modulus and the yield stress increased in the presence of a surface treatment; (ii) the Young's modulus and the yield stress were better with the silane treatment compared to epoxy treatments; (iii) no significant variations in the yield stress were obtained for
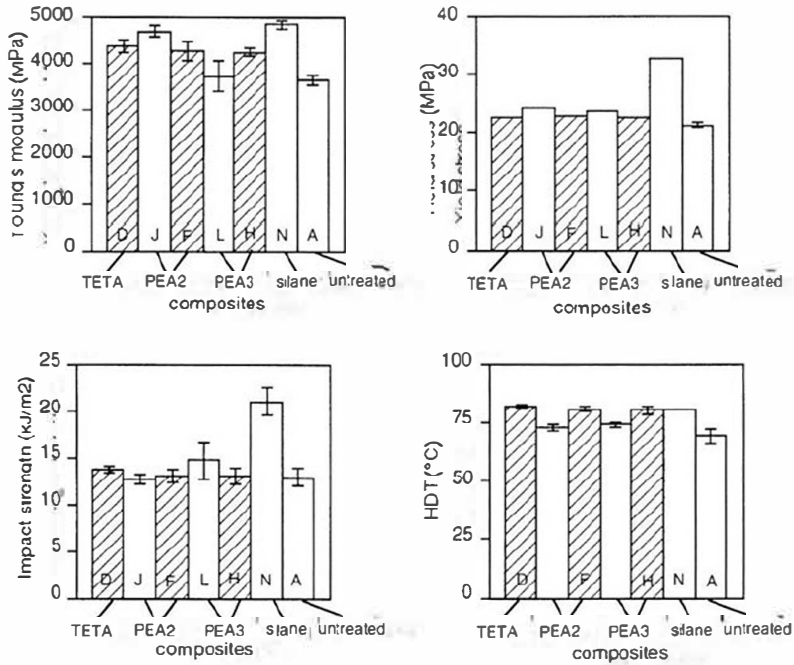
Figure 7. Influence of the coating process and of the nature of the surface modifier (□) dry process (▨) wet process on the mechanical characteristics of composites (coating amount: 1% — curing: 80°C — epoxy resin/curing agent ratio: 9/1) compared to silane-coated composite (composite N) and to untreated fillers reinforced composite (composite A).

epoxy systems; (iv) the Young's modulus of the epoxy-coated mica flakes reinforced composites did not vary when the wet deposition process was used; (v) the PEA2-cured epoxy treatment gave the highest Young's modulus compared to the PEA3-cured epoxy treatment when the dry coating process was used; (vi) moreover, the Young's moduli of composites D, F and H which were wet-coated were between the Young's moduli of the composites J (PEA2) and L (PEA3) which were both dry-coated.

For the impact results, data show that: (i) composites reinforced by silane-coated fillers have the highest impact strength; (ii) except for PEA3-cured epoxy-treated mica reinforced composites (dry process), the impact strength of composites reinforced by epoxy-coated mica flakes is similar to those of composites reinforced by untreated fillers; (iii) the PEA2 curing agent leads to lower impact properties than the PEA3 curing agent for the dry coating process.

For HDT results, data show that: (i) the HDT values increased in the presence of a surface treatment; (ii) for epoxy systems, HDT values are higher when the wet process is used and these values are similar to those of silane-coated composites.

Some difficulties can exist in attempting to get insight into the filler/matrix interaction by the determination of the Young's modulus. Nevertheless, the values of the yield stress depend on this interaction amongst others. Data show similar

yield stress values for composites reinforced by epoxy-coated fillers, whatever the deposition process, and for composites reinforced by untreated ones. Therefore, this could be due to a poor interaction between the epoxy-treated filler and the polymer matrix. Equally, the increase in the yield stress for the silane-coated mica reinforced composites gives evidence of a good adhesion.

The epoxy-coated mica/polyolefine composites have a greater Young's modulus than the untreated mica/polyolefine composites. This result could be due to a good dispersion of mica flakes in the polymer matrix and/or the presence of a stiff interphase arising from the epoxy resin crosslinking. Indeed, wettability tests showed that the epoxy-treated mica surface becomes hydrophobic, compared to the raw mica surface which is hydrophilic. Therefore, the presence of an epoxy treatment seems to improve the dispersion of mica particles compared to untreated particles.

Furthermore, when the dry coating process is used, the PEA2-cured epoxy-coated and the silane-coated mica reinforced composites have a similar Young's modulus. But this is higher than the Young's modulus of PEA3-cured epoxy-treated mica reinforced composites. On the one hand, wettability results show that the hydrophobicity of the PEA2-cured epoxy-coated mica surface is higher than that of the PEA3-cured epoxy-coated mica surface. Therefore, the PEA2-cured epoxy-treated mica flakes should be better dispersed in the polymer matrix than the PEA3-cured epoxy-treated ones. But, on the other hand, the curing agent PEA3 has been supplied to be more flexible than the curing agent PEA2. It should involve a softer interphase. This last assumption seems to be in good agreement with the impact tests.

When the wet coating deposition is used, these previous differences in Young's modulus are smoothed because this wet process is expected to induce a more homogeneous encapsulation of the mica flakes by the epoxy resin. Moreover, quite a good dispersion of mica flakes in the polymer matrix might exist regarding to the HDT tests.

5. CONCLUSIONS

This study deals with the use of an epoxy resin as surface modifier of mica flakes before their incorporation in a polyolefine. The results show that the curing temperature of the epoxy resin, as well as the epoxy resin/curing agent ratio have no significant influence on the mechanical properties. Thus, a curing temperature of 80°C and an epoxy resin/curing agent ratio of 9/1 were chosen. Nevertheless, an increase in the amount of coating added to particles resulted in a considerable decrease in impact strength. Therefore, an amount of coating of 1% corresponding to a partial encapsulation of mica flakes was chosen. Moreover, the nature of the curing agent and the deposition process have a great influence on the mechanical characteristics. The epoxy treatments presented in this paper appear to create a stiff

and brittle interphase leading to a slight increase in tensile properties but to a drastic fall in impact properties.

Research will be carried out in order to use other curing agents which are much more flexible in order to obtain a less brittle interphase. Nevertheless, this soft curing agent should be combined with a commonly used one (for example, a tetraethylenetetramine curing agent) in order to improve impact properties without modification of tensile properties. Concerning the deposition process, the results appear to advocate the wet process. But the high value of the Young's modulus obtained for the PEA2-cured epoxy-coated mica reinforced composites when these fillers are dry-treated should lead us to keep this last process under consideration.

Acknowledgement

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