

MODIFIED ORGANOPHILIC MONTMORILLONITES/LDPE NANOCOMPOSITES

Preparation and thermal characterization

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In this work a commercially available organophilic Montmorillonite (Cloisite 30B) was modified by interaction with different surfactants, namely dodecylsuccinic anhydride (DSA), octadecylamine (ODA), octadecanoic alcohol (ODOH) and octadecanoic acid (ODAc), in order to increase its basal spacing and to achieve a better dispersibility in LDPE. The morphology of the dispersions was investigated through XRD and TEM analyses. Intercalation phenomena were found for all the systems investigated. The thermal properties of the obtained nanocomposites were studied by means of DSC and TGA measurements. No variation of T_m and crystallinity of LDPE was found after the addition of the nanoclays (5 mass/mass%). A significant increase of the air thermal stability of LDPE was achieved in the presence of the modified nanoclays.

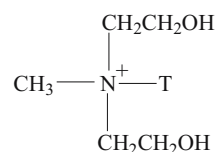
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Introduction

The emphasis in the research involving nanofillers dispersed in polymers is mostly due to their peculiar phase morphology and interfacial properties which determine an improvement of the performances of the nanocomposites. Nanoclays are particularly explored as matrix reinforcing components for their high aspect-ratio, plate morphology, natural availability and low cost. They are known to enhance properties such as stiffness, modulus, barrier properties toward different gases and flame retardancy [1–5]. Some restrictions in their use however arise from their tendency to form agglomerated tactoidal structures, having high cohesive energy which causes problems in the dispersion at a nanometric level in non-polar polymer matrices such as polyolefins. For this reason it is necessary to perform modifications on the structure of the nanoclays in order to decrease their polarity. The most common way is the ion exchange functionalization with quaternary ammonium salts, which lower the surface energy and the hydrophilic character of the nanoclays, and make them more compatible toward polyolefins [6–10]. As a result, it is possible to increase the interlayer distance of the platelets and to allow better interactions with the polymeric matrix. The morphology of the clay in the matrix, indeed, plays an important role on the final properties of the nanocomposite material, such as its mechanical behavior and thermal resistance. The most effective

configuration corresponds to that where the silicate layers are individually and homogeneously dispersed in the polymer matrix (exfoliated structure). It is difficult, however, even by using compatibilizers, to obtain this type of morphology in the presence of polyolefins, due to their non-polar structure. The most common compatibilizers employed for this purpose are maleinized polymers, EVA (poly(ethylene-co-vinyl acetate)) and ionomers [11–16]. Usually intercalated structures are obtained, which, anyway, can improve the mechanical strength and the thermal stability of the nanocomposites.

In this work we used a commercially available organophilic Montmorillonite, namely Cloisite 30B. It contains the alkyl ammonium ion whose structure is reported in Fig. 1. The nanoclay was further modified by interaction with different additives bearing C₁₂–C₁₈ alkyl chains and functional groups able to interact with the hydroxy-ethyl groups present in Cloisite 30B. Thus it was possible to further decrease the surface tension of the nanoclay, and to make it more compatible toward LDPE.



(T=Tallow: 65% C₁₈, 30% C₁₆, 5% C₁₄)

Fig. 1 Structure of the alkylammonium ion in Cloisite 30B

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For this purpose dodecylsuccinic anhydride (DSA), octadecylamine (ODA), octadecanoic alcohol (ODOH) and octadecanoic acid (ODAc) were used. They can be considered as model compounds of the compatibilizers reported above [17–19].

The basal spacing values of the obtained products were evaluated by means of XRD analyses. The modified clays were dispersed in LDPE using a Brabender mixing unit (5 mass/mass%). The morphology of the nanocomposites was examined through XRD and TEM investigation. Their thermal properties were evaluated through DSC and TG analyses.

The aim of the work was to compare the behavior of the different modified clays as nanofillers dispersed in LDPE.

Experimental

Materials

A commercially available organo-modified Montmorillonite nanoclay, namely Cloisite® 30B, was purchased by Southern Clay Product Inc. (USA).

Dodecylsuccinic anhydride (DSA), octadecylamine (ODA), octadecanoic alcohol (ODOH) and octadecanoic acid (ODAc) were Aldrich products, used as received.

The modified clays were added to LDPE (Riblene® FC30, density: 0.922 g cm⁻³, MFI: 0.27 g/10' @190°C/2.16 kg), kindly supplied by Polimeri Europa (Italy). Irganox 1076 (Ciba Specialty Chemicals) was added as antioxidant (0.1 mass/mass).

