

Compatibilization and Development of Layered Silicate Nanocomposites Based of Unsaturated Polyester Resin and Customized Intercalation Agent

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ABSTRACT: In this study a procedure for the preparation of compatibilized nanoclays was used to produce effective nanocomposites based on unsaturated polyester (UP) resin. A compatibilization procedure of the filler with a selected surfactant has been developed and optimized, the effect of organic modifiers on the synthesized nanocomposites properties was studied. Moreover, polyester/clay nanocomposites were prepared. In particular, samples were prepared using two different mixing methods. The properties and formation processes of the nanocomposites obtained using the two methods were compared. X-ray diffraction studies revealed the formation of intercalated/exfoliated nanocomposites structures. The effect of processing parameters, used for both the compatibilization procedure and the preparation of nanocomposites, was studied. Dynamic mechanical, thermal analysis, and rheological tests were performed to investigate the formation mechanism of UP/montmorillonite

nanocomposite. In particular, mechanical properties of nanocomposites were studied using dynamic mechanical analysis and tensile tests. Mechanical, rheological, and thermal characterization have confirmed the validity of the used approach to compatibilize the nanoclay and to produce nanocomposites. Tensile strength and Young's modulus were modified by the loading of the organoclays. Furthermore, the rheology of the nanocomposite formulation provided processing information, while mechanical and dynamic mechanical characterization was performed on the nanocomposites produced with the newly compatibilized formulation. The results have shown that nanocomposites with better mechanical properties can be obtained through the selection of an appropriate compatibilization process. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3659–3666, 2010

Key words: compatibilization; nanocomposites; polyester

INTRODUCTION

In the last years a growing attention was dedicated to polymer based nanocomposites. In particular polymer/silicate nanocomposites represent an alternative to conventionally filled polymers and also a possible matrix for fiber reinforced composites. In the open literature^{1–18} and in the commodity polymer industry, it has been demonstrated that the addition of nanometer sized fillers can be used to significantly enhance the mechanical properties of thermosetting and thermoplastic polymers. For example, in the case of thermosetting polymers, it has been observed that the enhancement in fracture toughness of the nanocomposites can be directly related to the size of nanoreinforcements, with smaller particle sizes resulting in greater increase in fracture toughness.^{3,7–9} The dimension, microstructure, and the geometric characteristic of the particles

can significantly affect the proprieties of the filled polymers. Since a fair dispersion of silicate nanoreinforcements can produce materials with higher mechanical properties and good gas barrier and flame reaction¹² polymer/clay nanocomposites have been intensely investigated.

The increase of the aforementioned properties is mainly due to the high aspect ratio of clay nanolayers, conversely it is not easy to disperse the nanolayers in a polymeric matrix because of the intrinsic hydrophobic behavior of most polymers. It is therefore necessary to compatibilize the clay mineral and/or the polymeric matrix. The difficulties to uniformly disperse the nanofiller hold both in the case of thermoplastic and in the case of thermosetting resin such as unsaturated polyester (UP).

The properties of UP/montmorillonite (MMT) nanocomposite greatly depend on the preparation procedure because of the chemical reactions and physical interactions involved.⁴ Furthermore, to obtain an exfoliated UP based nanocomposite it is necessary that, before the polymerization, the polyester molecules shall intercalate the gallery of the silicates, and that the polymerization reaction can start

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Figure 1 Structure of Hyamine[®] 1622.

and propagate from these galleries. If most of the chains react outside the galleries, the shrinking caused by the crosslinking generates a force which works against the exfoliation of the layered silicates. Therefore, to obtain partially or completely exfoliated nanocomposites, also the molecules of the compatibilizer which are firstly intercalated should be able to promote or to take part to the polymerization reaction.^{19,20}

To compatibilize the nanoclay with the polyester matrix, a surfactant must be used. The choice of the surfactant is mainly driven by the need to introduce in the nanoclays galleries, a molecule able to increase the interlayer distance. Furthermore it should somehow affect the reactivity and the affinity with the polyester matrix. The main aim of this study is to compatibilize sodium MMT using a salt which is able to intercalate the clay silicates and at the same time can promote the polymerization of the resin inside the silicate galleries. The first part of the study is dedicated to the process of compatibilization of the MMT, in this part the effects of the compatibilization conditions such as amount of compatibilizer, solvent-salt ratio, and mixing temperature is evaluated. In the second part a preliminary characterization of a nanocomposite based on polyester resin and the optimized MMT is performed. A compatibilization procedure of the filler with a surfactant has been developed and optimized and the effect of organic modifiers on the synthesized nanocomposites properties was studied. Moreover, polyester nanocomposites with an elevated degree of intercalation, were obtained using a mechanical mixing and sonication at the same time.

