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Preparation and Flame Retardancy Properties of Novel PA12 and PE/Layered Titanoniobates Nanocomposites

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Summary: We report herein a study performed on a layered titanoniobate $KTiNbO_5$ modified by octadecylamine to evaluate the fire retardancy properties of this novel hybrid nanofiller dispersed in PA12 and LLDPE, by polymer melt intercalation. The nanocomposites have been characterized using Electron Microscopy techniques to evaluate the degree of exfoliation and the morphologies. Thermogravimetric analyses and cone calorimeter tests have been carried out to assess the fire retardant performances.

Keywords: fire retardancy; hybrid layered material; Nanocomposite; STEM; TEM; thermal stability; titanoniobate

Introduction

Layered silicates, used as nanofillers in polymer nanocomposites, are known to enhance performances of polymers, especially the fire retardancy properties[1] which was explained by surface ceramisation and charring leading to reduction in heat release rate.[2,3]

This study provides an alternative route to conventional flame retardant fillers. According to its layered structure, the pristine oxide $KTiNbO_5$,[4] offers the possibility of a cation exchange, allowing the insertion of organic molecules in the interlayer space.[5] In previous studies, $KTiNbO_5$, intercalated with octadecylamine, has been dispersed via polymer melt intercalation in polyamide-12 (PA12)[6] and linear low density polyethylene (LLDPE).[7] The structural characterization and the trend shown by the physical properties have revealed the ability of this nanofiller to be exfoliated when appropriately modified. Moreover, the influence of the polarity of the host polymer on the structure of the nanocomposite has been evidenced, since exfoliated nanocomposites have been obtained with PA12 and intercalated morphologies have been observed in polyethylene.

Experimental Part

Preparation of the Hybrid Material

$KTiNbO_5$ ($M = 259.8\,g \cdot mol^{-1}$) was prepared by solid state reaction of a TiO_2:Nb_2O_5:K_2CO_3 mixture (2:1:1) adapted from[7] with oxide powders from Prolabo. The N-alkyl amine intercalation has been made following the experimental procedure described in our previous work[7] using octadecylamine (ODA) (Aldrich). The obtained hybrid material is named: $C_{18}HTi$.

Preparation of the Composites

Polyamide-12 composites have been obtained by melt incorporation of 1 wt%, 5 wt% and 10 wt% of $C_{18}HTi$ in polyamide-12 Rilsan® AECHVO, supplied by

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ARKEMA (Serquigny, France), using a twin screw 15cc DSM Xplore® microcompounder equipped with corotating intermeshing conical screws. The mixture was sheared 1 minute at 100 rpm at 210 °C and injected with a 10 cc molding device in a mould at 70 °C to obtain dumbbell-shaped specimens. Polyethylene composites have been obtained by melt incorporation of 1 wt%, 5 wt% and 10 wt% of C_{18}HTi in polyethylene Flexirene® MR50, supplied by Polimeri Europa, using the same microcompounder than previously. The mixture was sheared 1 minute at 100 rpm at 190 °C and injected with a 10 cc molding device in a mould at 30 °C to obtain dumbbell-shaped specimens. PA12 and the fillers have been dried overnight under vacuum at 80 °C before use. The samples are named: PA12: pure polyamide-12, PA-1%, PA-5%, PA-10%, PE for pure polyethylene, PE-1% PE-5% PE-10% according to the filler content incorporated.

Characterization

The microstructure and the dispersion of the nanofiller in the two different matrices have been investigated by Scanning Electron Microscopy (SEM) using a Zeiss supra 55 and a JEOL 2010 FEG STEM, Transmission Electron Microscope (TEM) operated at 200 kV. Energy Dispersive Spectroscopy (EDS) analyses have been performed with EDAX Si/Li detectors coupled on both microscopes.

