

## Preparation and UV weathering of polyethylene nanocomposites

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### Summary

Polyethylene / montmorillonite (PE/MMT) nanocomposites films were prepared by blending in the molten state: Low-density polyethylene (LDPE), montmorillonite clay, and polyethylene grafted maleic anhydride (LDPE-g-MA) or zinc neutralized carboxylate ionomer (Surlyn B) as compatibilizers. A chemically modified clay Cloisite 20A has been used. Nanocomposites were prepared by melt blending in a twin-screw extruder by using two-step mixing. Characterization of the nanocomposites was performed by mechanical properties, X-ray diffraction, light transmittance, infrared spectroscopy (FTIR) and transmission electronic microscope (TEM) techniques. Changes in UV irradiated nanocomposites film samples were characterized by FTIR. The results were analyzed in terms of the effect of the compatibilizing agent in the clay dispersion, and UV degradation of the nanocomposite.

### Introduction

The hybrid organic-inorganic nanoscale composites have received special attention, both in industry and in academia, because of their improved properties at very low loading levels compared with conventional filler composites. They often exhibit improved properties such as mechanical, dimensional, barrier to different gases, thermal stability and flame retardant enhancements with respect to the bulk polymer [1-4]. One of the most promising composites is the hybrid based on organic polymers and inorganic clays consisting of layered silicates. The hydrophilic clay needs to be modified prior to its introduction in most organophilic polymer matrices, in order to achieve good interfacial adhesion and therefore a better mechanical performance. Polyethylene is one of the most widely used polyolefin polymers because of its low cost, low weight, low-temperature toughness, low moisture absorption, good optical properties and ease of processing and recycling. However because it does not include any polar group in its backbone, it is difficult to get the exfoliated and homogenous dispersion of the clay layer at the nanometer level in the polymer matrix. Then preparing nanocomposites by melt compounding, the exfoliation and dispersion of

nanoclays in polyolefins depend on the organic modifier of the nanoclay, the initial interlayer spacing, the concentration of functional groups in the compatibilizer and its overall concentration in the composite, the viscosity of the plastic resin, and the operational conditions, such as screw configurations of extruders, rpm, temperature, residence time, etc. Recent studies have focused on the uniform dispersion of modified clay particles in the nonpolar matrix to increase their physical and mechanical properties. Among these improved properties are mechanical, dimensional, barrier to different gases, thermal stability and flame retardant enhancements with respect to the bulk polymer [5-8].

Copolymers of ethylene with monomers containing acid groups are important commercial products with a metal cation as the neutralizing agent for the acid group. The later are termed ionomers, and typically the amount acid groups neutralized with a metal cation is not stoichiometric, that is that only some of the acid groups are neutralized with metal cation. There are several studies of the improvement in miscibility of PA6 with different Polyolefins when a ionomeric compound was used [9-11]. For these reason it seems possible that the ionic groups on the ionomer could undergo favorable interactions with the ammonium salt of the organoclay. There are few reports on nanocomposites using such ionomers [12-14]. Fire retarded materials are now expanding into new areas where permanent exposure to UV light might occur [15,16]. Besides the using of PE as greenhouse cover films and other UV light exposure applications has spread worldwide. It is important to investigate the thermal insulating and photo-aging behavior of PE nanocomposites. In this work zinc neutralized carboxylate ionomer and maleic anhydride grafted PE (LDPE-g-MA) has been used as a compatibilizers. Maleic anhydride (MA) has been widely used as a compatibilizing agent for this kind of systems and is used as reference on this work. The LDPE-Clay nanocomposites have been obtained by melt compounding with a commercial montmorillonite clay, in a twin-screw extruder by using two-step mixing and then tubular blown films were prepared. Characterization of the films nanocomposites was performed by X-ray diffraction, infrared spectroscopy (FTIR) and transmission electronic microscope (TEM) techniques in order to determine the effect of compatibilizing agent on clay dispersion.