Tensile strength and Young's modulus were modified by loading the organoclays. In particular, nanocomposite samples were prepared to investigate the properties and formation mechanism of UP/MMT nanocomposite using two different mixing procedures. The properties and formation processes of the nanocomposites obtained using the two procedures are compared.

The structure of UP/MMT nanocomposites was investigated by X-ray diffraction (XRD). Dynamic mechanical analysis, thermal analysis, and rheological tests were performed, to characterize the nanocomposite obtained. In particular, mechanical properties of nanocomposites were studied using dynamic mechanical analysis and tensile tests. Me-

chanical, rheological, and thermal characterization have confirmed the validity of the used approach to make compatible the nanoclay and to produce effective nanocomposites.

MATERIALS AND EXPERIMENTAL

AROPOL Q6585 polyester resin, supplied by Ashland Composite Polymer (Covington, Kentucky), was used in this study. AROPOL Q6585 is a high reactivity resin, and it is designed for use in low profile and controlled shrinkage applications. Butyl peroxide (BPO) was used as initiator.

The fillers used in this study are derived from Bentonite and are commercialized with the name of DELLITE from Laviosa Chimica Mineraria S.p.a. In particular, this research has adopted the DELLITE[®] LVF which is a nanoclay derived from a natural sodium MMT.

XRD analysis performed to determine the interlayer distance of the DELLITE[®] LVF revealed a value of $d_{001} = 9.9 \text{ \AA}$ was obtained for the layered silicate in the non hydrated state while a value of $d_{001} = 12.5 \text{ \AA}$ for the hydrated state was measured.

In this study an ammine based salt, Hyamine[®] 1622 from Sigma-Aldrich, was used. This choice was mainly made because of its availability, the size of the macromolecule, and its effect on the reaction of the polyester. In Figure 1 the structure of the ammonium salt is shown. The presence of a hydrophilic group and of an organophilic group make this salt ideal to be used as a substitute of the metallic cation of the layered silicate.

The rheological and dynamic mechanical tests on reacted resin were performed using a Rheometric Scientific ARES dynamic viscosity spectrometer, parallel plates with a diameter of 12.5 mm, were used for the liquid systems. XRD analysis was performed using a Rigaku Ultima+, using Cu-K α radiation in reflection mode ($\lambda = 0.154 \text{ nm}$).

Thermogravimetric analysis (TGA) was performed using a SEIKO ESTAR 2000 TGA, test on pure materials and nanocomposite were performed in dynamic mode up to the final degradation temperature of the resin and at different heating rates ranging from 2 to 20°C/min.

Mechanical tests were performed using an universal dynamometer Lloyd LR30, tensile tests were

TABLE I
Main Characteristics of the Different Compatibilization Processes

Sample	Mixing method	Temperature (°C)	Mixing time (h)	Weight surfactant/weight solvent (g/mL)	Weight surfactant/weight nanofiller (%)
A	Manual	Room temperature	Istantaneous	1 : 160	60
B	Ultrasound	70	1	1 : 160	60
C	Ultrasound	70	2	1 : 160	60
D	Ultrasound	70	3	1 : 160	60
E	Ultrasound	70	10	1 : 160	60
F	Manual	Room temperature	Istantaneous	1 : 160	30
G	Manual	Room temperature	Istantaneous	1 : 160	100
H	Manual	Room temperature	Istantaneous	1 : 160	60
I	Manual	Room temperature	Istantaneous	1 : 20	500

performed according to ASTM D638M with cross-head speed of 5 mm/min, while flexural test were performed according to ASTM D790M with a cross-head speed of 1.7 mm/min. The values of the Modulus were calculated as the tangent of the curve stress–strain in the small deformations range.