Nanocomposite specimens for SEM observations have been prepared by breaking fragments of the filled polymer at low temperature (in liquid nitrogen). They have been directly observed using very low beam conditions (<5 kV at low vacuum). For TEM studies, thin slices of filled polymer have been cut in liquid nitrogen, selected and placed between two 0.8 mm aperture Ni grids on the sample holder and the thinnest parts (near the slice edge) have been then observed and analyzed by Scanning Transmission Electron Microscopy (STEM) and EDS techniques.

Thermal degradation of the modified oxides and nanocomposites has been studied using a Perkin-Elmer TGA 7 under nitrogen gas flow (80 mL/min) from 50 °C to 900 °C at 20 °C/min. A TA Instrument Q500 V6.7 thermo-balance using platinum pans at 10 °C/min under air or nitrogen gas flow (60 mL/min) has also been used.

Cone calorimeter tests have been performed using a Fire Testing Technology (FTT) cone calorimeter apparatus: $100 \times 100 \times 3\,mm^3$ samples were irradiated at $35\,kW/m^2$ heat flux, representing conditions of a declared fire. The tests were performed in the horizontal position. Specimens were wrapped in aluminium foil leaving an upper edge of 3 mm and placed on ceramic backing boards at a distance of 25 mm from the cone base. All tests were performed at least in triplicate and the average values are reported in the following tables.

Results and Discussion

Characterization of the obtained C_{18}HTi hybrid by X-ray diffraction (XRD) and electron microscopy indicate that the d-spacing of the pristine $KTiNbO_5$ has been raised from 9 to 41 Å by the alkyl ammonium intercalation. Moreover, 60% of the available sites have been exchanged which represent a cationic exchange capacity (CEC) of 300 meq/100 g.

Morphologies

SEM and TEM studies have been carried out in order to characterize the hybrid exfoliation and dispersion in the polymer matrices at micro- and nanoscale. On Figure 1 we present the TEM image obtained on the PA-5% composite. It indicates that the exfoliation of the mineral oxide layers has been quite well achieved suggesting the formation of nanocomposites. It confirms the disappearance of any 00l reflexions on this material when characterized by XRD.[7] TEM observations performed on this nanocomposite coupled with EDS mapping using the STEM option

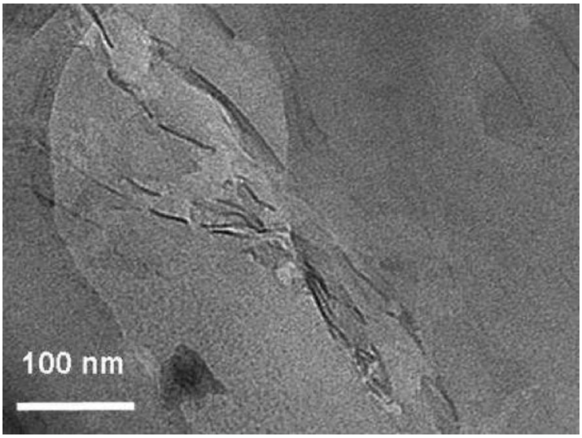

Figure 1.
TEM images of the nanocomposite PA-5% showing the exfoliated morphology of the filler. Sheets viewed perpendicularly to the sheet plane (black lines).

of the TEM confirmed all these points. The image presented on Figure 2 shows the sheet-like lamellar nature of the hybrids and its chemical composition.

XRD diffraction experiments on PE based composites showed the persistence of 00l hybrid reflexions despite its dispersion in the polymer.[7] The SEM observations of the hybrid material introduced in a polyethylene matrix (PE-5%) is presented in Figure 3-a,b. In the major part of the sample, thin but still visible micron-sized tactoïds are evidenced (arrows Figure 3-a).