## **Experimental**

### *Materials*

Commercial LDPE, PX22004 from Pemex with an MFR of 0.4 g/10min, was used. Two different coupling agents were used: a commercial zinc neutralized carboxylate ionomer, made from ethylene-acid copolymer, in which the acid groups are partially neutralized with zinc ions, Surlyn 1652 from DuPont with an MFR of 5.8 g/10min, density of 0.94g/cm<sup>3</sup>, 6.5 wt% of methacrylic acid, ion type zinc and a commercial LLDPE-g-MA, with 0.9% of MA, CXA4107 from DuPont. An a quaternary ammonium salt modified clay (Cloisite 20A) from Southern Clay Products Co. was used.

### *Preparation of polypropylene-clay nanocomposites*

Nanocomposites were obtained by previous preparation of a master batch of compatibilizing agent (PE-g-MA or Surlyn) and clay (60/40) by mixing in a Werner

and Pfeleiderer twin screw extruder, with an L/D = 29:1 and D= 30 mm, operating with a temperature profile from 180 to 190°C and 50 rpm in corrotating mode. The clay was added through a side feeder. Subsequently, the desired amount of pure PE, master batch and compatibilizing agent were mixed in the twin screw extruder with a temperature profile from 190 to 200°C and 100 rpm for the one step mixing. Then the samples were pelletized and mixed again passing through the twin-screw extruder in a two-step mixing with a temperature profile from 190 to 200°C and 200rpm.

Films of different PE samples, after being dried at 80°C for 16 h, were prepared with tubular blown PE film equipment at a 2.0 blow-up ratio. The equipment had a screw with a 31.75 mm diameter, a L/D ratio of 24, and spiral die with a die gap of 1.8 mm. The film thickness was controlled to be 35  $\mu\text{m}$ . The processing temperature was kept at 175-220°C.

### *Evaluation of nanocomposites*

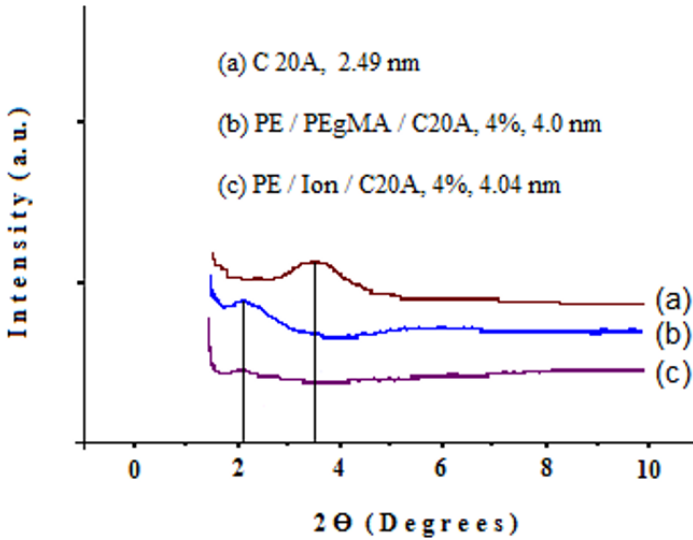
X-ray diffraction of the clays and nanocomposites, in order to evaluate the evolution of the clay  $d_{001}$  reflection, was performed in a Siemens D5000 using  $\text{CuK}\alpha$  X-ray radiation. The X-ray samples were obtained from compression moulding in order to avoid the preferred orientation of the clay when samples are prepared from the films extrusion. Mechanical properties of the resulting nanocomposites were measured according to ASTM D 638 with an Instron Model 4301. UV/condensation exposure test was carried out in a QUV panel chamber. The working temperature was controlled at  $70/50 \pm 2^\circ\text{C}$  and the wavelength of radiation was 340 nm. The rate of photo oxidation of the UV degraded films was followed by measuring carbonyl oxidation products through FTIR by using a Nicolet FTIR Magna 550 IR analyzer. Optical properties of light transmission was determined according to ASTM D1003. Ultrathin section for TEM analysis, approximately 70-100 nm in thickness, were cut from compression moulded samples, with a diamond knife at a temperature of  $-95^\circ\text{C}$  using a Leica microtome attached to a closed chamber with circulating liquid  $\text{N}_2$ . The TEM observations were performed for the thin films with a Jeol-2000EX microscope with a field emission gun at a accelerating voltage of 200 kV.