Modification of Cloisite 30B

5 g of Cloisite 30B were dispersed in 2,2-dimethoxyethane at 75°C for 2 min. The modifier was then added and the dispersion was heated at 75°C for 2 h under vigorous stirring. The mixture was washed with fresh solvent and filtered at room temperature. The obtained product was then placed in an oven at 70°C for one night until constant mass was reached.

Preparation of the nanocomposites

The dispersion of the nanoclays into LDPE was performed using a Brabender Mixing Apparatus Plastograph W30 1E (temperature: 160°C; time: 4 min, 100 rpm).

The modified Cloisites were added in the molten LDPE at 5 mass/mass concentration. The obtained nanocomposites were then hot-pressed by using a laboratory plate press Collin Teach Line 200T working at 160°C and 100 bar (heating time: 4 min; cooling time: 3 min).

Analyses and characterization techniques

RX measurements were performed both on the clays and on the composites using a Philips X'Pert-MPD diffractometer (CuK_α radiation; 2θ range: 2–30°; Δ2θ step: 0.02°; step time: 2 s).

Wide angle X-ray scattering (WAXS) analyses were conducted on all the modified clays in order to confirm the basal spacings. Scanning was performed from 1 to 5°, with 0.01° Δθ step and 20 s step time.

DSC measurements were performed using a Mettler DSC 30 (Switzerland) apparatus, equipped with a low temperature probe (heating rate: 10°C min⁻¹).

TG analyses were performed using TGA/SDTA 851 analyzer. The analyses were carried out under both nitrogen and air at a flow rate of 60 cm³ min⁻¹ from room temperature up to 800°C (heating rate: 5°C min⁻¹).

TEM analyses were performed using an EM 420T TEM 140 microscope on ultramicrotomed specimens (with a diamond knife on a Leika Ultracur UCT microtome; thick section: 70 nm) without any specific staining.

Results and discussion

In Table 1 the basal spacing d_{001} data of the modified clays, together with the increase of the spacing Δd_{001} with respect to Cloisite 30B are collected, as obtained by XRD analysis.

In Fig. 2 some XRD patterns related to Cloisite 30B, Cloisite 30B+DSA and Cloisite 30B+ODOH are reported. A clear shift of the diffraction peaks of the planes (001) towards lower angles after the treatment with the different surfactants is evident. The modified

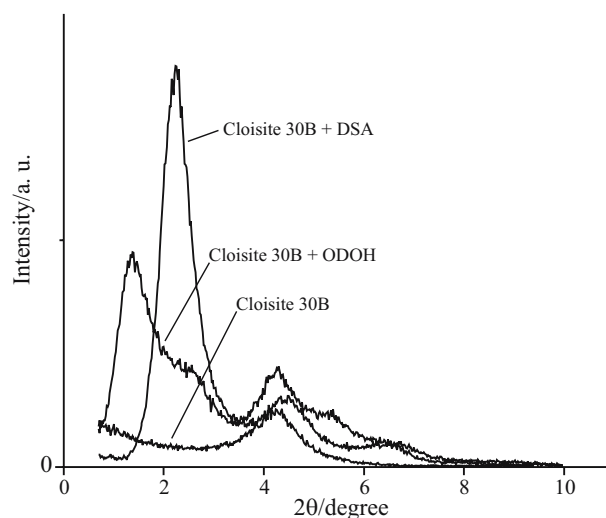


Fig. 2 XRD patterns for Cloisite 30B, Cloisite 30B+DSA, Cloisite 30B+ODOH

Table 1 d_{001} and Δd_{001} data for the different nanoclays

Nanoclay	Interlayer distance $d/\text{\AA}$	$\Delta d/\text{\AA}$
Cloisite 30B	18.4	–
Cloisite 30B+DSA	38.9	20.5
Cloisite 30B+ODOH	64.4	46.0
Cloisite 30B+ODAc	39.2	20.8
Cloisite 30B+ODA	40.3	21.9

Cloisite with DSA shows a more defined peak probably due to the reaction of OH groups with the succinic anhydride groups of DSA, which strengthen the interactions with the nanoclay. Actually previous FTIR investigations showed the disappearance of the anhydride group signal and the appearance of an ester group band at 1742 cm^{-1} after the modification treatment [20].

Moreover it can be noted that every treatment with the surfactants increases the basal spacing of Cloisite 30B of about 20 \AA . Otherwise the system treated with ODOH gives an increase of the basal spacing clearly higher with respect to the other additives ($\Delta d=46\text{ \AA}$), probably due to the formation of stronger H bonds.

