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Photooxidation of Polymeric-inorganic nanocomposites: Chemical, Thermal Stability and Fire Retardancy Investigations

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Abstract

Nanocomposites of polypropylene-*graft*-maleic anhydride/clay and polypropylene/clay were prepared by melt blending using two different approaches. X-Ray diffraction results showed an intercalated structure. Samples of nanocomposites were exposed to UV light under atmospheric oxygen and their photo-oxidative stability was studied using FTIR and UV spectroscopy. The consequences of this photo-oxidation on the thermal stability and fire retardant performance of the nanocomposites were also addressed from thermogravimetry analysis and Cone calorimetry.

Keywords

Polypropylene, Nanocomposites, Thermal stability, Fire retardancy

1. Introduction

Because of the many demands made upon modern engineering materials, individual polymers no longer have the performance or the desired properties suitable for their required tasks. Since the successful attempt to develop a montmorillonite reinforced polyamide nanocomposite by the Toyota group [1], a new approach to this problem has emerged and polymer layered silicates nanocomposites have recently received considerable attention. Polymer–clay nanocomposites usually display a variety of desirable properties, compared to both conventional composites and unreinforced bulk polymer, including mechanical strength, impermeability to gases, flame retardancy, etc. However, there has been a restriction on the polymer used for the nanocomposite. Polymers, such as polydimethylsiloxane, polystyrene, polycarbonate, poly(methyl methacrylate) and polysphosphazines [2], [3] have been produced as nanocomposites through a chemical modification of the silicate surface. A polyethylene oxide nanocomposite can be produced without surface modification of the silicate layers. As a consequence of the progress in this field, a new class of nanocomposites containing non-polar polymers, such as polypropylene and polyethylene has been developed [4], [5], [6].

Nanocomposites can be produced by both an in situ polymerization or by melt or solution blending. The particular blending process which is used, as well as the time of annealing after the nanocomposite has been formed, can have a significant influence on the structure, and hence the properties of the nanocomposite. When registry between the layers is maintained, the material is described as an intercalated material. When this registry is lost, and the clay layers are more randomly distributed throughout the polymer matrix, the system is described as an exfoliated or delaminated nanocomposite. Of course, if the clay is not dispersed, it is simply a filler and a nanocomposite is not formed [7].

In the present work, thermal stability and flammability tests were conducted on polypropylene-nanocomposites (PP-nanocomposite) using thermogravimetry analysis, TGA, and Cone calorimetry. These nanocomposites were produced using two different approaches, as will be described later. Fire retarded materials are now expending into new areas where permanent exposure to UV light might occur. Therefore, it is important to investigate the photo-aging behavior of nanocomposites. Some results concerning the photo-stability of nanocomposites are presented herein along with the effect of photo-aging on the thermal stability and fire retarded properties of PP-nanocomposites.

2. Experimental

2.1. Materials

Polypropylene-*graft*-maleic anhydride (PP-g-MA) was acquired from Aldrich Chemical Company and contains a mass fraction of 0.6% maleic anhydride (melt index at 190°C/2.16 kg is 115g/10 min). The organically-modified montmorillonites used were provided by Southern Clay Products, Inc. and Nanocor. All clays contained an ammonium salt which replaced the sodium cation present in the natural clay. The typical ammonium salt contains at least one long chain alkyl substituent, typically of 16 or more carbons; this may be saturated, referred to as hydrogenated tallow, HT, or unsaturated, referred to as tallow, T. The remaining substituents consist of methyl groups, M, benzyl groups, B, and 2-hydroxyethyl, EtOH.

2.2. Preparation of the nanocomposites

The first series of PP-nanocomposites was obtained by melt blending PP-g-MA with various organic-modified montmorillonites in a Brabender mixer, following the procedure of Gilman [4]. This melt blending process was carried out under a flow of nitrogen to minimize any possible oxidation. The resulting material was pressed at a temperature between 160 and 180°C for 30 min, followed by annealing in a vacuum oven overnight at 80°C.

Another series of PP-nanocomposite was prepared using the solution blending method proposed by Kurokawa et al. [5]. In brief, 20 g of organically-modified clay was mixed with toluene (160 g) at 30°C for 24 h. Then a 0.1 g of 2.2'-azobis(isobutyronitrile) (AIBN), dissolved in 10 g of toluene, was added as a polymerization catalyst. AIBN is believed to intercalate into the montmorillonite after 1 h stirring at 30°C. Diacetone acrylamide (DAAM) (20 g), dissolved in 90 g toluene, was then added; stirring at 30°C for 1 h allows DAAM to intercalate and heating with stirring at 75°C for 1h under N_2 effects the polymerization of DAAM. This is followed by the addition of 2 g of maleic acid-modified PP, PP-g-MA, dissolved in 100g toluene, into the sol at 100°C with stirring for 1h. The resulting polymer was precipitated by the addition of methanol, followed by washing, centrifuging and oven drying at 60°C overnight. This polymer was then blended with polypropylene to produce the nanocomposite. In both modes of preparation, the conditions allowed the production of PP-clay nanocomposites with clay mass fraction of 5%.