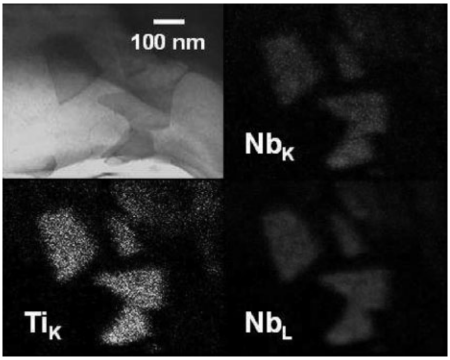

Figure 2.
EDS mapping of the PA-5% nanocomposite using the STEM option. Ti and Nb maps respectively recorded using Ti$_K$, Nb$_K$ an Nb$_L$ lines show that, the chemical composition of the mineral layers has not been deteriorated by the exfoliation process in the PA matrix. Here the sheets are viewed on the sheet plane.

Moreover, bigger aggregates of non exfoliated material are present suggesting we are in presence of an intercalated morphology (Figure 3-b).

Thermogravimetric Analyses

The weight loss of the polyamide nanocomposites under nitrogen is plotted as a function of temperature (Figure 4-a). First, it can be noticed that all the nanocomposites have a degradation temperature (T_d) much lower than the pure polyamide.

We reported in our previous paper[6] that the value of T_d for polyamide nanocomposites is probably ruled by a balance between the beneficial effects of a diffusion barrier due to the exfoliated morphology and the T_d-lowering effect due to a filler-catalyzed degradation process of polyamide by the presence of acidic sites on the platelets surface. These sites are induced by the Hoffman degradation of octadecylammonium. Since our lamellar hybrid have a CEC three times higher than MMT (Montmorillonite), the presence of numerous acidic sites coupled to the apparently good state of dispersion of the platelets in the matrix is strongly likely to be responsible of the observed decrease in thermal stability.

The weight loss curves under air and under nitrogen of the pure polyethylene and of the PE-5% sample are plotted in

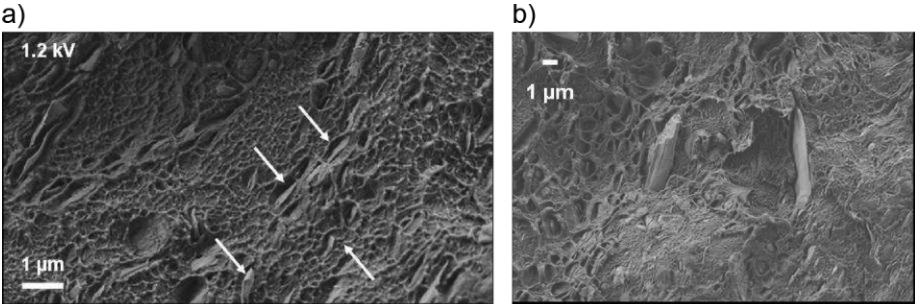

Figure 3.
SEM images of PE-5% showing the coexistence of (a) tactoïds (size >5 μm) and (b) aggregates of non exfoliated hybrid (size <1 μm).

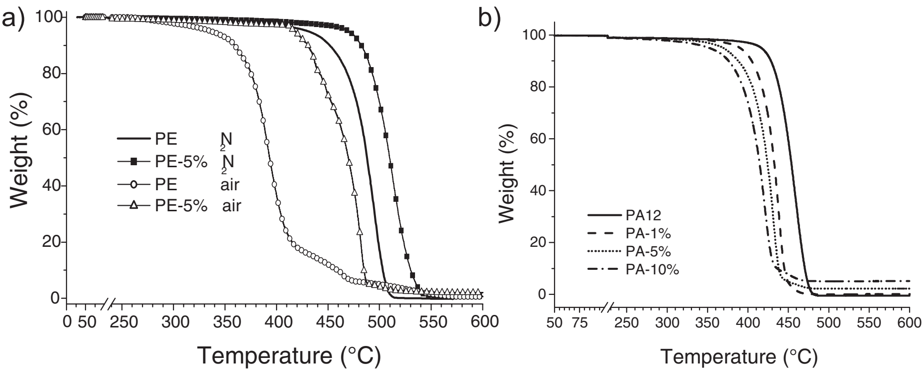

Figure 4.
Thermogravimetric analyses of (a) the PA12 and the various nanocomposites showing the influence of the C_{18}HTi content under nitrogen, and (b) the PE and the PE-5% samples under air and under nitrogen.