The modified clays were then dispersed into molten LDPE at a 5 mass/mass% concentration, using a Brabender Apparatus. All the prepared samples showed a homogeneous dispersion of the clays. In Fig. 3 the XRD patterns of Cloisite 30B, Cloisite 30B modified with ODOH and Cloisite 30B modified with DSA are reported. In Table 2 the results of XRD analyses performed on the composites are collected. It can be noted that the d_{001} spacing value related to Cloisite 30B does not change after its dispersion in LDPE. On the other hand, all the other systems give rise to intercalation effects. Cloisite 30B+ODOH evidences a de-

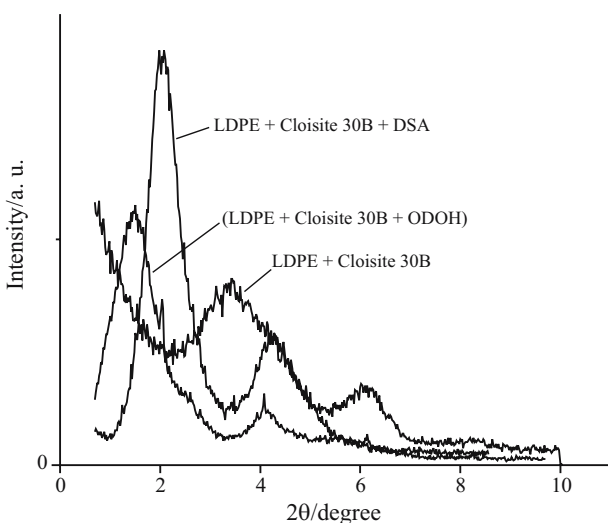

Fig. 3 XRD patterns for Cloisite 30B, Cloisite 30B+DSA, Cloisite 30B+OD based nanocomposites

Table 2 d_{001} data for the different LDPE nanocomposites (5 mass/mass%) compared to the used clay

Nanocomposite	$d_{001}/\text{\AA}$	$d_{001}/\text{\AA}$ of the used clay
LDPE/Cloisite 30B	18.4	18.4
LDPE/Cloisite 30B+DSA	39.2	38.9
LDPE/Cloisite 30B+ODOH	59.4	64.4
LDPE/Cloisite 30B+ODAc	38.1	39.2
LDPE/Cloisite 30B+ODA	41.3	40.3

Table 3 LDPE crystallinity and T_m values (from DSC) of the different nanocomposites (5 mass/mass% of clay)

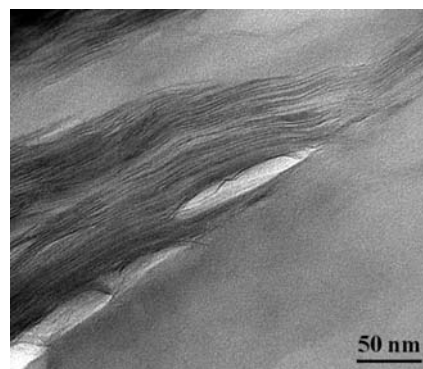
Nanocomposite	$X/\%$	$T_m/^\circ\text{C}$
LDPE	32.1	110
LDPE/Cloisite 30B+DSA	31.8	111
LDPE/Cloisite 30B+ODOH	32.2	111
LDPE/Cloisite 30B+ODAc	32.4	112
LDPE/Cloisite 30B+ODA	31.9	110

crease of the basal spacing, indicating that the intercalation effect of ODOH is not maintained when the clay is dispersed into LDPE. The same behaviour can be observed for Cloisite 30B+ODAc/LDPE systems. We can conclude that the polar interactions between ODOH or ODAc and ammonium ions are slightly reduced during the dispersion of the clays in molten LDPE.

In Table 3 the crystallinity and T_m values of the different nanocomposites are collected; they clearly indicate no variation of these parameters in the presence of the nanofillers.

The XRD data were confirmed by TEM analyses. In Fig. 4, a typical TEM micrograph, related to a LDPE/Cloisite 30B+ODA nanocomposite, is reported; it shows an intercalated morphology with the presence of tactoids.