## **Results and discussion**

### *Effect of compatibilizer on intercalation behavior*

The X-ray diffraction patterns of the neat clay (C20A) and nanocomposites with different compatibilizing agent, are shown in figure 1. It can be observed that the original basal reflection peak of cloisite 20A in samples with ionomer and MA is quite low and shifted to lower angles. All the samples show a shift of the diffraction peak to lower angles and higher intergallery spacing of about 4 nm for the 4% C20A with MA sample and 4.04 nm for the 4% C20A with ionomer, compared with 2.49 nm of the clay 20A. It can be observed that, even the peak appears almost at the same angles for both compatibilizing agents, the peak for ionomer is less notorious indicating perhaps a more homogeneous clay intercalation or exfoliation. This fact reveals that the clay were intercalated and dispersed in the PE matrix. This confirms the fact that both MA and Ionomer, because of their functional polar groups, could be interacting

with the functional groups in the surfactant allowing more intercalation and, better mechanical properties, as will be seen below.



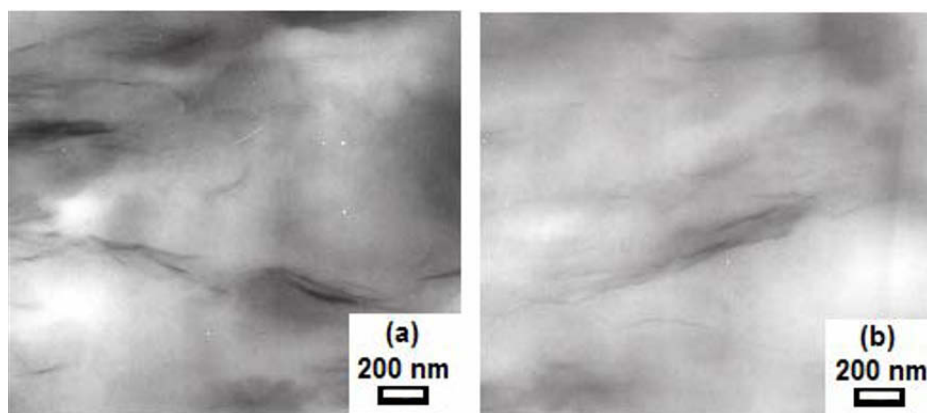
**Figure 1.** X-ray diffraction patterns of nanocomposites of PE/C20A with PEGMA or Ionomer as compatibilizing agent.

Figure 2 shows the TEM images that are in good agreement with observed X-ray results. It can be seen that for both MA and ionomer compatibilizing agents a well dispersed morphology can be obtained. The use of PEGMA or Ionomer as compatibilizers were efficient to push apart the clay layers which form stacks or tactoids of several platelets. It can be observed that the samples with MA (a) and ionomer (b) show almost similar morphology among them with a higher degree of disordered structures and more intercalated/exfoliated layers. Only a slightly more homogeneous dispersion can be appreciated with the ionomer sample. This photograph shows that the thickly stacked layer structures were separated into thinner ones when using MA and Ionomer through the processing of the nanocomposite.

#### *Effect of compatibilizer on mechanical properties*

Table 1 shows mechanical properties of the nanocomposites obtained with the two compatibilizing agents, specifically Young's modulus, tensile strength and tensile strain. It can be seen that in the PE/Compatibilizing agent blends, modulus is not significantly increased. Mean while the C20A nanocomposite samples with PE-g-MA and Ionomer as a compatibilizing agents have higher modulus than the pure PE, specially for the higher clay content, being only slightly higher for the ionomer samples, with an increase of around 60%, compared with an increase of around 50% for the PEGMA. This means that the addition of C20A increased the stiffness of the PE more when using ionomer as compatibilizing agent.