The method developed to compatibilize and functionalize the nanofiller was based on the substitution of the metallic cations, which lay in between the silicate galleries, with the organic cation of the selected compatibilizer. This method exploited the solubility in water of both the compatibilizer salt and the MMT.^{21,22} Therefore two solutions in deionized water were firstly prepared. The first one was made dispersing the nanofiller and the second one contained different amounts of surfactant. Subsequently, the two solutions were mixed together, to allow the exchange between the sodium cations of the dispersed MMT and the cations of the alkyl ammonium salt. Once the two solutions were completely mixed, the solution was filtered with a porosity of 90 μm , and the so obtained compatibilized silicate was washed in deionized water to eliminate the excess surfactant. The organo-modified clay compound was then dried in a ventilated oven at 40°C and milled to reduce the platelet stacking. Different processing variables were changed to find the more adequate processing conditions. In particular, the effects of the mixing time, mixing temperature, and mixing modality were studied. Once determined the optimum of these variables, the clay/surfactant ratio was also optimized. The first solution, characterized by a ratio clay/deionized water, of 1 g of clay over 100 mL of water, was considered the best compromise between the need of obtaining a good dispersion of the clay in the liquid, and the need of minimizing the amount of water used.

RESULTS AND DISCUSSION

Table I reports the number of samples produced and the respective treatments used, in this table, the letters refers to the different procedures followed dur-

ing the compatibilization process. In the procedures A, B, C, D, and E, the concentration of the solution of the compatibilizer in water is 1 g over 160 mL, whereas the net weight percentage of the surfactant respect to the neat clay when the two solutions are mixed was 60%. The differences between each procedure lay in the method with which the nanoclay dispersion and the surfactant solution are blended together. In procedure A, the surfactant solution and the nanoclay dispersion are mixed manually, in the procedure B, the two solutions have been mixed using ultrasound for 1 h at 70°C. in the procedure C, the same conditions as B were used, but the mixing in ultrasounds lasted 2 h, in the procedure D, the ultrasound mixing was held for 3 h and in the procedure E, it was 10 h. The sample clays, indicated by the procedures F, G, H, and I, were produced after the first optimization to evaluate the effects of the clay/surfactant ratio and were mixed manually at room temperature. The amount of surfactant with respect to the pure clay was in this case, 30, 60, 100, and 500% respectively.

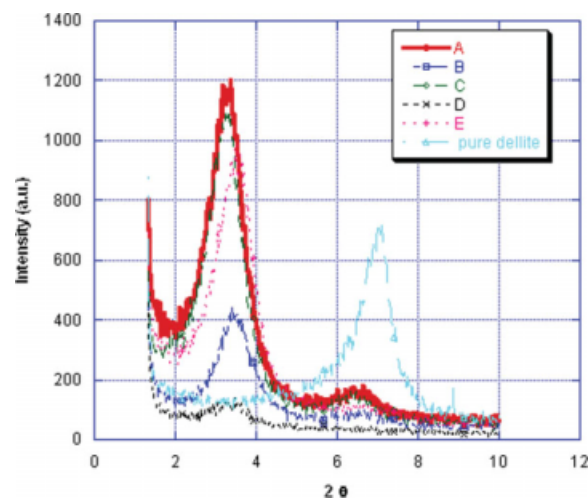


Figure 2 XRD diffraction peaks of natural clay and of compatibilized clays at different sonication time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
XRD and TGA Results for the Modified Clay

Sample	2 θ	d_{001} (Å)	Surfactant adsorbed (wt %)	Organic cation exchanged (meq/100 g)
Pure dellite	8.86	9.9	–	–
A	3.18	27.7	22	49
B	3.37	26.1	21	47
C	3.36	26.2	22	49
D	3.61	24.5	21	47
E	3.46	25.5	19	42
F	3.64	24.3	14	31
G	2.91	30.3	24	54
H	3.25	27.2	23	51
I	3.18	27.8	27	60