Figure 4-b. We observe that under air the composite is much more stable than the pure matrix and that it is almost as stable as the pure polyethylene under nitrogen. This test shows that the presence of mineral platelets allows preventing dioxygen to go through the material. The barrier effect is demonstrated in that case. This phenomenon is also characterized by the increase of the degradation temperature of about 20 °C for the PE-5% sample under nitrogen compared with its pure counterpart.

Cone Calorimeter Tests

Visual Observations

Concerning the polyamide-12, the pure matrix burns relatively rapidly and extensive bubbling was observed. The image Figure 5-a shows a thin residue in the aluminum pan probably due to the formation of nitride aromatic species. The other formulations behave more like solids with only minor bubbling when the filler content increases. Images of the residues shown in Figure 5-b,c,d reveal isolated islands more or less well dispersed.

Concerning the polyethylene nanocomposites, no residue was observed for the pure matrix (Figure 6-a) and very little for the PE-1% sample (Figure 6-b). For the composites containing 5wt% and 10 wt% of C_{18}HTi, a large quantity of residues is observed (Figure 6-c, d). Their densities are not homogeneous confirming a non optimal dispersion of the hybrid in the polyethylene matrix during the nanocomposites processing.

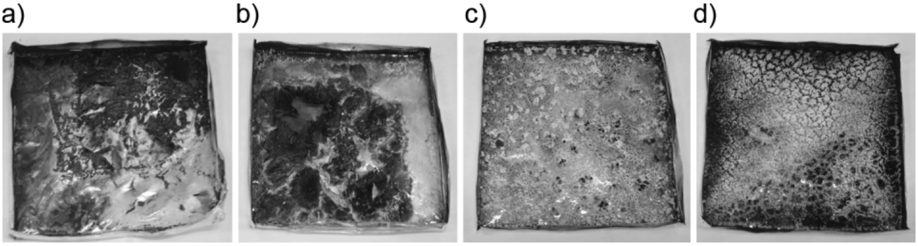

Figure 5.
Images of the residues for the polyamide nanocomposites: (a) pure PA12, (b) PA-1%, (c) PA-5% and (d) PA-10%.

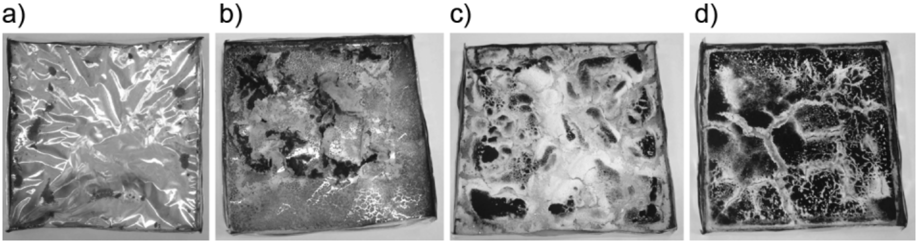

Figure 6.
Images of the residues for the polyethylene nanocomposites: (a) pure PE, (b) PE-1%, (c) PE-5% and (d) PE-10%.

Ignition Times

The average ignition times are presented in Table 1 for polyamide based composites and Table 2 for polyethylene systems. We do not observe any change for the PA and PA-1% samples whereas this time strongly decreases with 5 wt% and 10 wt% of nanofillers. This can be attributed and relied to the decrease in thermal stability of the hybrid shown by TGA. The presence of acidic sites catalyses the polyamide degradation and therefore the ignition arrives early in the HRR history. For polyethylene, the trend is different. The ignition time increases with 1wt% of hybrid filler, doesn't change with 5 wt% and decreases with 10 wt% of filler.