The tensile strength of the films is shown in this table 1. Just as for the modulus the samples with C20A and compatibilizing agents have the better tensile strength values than the pure PE being slightly higher for the samples with ionomer as a compatibilizing. The elongation at break in all the samples was lower than the pure PE and the samples with C20A and compatibilizing agents showed a reduction in deformation of around 7% less than the pure PE for the MA samples and around 8% less for the samples with Ionomer. This reduction in deformation is attributed to the fact that the inorganic filler particles are rigid and could not be deformed by external stress in the specimens but acted only as stress concentrators during the deformation process.



**Figure 2.** TEM images of nanocomposites samples using: (a) PEGMA and (b) Ionomer as compatibilizer.

**Table 1.** Mechanical Properties

Sample	Modulus (Mpa)	Tensile strength MD (Mpa)	Elongation at break MD (%)
PE (100)	200 ± 10	14 ± 1.0	505 ± 10
PE/PEGMA (84/16)	210 ± 08	15 ± 0.9	500 ± 05
PE/Ion (84/16)	212 ± 05	16 ± 0.5	500 ± 10
PE/PEGMA/C20A (84/12/4)	284 ± 07	18 ± 0.7	480 ± 05
PE/PEGMA/C20A (76/18/6)	305 ± 08	22 ± 1.0	470 ± 11
PE/Ion/C20A (84/12/4)	303 ± 04	20 ± 0.8	480 ± 08
PE/Ion/C20A (76/18/6)	328 ± 06	24 ± 0.6	465 ± 10

#### *Effect of clay on optical properties*

One basic requirement concerning agricultural films for greenhouse covers, is to ensure that the plants obtain the maximum quantity of visible solar radiation. The economic efficiency of agricultural films mainly depends on the transmission of visible light, which is responsible for the growth of plants, and on the possibility of

retaining thermal energy accumulating inside the cover. Table 2 shows the visible light transmission of the films. It can be observed only slightly lower values of light transmission in the samples with higher clay content. Since total transmittance is the ratio of total transmitted light to incident light, it can be seen that the transmitted light is not greatly affected by the clay content in neither of the compatibilizing agents used. This suggests that the C20A inclusion did not adversely influence the polymer optics perhaps because of its dispersion on the order or even smaller than the wavelength of visible light.

**Table 2.** Light Transmission of the films

Sample	Light Transmission ( % )
PE (100)	91.5 ± 0.4
PE/PEgMA (84/16)	90.5 ± 0.2
PE/Ion (84/16)	90.5 ± 0.4
PE/PEgMA/C20A (84/12/4)	90.0 ± 0.6
PE/PEgMA/C20A (76/18/6)	88.5 ± 0.5
PE/Ion/C20A (84/12/4)	90.5 ± 0.2
PE/Ion/C20A (76/18/6)	89.0 ± 0.4

#### *Effect of clay on thermal insulating properties*

The basic requirement concerning greenhouse films is to ensure that the plants obtain the maximum quantity of visible solar radiation during the day and to protect the plants against abrupt drops in temperature during the night by reducing IR light transmission, creating the so-called greenhouse effect. The thermal insulating properties of a film screen, which are a function of the transmission of infrared light, depend on the kind of polymer but also in the structure of the film. Table 3 shows the thermal insulating properties of the films. As expected the neat PE shows the highest transmission of infrared light in the zone 700-1400  $\text{cm}^{-1}$ . It can be observed that the nanocomposites with clay shows lower transmission of IR light in this zone which can be explained with the fact that the nanoclay absorbs this light in this zone and can impart thermal properties to the films similar than the micrometric size clays do. It can be observed that the higher the clay content the lower the transmission of IR radiation in this zone.