X-ray patterns are reported for samples A to E in Figure 2, and data of the pure clay are also plotted as a reference. The difference in the intensities of the diffraction peaks is mainly due to the different concentration of the material used during the test. From this plots, it is possible to observe that all the procedures revealed an intercalation the clay, as the peak of the interlayer distance shifts to lower diffraction angles. Each treatment has produced a different interlayer distance as a result of an increased capacity of cation exchange (CEC), and in some case the treatment was able to triplicate the d_{001} value (Table II). This remarkable increase of the interlayer distance indicates that the process of cationic exchange took place, and that all compatibilization treatments were, to some extent, effective. Quantitative measurements of the amount of surfactant exchanged were performed using TGA. Figure 3 reports different dynamic scans performed on samples A through E, on pure Hyamine and on the neat clay. All the plots except the one of Hyamine are characterized by a two steps degradation process. The first degradation step, which in the case of pure Dellite take places around 100°C, is due to the interlayer water associated with the exchangeable Na⁺ ions with minor contribution of free water held in interparticle pores. The second step in the 700–800°C range is associated with the loss of structural water through dehydroxylation of the MMT layers.^{23–25} It is possible to observe that the treatment with Hyamine has modified the thermal behavior of the clay. Comparing the TGA results with the X-rays, which indicate an increase of interlayer distance, it is possible to draw further insight on the effective compatibilization of the clays. The shift to higher temperatures of the onset of the weight loss respect, both the pure clay and the Hyamine, indicates that the surfactant is bonded to the surface, or better, into the interlayer galleries of the clay platelets, since more energy is necessary to allow its evaporation and/or degradation. Fur-

thermore all the compatibilized samples present a smaller residue at 1000°C which can be directly associated to the amount of surfactant adsorbed. With these data, it has been possible to calculate the amount of exchanged cation CEC for each of the samples. The comparison of the results obtained has shown that the mixing at higher temperature does not produce substantial improvement of the compatibilization, whereas the best results were obtained by mixing at room temperature without the use of ultrasounds (method A). These results are interesting under a processing point of view since this is the simplest and cheapest method.

The effect of the different clay/surfactant ratio was therefore evaluated, taking as a reference the sample made with method A. Samples F, G, and H were produced mixing at room temperature without ultrasound the two solutions varying only the ratio Hyamine/filler, as indicated in Table I. Figure 4 reports the X-ray patterns obtained on the aforementioned samples, all the different procedures produced an increase of the interlayer distance d , indicating that the surfactant was able to intercalate the layers of the clay silicate and exchange with the metallic cations. TGA test confirmed the results obtained by X-ray (Fig. 5), where the TGA dynamic scans of samples at different clay/surfactant ratio A, F, G, and H are reported. Table II summarizes the results obtained. Plotting the amount of surfactant absorbed and the cations exchanged as a function of the clay/surfactant ratio used during the compatibilization (Fig. 6), allows to make some interesting consideration about the compatibilization conditions.

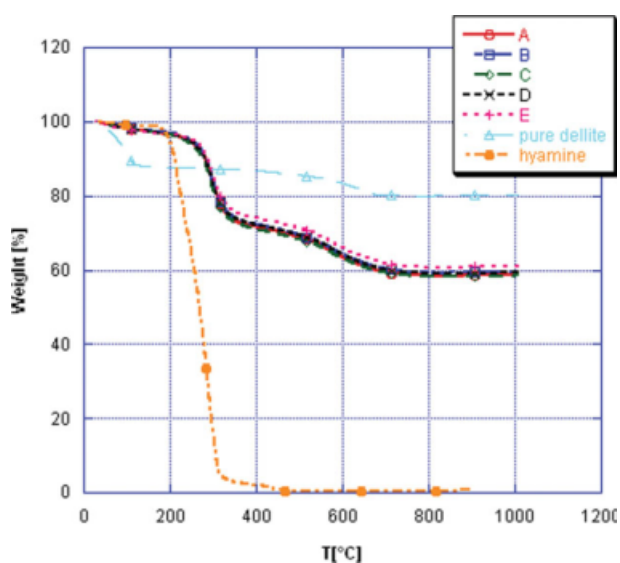


Figure 3 Thermogravimetric curves of the pure clay, surfactant, and of modified clay at different sonication time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