2.3. Instrumentation

Fourier transform spectra were obtained on a Nicolet 560 Magna instrument at 4 cm^{-1} resolution while ultraviolet spectra were obtained using a Shimadzu UV-2501PC instrument. X-ray scattering measurements of PP-nanocomposites were performed on a Rigaku powder diffractometer, with a Cu tube source at 1 kW. Thermogravimetric analysis, TGA, was performed using an Omnitherm 1000 unit under a flowing nitrogen atmosphere at a scan rate of 10° per minute between 20 and 600°C. Temperatures recorded from TGA data are reproducible to±3°C while the amount of char is reproducible to±2%. The Cone calorimetry measurements were carried out using a Stanton-Redcroft/PL Thermal Sciences instrument according to ASTME-1354-92 at an incident flux of 35 kW/m^2 using a cone shaped heater. Exhaust flow was set at 24 L/s and the spark was continuous until the sample ignited. Cone samples were prepared by compression molding (30–40 g) into square plaques, using a heated press. Typical results from Cone calorimetry are reproducible within about 10%. These uncertainties are based upon many runs in which thousands of samples have been combusted [7].

Thin films (100–200 μm) were used for the photo oxidation study. UV exposure was carried out in a home-made black box equipped with Mazda lamps. The working temperature was roughly controlled at (50±2)°C and the radiations of wavelengths shorter than 300 nm were eliminated using filters. The rate of photo oxidation of the UV degraded samples was followed by measuring the build up in non-volatile carbonyl oxidation products in the non-volatile fraction of the sample, using infrared bands near 1715 cm^{-1}.

3. Results and discussion

3.1. X-ray measurements

X-ray diffraction data of the products obtained show an inter-gallery spacing varying from 30 to 43 Å (2ϑ from 2.05 to 2.83). This is a noticeable increase of the 9.6 Å basal plane spacing of Na-montmorillonite, and from the spacing in the virgin organically-modified clay, which is about 17 Å, indicating that the polymer and clay form a nonocomposite. According to the literature, the intercalated form of nanocomposite in which the gallery spacing has increased to accommodate the polymer has been produced in this study [4], [5]. Without TEM examination that was not available, X-ray data can not exclude that also delamination was produced.

Further evidence for the presence of an inorganic-organic mixture can be obtained from the analysis of FTIR spectra recorded for the nanocomposites. The presence of both the characteristic bands of montmorillonite and PP-g-MA, at 1050 cm^{-1} (Si–O stretching vibrations) and 1782 cm^{-1} (carbonyl of the cyclic anhydride group) were observed and thus show the presence of both species.

3.2. Photo-oxidation of nanocomposites

Fig. 1 shows the evolution of the infrared spectrum in the carbonyl region upon UV irradiation. All spectra were obtained by spectral subtraction of the spectrum of the unirradiated film. At the beginning of the UV irradiation (the three spectra at the bottom of Fig. 1), the band at 1780 cm^{-1} was negative indicating the disappearance of maleic anhydride. At the same time, a small band around 1740 cm^{-1} begins to increase. This band is much more noticeable after 40 h of UV irradiation. The broad nature of the band at 1740 cm^{-1} indicates a mixture of different carbonyl species, among them ester entities. The role of the anhydride groups in the photo-oxidation of nanocomposites is open to speculation. It seems that their photo decomposition may yield ester species. However a more detailed study is necessary to validate this assumption because different mechanisms of maleic anhydride photodegradation have been proposed [8], [9].
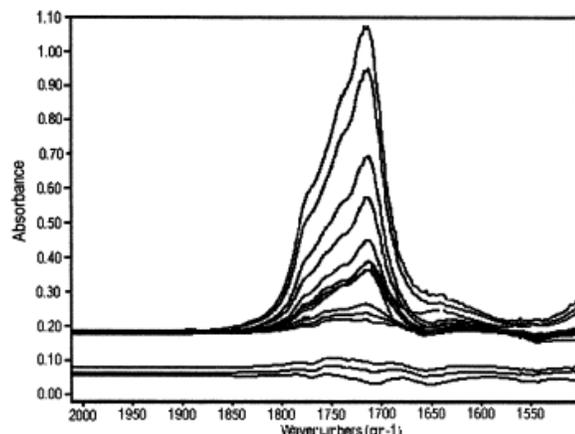

Fig. 1. Evolution of the infrared spectra at different times of UV irradiation of a PP-nanocomposite in the carbonyl region (from bottom to top, the irradiation time varies from 10 to 180 h). All spectra obtained by spectral substraction of the spectrum of the non oxidized film.