The thermal properties of the nanocomposites were investigated by TG analysis. The obtained re-


Fig. 4 TEM micrograph of an intercalated LDPE-Cloisite 30B+ODA nanocomposite

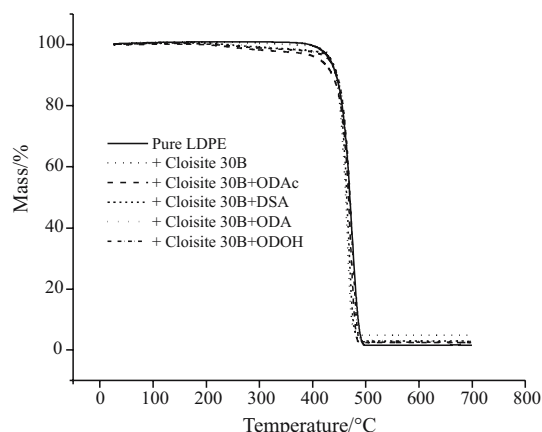


Fig. 5 TG curves for LDPE and for the nanocomposites performed in nitrogen

sults showed that the presence of nanoclays had a clear effect on the thermal stability and in particular on the thermo-oxidative behavior of the samples. As revealed by the TG curves performed in nitrogen atmosphere (Fig. 5), the LDPE decomposition takes place in a single step between 400 and 500°C while the same experiment carried out in air (Figs 6 and 7), displays a two-step degradation process starting at a lower temperature (250°C). The first step is attributable to the main degradation reaction and involves the pyrolysis and the subsequent formation of volatile ox-

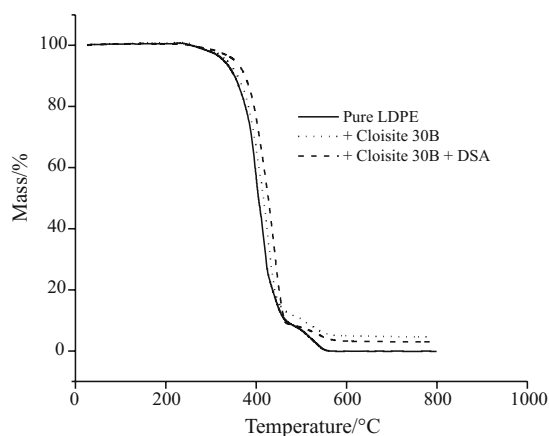


Fig. 6 TG curves for LDPE and for the nanocomposites performed in air

Table 4 T_{10} and T_{50} as determined through TG experiments in air for the different nanocomposites

Sample	$T_{10}/^{\circ}\text{C}$	$T_{50}/^{\circ}\text{C}$
LDPE	350	404
LDPE/Cloisite 30B	357	415
LDPE/Cloisite 30B+DSA	375	427
LDPE/Cloisite 30B+OD	374	417
LDPE/Cloisite 30B+ODAc	355	416
LDPE/Cloisite 30B+ODA	358	425

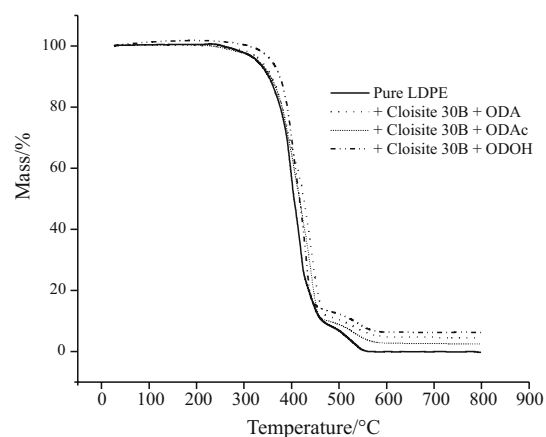


Fig. 7 TG curves for LDPE and for the nanocomposites performed in air

idized products; the second one takes place in a more complex process, due to the reaction of the degrading polymer radicals with oxygen in air. Such behavior is well described in the literature [21]. Moreover, the presence of the nanofiller shifts the degradation phenomena toward higher temperatures, as also shown in Table 4, thus indicating a higher thermo-oxidative stability of the nanocomposites with respect to the neat polymer. These results can be attributed to the slowing down of the oxygen diffusion, since the presence of the intercalated nanofillers determines an increase of the path length of the gas molecules through the nanocomposite.

Conclusions

A commercially available organophilic montmorillonite, Cloisite 30B, was modified with different surfactant additives bearing C_{12} – C_{18} alkyl chains, namely dodecylsuccinic anhydride, octadecylamine, octadecanoic alcohol and octadecanoic acid and then dispersed in molten LDPE.

After the treatment with the surfactants, the clays exhibited an increase of their basal spacing values, indicating a strong interaction between the two components. The morphology of the LDPE nanocomposites was investigated through XRD and TEM analyses. Intercalation phenomena were found for all the systems investigated.

The thermal properties of the obtained nanocomposites were studied by means of DSC and TG measurements. No variation of T_m and crystallinity of LDPE was found in the presence of the nanoclays (below 5 mass/mass%). A significant increase of the thermal stability in air of LDPE nanocomposites was achieved.

Acknowledgements

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