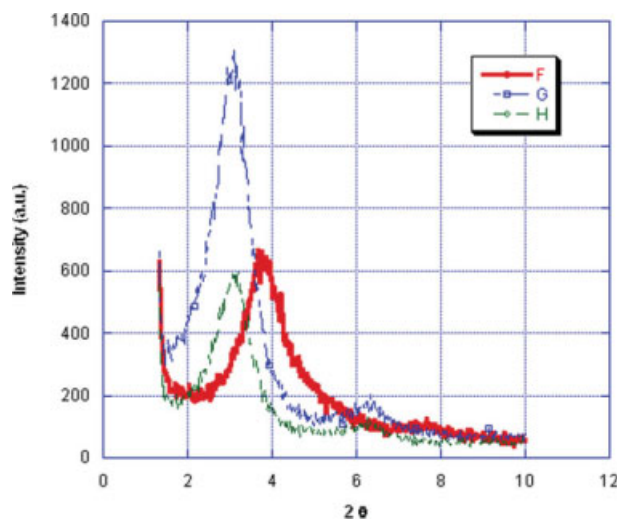


Figure 4 XRD diffraction peaks of compatibilized clay at different Hyamine/filler ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The curve obtained are, infacts, clearly asymptotic indicating that, a clay/surfactant ratio slightly higher than 100%, produced the maximum compatibilization and therefore it is not necessary to use higher mixing ratios.

Finally the effect of the dilution of the surfactant solution was analyzed. A new sample (sample I) was prepared using a more concentrated solution of compatibilizer and it was mixed with the nanoclay solution with the same modalities of sample A. In Figures 7 and 8 are reported the XRD plot and the TGA scan of both the samples, the values of the interlaminal distance and of the cation exchange capacity (CEC)

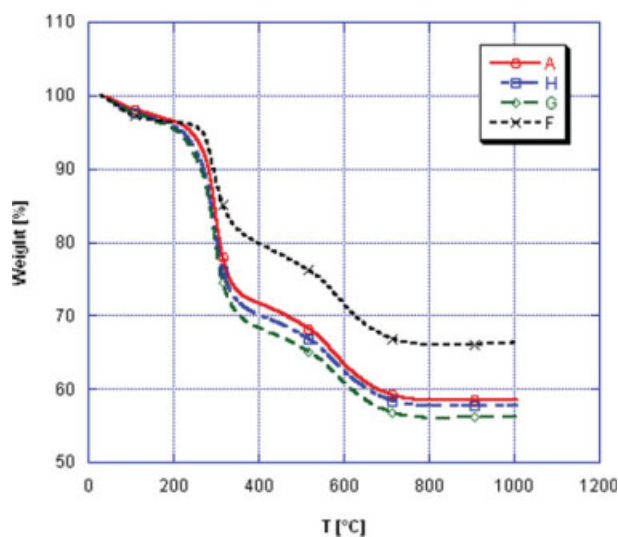


Figure 5 Thermogravimetric curves of the modified clay at different Hyamine/filler ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

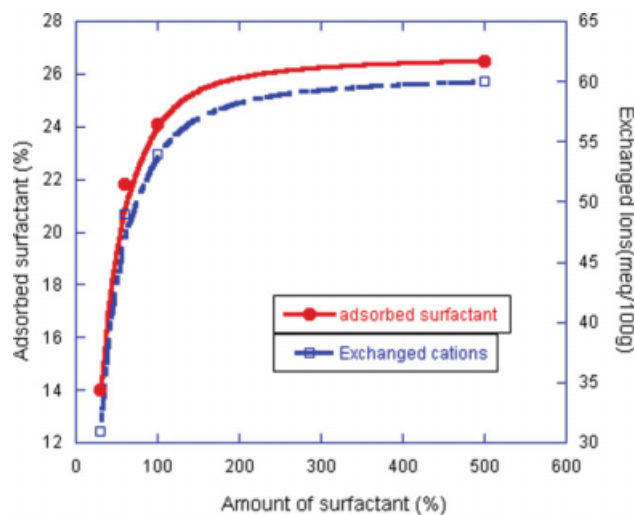


Figure 6 Amount of surfactant absorbed and cations exchanged as a function of the ratio clay surfactant used during the compatibilization. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

are also reported in Table II. It is possible to notice that the results obtained are very similar indicating that it is also possible to use a more concentrated solution of compatibilizer without compromising the CEC of the clay. Method G of Tables I and II was therefore considered the optimum method.