As the time of UV irradiation is increased, a progressive formation of bands at 1715 cm^{-1} (ascribed to a mixture of ketones and carboxylic acids) and at 1780 cm^{-1} (γ-lactones) is observed [10]. At this point, the nanocomposite degrades like virgin PP giving classical products of oxidation in both carbonyl and hydroxyl regions. Indeed, in this last region, a broad band centered at 3400 cm^{-1} increased regularly with UV irradiation time. In previous work, this band was assigned to a mixture of alcohol and hydroperoxide species (10).

The ultraviolet spectra of the nanoncomposite films upon UV irradiation showed an increase in absorbance over the range from 235 to 500 nm. Several degradation products containing carbonyl and unsaturated groups may absorb in this region.

The rates of photo-oxidation of the nanocomposites, PP-g-MA and pure PP processed in the same conditions as the nanocomposites were compared by measuring the formation of non volatile carbonyl oxidation products at 1715 cm^{-1}, as shown in Fig. 2. Nanocomposites and PP-g-MA showed a higher propensity towards photo-oxidation, as shown by a dramatic reduction of the induction period compared to pure PP; the data is shown in Table 1. This is true regardless of the mode of preparation of the nanocomposite or the type of montmorillonite which is used. These results suggest that the higher sensitivity to UV radiation of the nanocomposites may arise from the clay and/or the structural form of the nanocomposite. Additional investigations are necessary to clarify this point.
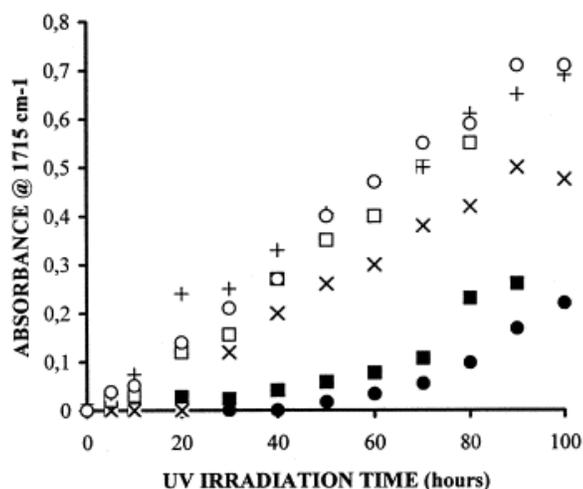
Fig. 2. Variations in the absorbance at 1715 cm^{-1} during the photo-oxidation of thin films of: (•) Pure PP, (■) PP-g-MA, (○) G-MTEtOH, (□) G-M$_2$BHT, (×) K-MTEtOH, (+) K-M$_2$BHT. Values have been corrected for 100 µm to allow comparison.

Table 1. The induction period and changes of the TGA data during the photo-oxidation of the nanocomposite films. Samples labeled G were prepared by the Gilman method, those labeled K were prepared by the Kurokawa method

Sample	Induction period (h)	UV irradiation time (h)	$T_{10\%}$	$T_{50\%}$	DTGA	Char	
		0	428	480	485	3	
	Pure PP	45	40	405	460	472	11
		100	428	470	475	7	
	0	391	456	469	9		
PP-g-MA	20	40	441	478	481	12	
		100	427	470	474	9	
	0	458	488	489	5		
K-M$_2$BHT	10	40	437	478	478	8	
		100	396	469	479	7	
	0	463	486	489	6		
K-MTEtOH	0	40	431	480	483	7	
		100	406	474	484	7	
	0	471	496	496	12		
G-M$_2$BHT	0	40	438	481	484	16	
		100	423	477	480	13	
	0	460	487	488	16		
G-MTEtOH	0	40	425	472	477	17	
		100	431	476	481	14	
	0	473	498	498	10		

G-M$_2$HT$_2$	0	40	431	480	482	15		
		100	433	480	485	12		

3.3. Thermogravimetric analysis

Various data from the TGA of the nanocomposites are collected in Table 1; this includes the onset of the degradation, taken as the temperatures at which 10 and 50% degradation occurs, the peak in the derivative curve, corresponding to the maximum rate of degradation, and the fraction non-volatile at 600°C, referred to as char. One notes that the onset of the thermal degradation of most of the unirradiated nanocomposites shifts significantly towards the higher temperature range, relative to that of pure PP and PP-g-MA. It appears that the presence of the clay, in the form of a nanocomposite, exerts a shielding effect against thermal degradation. There appears to be no significant difference between the two modes of preparation. For the nanocomposites the onset temperature of the degradation decreases upon irradiation while for PP there is a decrease followed by an increase. The amount of non-volatile residue does not appear to change upon irradiation for the nanocomposites but it does for PP, however the amount of non-volatile residue is greater for the melt blended samples than for the solution blended samples. Finally, the enhancement of the thermal stability of the nanocomposites was not significantly dependent upon the particular type of organic modification that was used.