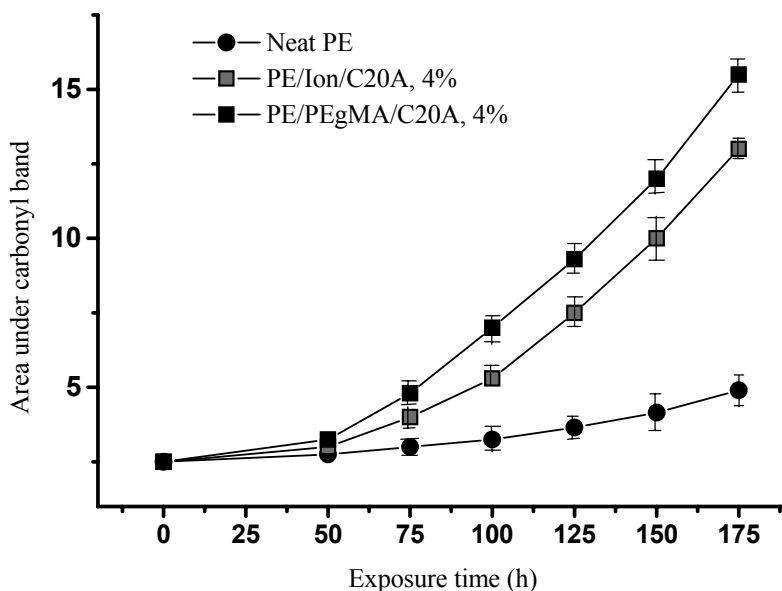
#### *Effect of clay on photo-oxidation process*

In order to compare the rates of photo-oxidation of PE in the different materials, the change of the area of absorbance in the carbonyl region as a function of irradiation time was considered as shown in figure 3. The area of the carbonyl region band could be seen as the quantity of the carbonyl. It can be seen as the measurement of photo-oxidative degradation of samples. It is reported that the increase in the carbonyl group is related with an increase in the degradation process of the polymer. It can be seen in this figure that the rate of photo-oxidation of all the nanocomposites is faster than that of pure PE. This could be explained with a higher degradation effect of both the clay and the ammonium modifier of the clay. It has been reported [16] that the ammonium

ion can lead to the formation of free radicals that can accelerate the degradation process of the polymer matrix. Another possibility is the metal ions contained as impurities in the nanoclay that could promote the polymer degradation, as was reported by La Mantia [17]. It also can be observed that when using ionomer as compatibilizer the sample degrades slightly slower than that with PEGMA, this could be attributed to the slightly more homogeneous dispersion of the clay obtained when using the ionomer compared with the PEGMA. We suggest that when a better dispersion is achieved there will be less concentration of aggregates of clay and ammonium ions and impurities that could accelerate the degradation process. However additional investigation are necessary to clarify this point.

**Table 3.** Thermal insulating properties of some films

Sample	IR light Transmission in 700-1400 $\text{cm}^{-1}$ (%)
Neat PE	$24.9 \pm 0.5$
Ionomer	$21.8 \pm 0.3$
PE/Ion/C20A (84/12/4)	$15.2 \pm 0.5$
PE/Ion/C20A (76/18/6)	$9.8 \pm 0.6$



**Figure 3.** Increase of area of carbonyl band during the photo-oxidation of films.

## Conclusions

In this study PE/clay nanocomposites using PEGMA or Ionomer as compatibilizer have been obtained. Nanoclay inclusion did not adversely influence the polymer light transmission and enhances the thermal insulating properties of the films by reducing

the transmission of IR light. Clay dispersion and interfacial adhesion are slightly affected by the kind of matrix modification. The using of ionomer as compatibilizing agent showed a slightly more homogeneous dispersion of the clay, only slightly better mechanical properties and a less rate of degradation.

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