Once determined the optimum compatibilization treatment, polyester based nanocomposite was produced. Samples for the mechanical test were produced curing a mixture of AROPOL resin with 1% of BPO at 60°C and then post cured at 110°C. Nanocomposites were then produced using two different

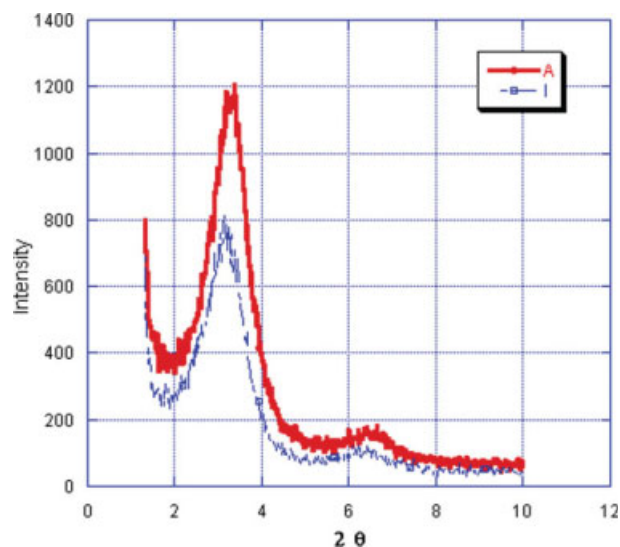


Figure 7 XRD diffraction peaks of the modified clay at different surfactant/nanoclay ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

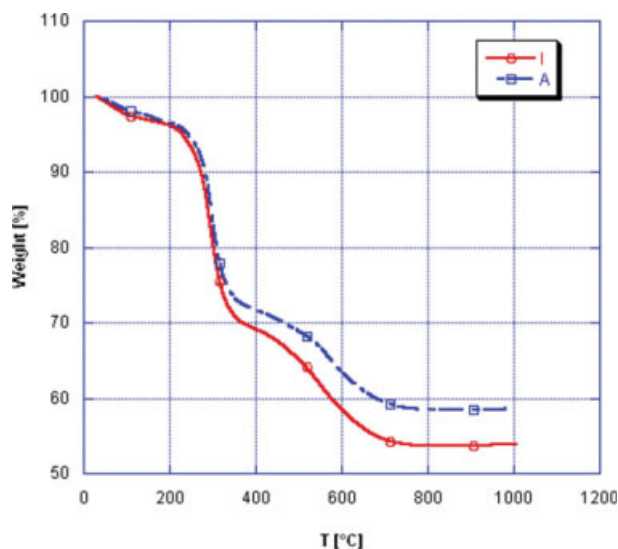


Figure 8 Thermogravimetric curves of the modified clay at different surfactant/nanoclay ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

methods of mixing: sequential mixing and simultaneous mixing. In the first case, the resin and a percentage of 2.5% of nanofiller were first mixed together and then introduced in an ultrasound machine for a certain amount of time then the obtained compound was further mixed in a centrifugal agitator at high rotation speed, the so obtained sample is indicated as (U + M). The second method consisted in preparing the solution of nanocomposite using the same time ultrasounds and mechanical mixing. The two mixtures were then cured and samples for mechanical properties were prepared. The mixing temperatures were chosen between room temperature and 70°C. The mixing time varied from instantaneous mixing up to 10 h. In the table and in the figures, sample produced with simultaneous mixing are indicated as [(UMC) ultrasound and mechanical compounding]. To evaluate the effectiveness of the different methods, XRD analysis was performed on samples produced with both the techniques. Figure 9 reports the XRD spectra obtained. Both systems show that it has been possible to increase the interlayer distance of the silicate. A diffraction peak still appears but it is shifted at lower

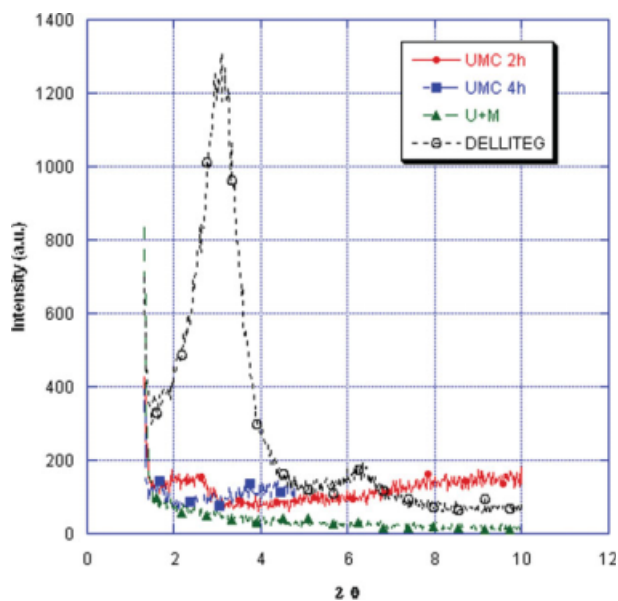


Figure 9 XRD diffraction of nanocomposites and of compatibilized nanoclay. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

angle and its small intensity indicates that a partially exfoliated structure is obtained.