It is understandable that the onset temperature of the degradation would decrease, since it depends on the strength of the bonds of the molecule. It may decrease because the photo-oxidation creates thermally weak bond (e.g. hydroperoxides and peroxides) that can initiate the thermal degradation. Since the formation of the nanocomposites appears to have no effect on the photo-stability, the decrease of the onset temperature with UV irradiation time is to be expected. During the photo-oxidation of PP [10], cross-linking reactions are more important than chain scissions at the beginning of UV exposure, but the reverse is true at later times in the irradiation. This leads to the suggestion that the cross-linking reactions which occur upon UV irradiation are responsible for the variation in char formation.

3.4. Cone calorimetry

An effect which has been repeatedly seen for nanocomposites is the reduction in the rate at which heat is released upon burning [7], [11]. This is sometimes considered to be the most important parameter for fire scientists. The average thickness and mass of the Cone samples were 6.3±0.1 mm and 25.6±1.9 g, respectively; the Cone data are collected in Table 2.

Table 2. Cone calorimetry for the PP-nanocomposites and their changes upon the photo-oxidation. Samples labeled G were prepared by the Gilman method, those labeled K were prepared by the Kurokawa method

Sample	UV irradiation time (h)	Time to ignition (s)	Time to peak heat release rate (s)	Peak heat release rate (kW/m^2)	Specific extinction area, (m^2/kg)
PP-g-MA	0	25	170	580	756
K-M$_2$BHT	0	30	165	673	735
G-M$_2$BHT	0	25	235	370	820
	200	25	235	403	825
	500	30	240	370	890
K-MT$_2$EtOH	0	30	165	610	806
G-MT$_2$EtOH	0	20	205	462	704
	200	15	200	455	770

	500	15	190	405	850
G-M$_2$HT$_2$	0	25	240	338	893
	200	30	240	277	862
	500	20	255	317	902

It must first be noted that the peak heat release rate, P_{HRR}, for unirradiated PP-g-MA is 580 kW/m^2 while other authors [11] obtained a value of 2028 kW/m^2. This discrepancy has been addressed by re-running the Cone samples in a second instrument, specifically that at which this much higher value was obtained. The results were confirmed. These good results can be explained by the absence of oxygen- that minimizes any oxidation- during the preparation of the nanocomposites.

It is apparent that the formation of the nanocomposite by the melt blending method brings about a significant reduction in the rate of heat release, ranging from 20 to 42%, depending upon the organic modification which has been made to the clay. At the same time there is an increase in the time at which this peak heat release is shown of 20–40%. Irradiation with UV light has little effect on any of the Cone parameters. This is probably due to the fact that oxidation occurs mainly in the first microns of the irradiated surface sample and do not reach the core. This was confirmed by taking a piece of the plaque for Cone calorimetry, after 500 h of irradiation, that was microtomed and subjected to analysis by infrared spectroscopy. The oxidation level decreased very rapidly with the distance from the irradiated surface. The oxidation profile obtained can be explained by a combination of the attenuation of the light absorption within the sample and oxygen starvation. This oxygen starvation may be accentuated by the well known reduction of gas permeability in the nanocomposite due to the presence of silicate layers [2]; explanation that needs to be confirmed.

The amount of smoke, specific extinction area, does not appear to change significantly in any of these samples. The results for the nanocomposites that were prepared by solution blending are quite different, the peak heat release rate is actually increased while the time at which this is observed is decreased. This indicates a clear difference between these two techniques; elucidation of the reasons for the difference will be the subject of future investigations.

A conclusion based upon the TGA results was that there was little effect based upon the ammonium salt which was used to modify the clay. On the other hand, there appears to be a difference from the Cone results. The clay with a hydroxyl functionality gives a higher peak heat release value than do those without functional groups. One may anticipate that the absence of this functional group may make the clay more like the polymer and give a more compatible material. This requires further investigation.

4. Conclusion

The intercalated form of PP-nanocomposites obtained in this study showed a noticeable enhancement of the thermal stability, compared to pure PP and PP-g-MA. This enhancement is attributed to the presence of silicate (mass fraction 5%); the presence of the clay is ineffective in retarding photo-oxidation. Indeed, the PP-nanocomposites degraded much more rapidly than pure PP as shown by the absence of an induction period. Photo-oxidation also had an adverse effect on the thermal stability of the nanocomposites.

The Cone calorimetric study on these nanocomposites shows a clear advantage for the samples prepared by melt blending. Irradiation of these samples appeared to have little effect on the Cone parameters.

Acknowledgments

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