Table 1.
Time To Ignition, peak of Heat Released Rate, Total Heat Released and Total Smoke Released for polyamide 12 nanocomposites

	TTI (s) ± S.D.	pHRR (kW/m^2)	THR (MJ/m^2)	TSR (m^2/m^2)
PA-12	112	952	100	669
PA-1%	108	995	100	701
PA-5%	66	758	97	810
PA-10%	70	599	93	1124

Table 2.
Time To Ignition, peak of Heat Released Rate, Total Heat Released and Total Smoke Released for polyethylene nanocomposites

	TTI (s) ± S.D.	pHRR (kW/m^2)	THR (MJ/m^2)	TSR (m^2/m^2)
PE	75	995	103	787
PE-1%	96	1117	104	805
PE-5%	80	667	99	1225
PE-10%	66	459	95	1303

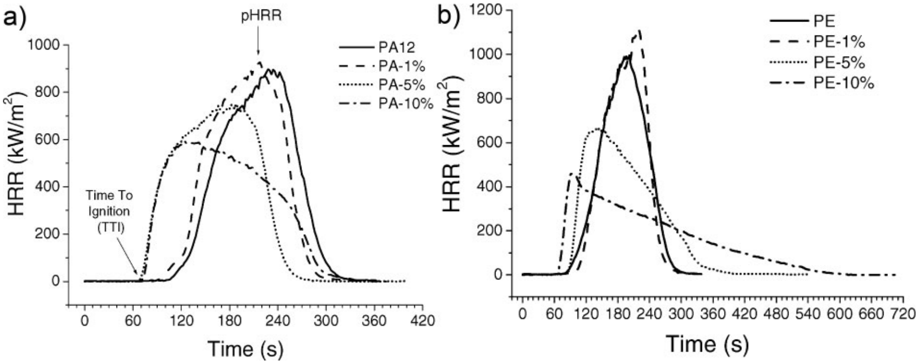

Figure 7.
HRR histories for (a) the polyamide nanocomposites and (b) the polyethylene nanocomposites.

Heat Release Rate and Production of Smoke
The peak of heat release rate of the polyamide nanocomposite is not affected by the presence of 1 wt% of nanofiller as can be seen in Figure 7-a. The value decreases with the filler content. It reaches 63% of the pure PA12 pHRR with 10 wt% of C_{18}HTi (see Table 1).

Figure 7-b displays the HRR histories for all the polyethylene formulations. It can be noticed that the peak of heat released rate decreases with the hybrid nanofiller content. The minimal pHRR value is for the PE-10% sample with a reduction of 50% (see Table 2).

For both systems, the total heat released is not affected by the incorporation of hybrid nanofiller (Table 1 and 2). However, the samples release heat over a longer period of time compared to the pure matrixes.

The results concerning the total smoke released, presented Table 1 and 2, are the same whatever the matrix is. In all cases, the quantity of smoke released strongly increases with the filler rate. This phenomenon is due to the formation of char with aromatic species which volatilize during the combustion and create smokes.

Conclusion

Fire retardancy of polymer nanocomposites based on a novel type of nanofiller (titanoniobate) was examined by means of thermogravimetric analysis and cone calorimeter experiments. This study has evidenced the competitive role of the nanocomposites morphology and of the thermal stability of the hybrid material towards the fire properties of these composites. Indeed, on one side the exfoliated morphology of the polyamide systems, provides protection towards the flame action reducing rate of combustion. On the other side, intimate contact of amide groups with acidic sites from thermal decomposition of alkyl ammonium moiety, leads to accelerated polymer decomposition in the ignition step which results in shortening of ignition time. On the other side, despite an intercalated morphology, the polyethylene nanocomposites have shown good results that are comparable with polyethylene/MMT ones.[8]

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