Tensile and flexural tests were performed to evaluate the better method. The results obtained are summarized in Table III. Regarding the tensile test, it seems that no substantial increase of the mechanical properties is observed. The reduction of the tensile strength can be attributed to the presence of micro defects and superficial defects whose effects are generally more marked on tensile properties. More interesting results were obtained from flexural tests, such tests showed an increase of the flexural modulus and of the flexural strength only for the samples obtained using simultaneous mixing technique at longer time, confirming that, with such technique, it is possible to produce a nanocomposite with increased properties. The better performance of the sample UMC4h, respect to others, indicates that prolonged mixing produces better intercalation.

Rheological tests were also made on the nanoreinforced compounds and on the pure resins. Dynamic, stationary, and transitory test were performed (Fig. 10). Rheological test on the unreacted resins were

TABLE III
Tensile and Flexural Properties of Cured Resin and of Cured Nanocomposites

Name	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)	Flexural modulus (GPa)	Flexural strength (MPa)
AROPOL	3.3 ± 0.5	35 ± 18	3.2 ± 1.4	2.5 ± 0.1	48 ± 15
AROPOL + 2.5 (U + M)	3.7 ± 0.2	20 ± 4	1.5 ± 0.6	3.6 ± 0.6	34 ± 5
AROPOL + 2.5% (UMC4h)	3.9 ± 0.3	30 ± 8	1.5 ± 0.7	4.3 ± 0.4	72 ± 15
AROPOL + 2.5% (UMC2h)	3.5 ± 0.4	21 ± 5	1.5 ± 0.2	3.5 ± 0.5	47 ± 15

made to investigate the microstructure and influence of the filler on the processing. It was observed that all the synthesized nanocomposite compounds exhibit a higher viscosity respect to that of the pure matrix. The characteristic shear thinning behavior, observed in layered silicate nanocomposite, is also observed both in the stationary and in transitory tests. However the difference in the rheological properties in low deformation range is compatible with the processing request.

Dynamic-mechanical characterization on the obtained samples were also made. A substantial improvement of the storage modulus was observed at higher temperatures. Figure 11 reports a comparison of the storage modulus and of the $\tan \delta$ of the pure resin and the nanocomposites obtained with different mixing methods. The effect of the nanofiller results in an increase of the behavior at higher tem-

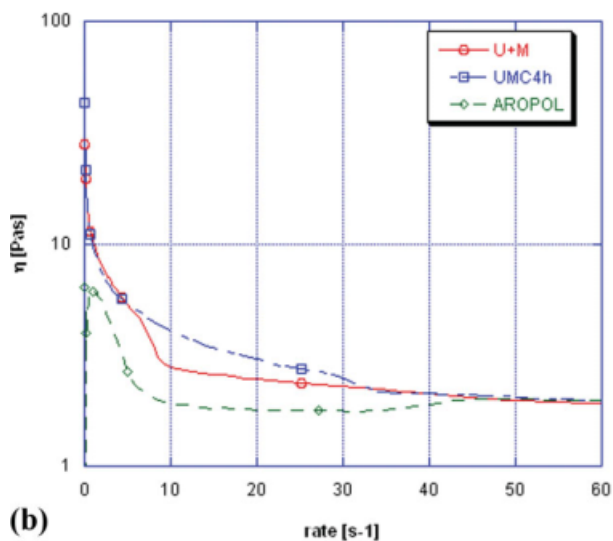
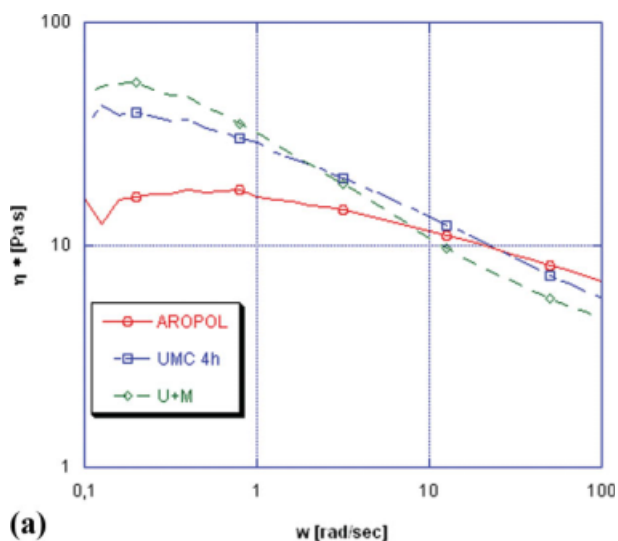


Figure 10 Flow curves of the prepared nanocomposites: dynamic (a) stationary (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

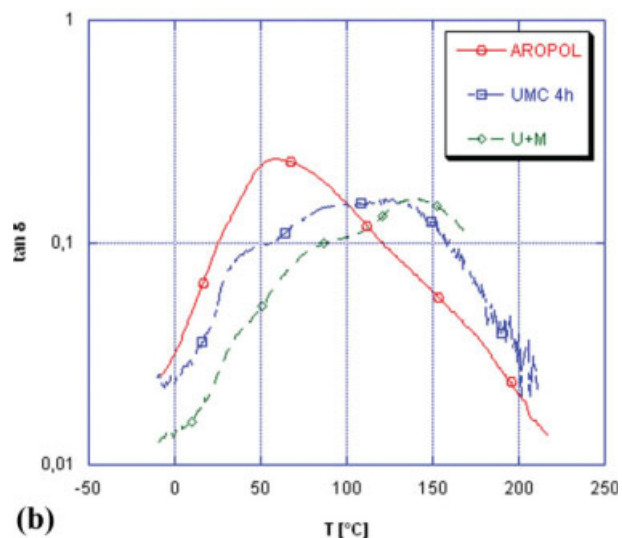
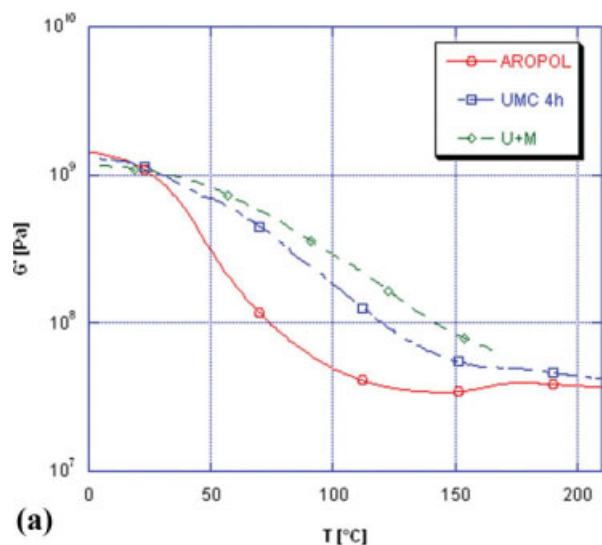


Figure 11 Storage modulus (a) and $\tan \delta$ (b) of the pure resin and of the nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

peratures for the nanocomposites made using the compatibilized filler. The $\tan \delta$ peak is shifted at higher temperatures confirming the hypothesis of a lower mobility and more rigid structure due to the reinforcing effect of the nanocharges. Furthermore the nanocomposites produced using simultaneous mixing method did not break at higher temperatures, up to 200°C, whereas the other samples broke at 170°C indicating that an appropriate mixing, coupled with a custom compatibilization treatment, result in a nanocomposites with better performances.

CONCLUSIONS

This study has compared different method of compatibilization of layered silicate for polyester resin.

TGA and X-ray were used to evaluate the effectiveness of the compatibilization process and to optimize the compatibilization parameters, in terms of amount of water used and clay/surfactant ratio. It was found that using a clay/surfactant ratio higher than 100% does not produce sensible increases of the cation exchanged. The two different mixing method used to produce nanocomposites with the compatibilized clays resulted in nanocomposites with improved mechanical properties, but only simultaneous mechanical and ultrasound mixing of the clay resin system produced an increase of both the flexural modulus and the flexural strength. The nanocomposites obtained with such method showed also an higher storage modulus at higher temperature and higher thermal resistance, confirming, together with the X-ray results, that it has been possible to obtain a partially exfoliated structure.

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