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Polyethylene and Polypropylene Nanocomposites based upon an Oligomerically-Modified Clay

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Abstract

Montmorillonite clay was modified with an oligomeric surfactant, which was then melt blended with polyethylene and polypropylene in a Brabender mixer. The morphology was characterized by X-ray diffraction and transmission electron microscopy, while thermal stability was evaluated from thermogravimetric analysis and the fire properties by cone calorimetry. The nanocomposites are best described as mixed immiscible/intercalated/delaminated systems and the reduction in peak heat release rate is about 40% at 5% inorganic clay loading.

Keywords

1. Introduction

It is believed that the presence of only a small amount of clay can greatly improve many properties of polymers, if nano-dispersion of clay in the polymer matrix is realized [1]. Generally there are two ways to make a nanocomposite: in situ polymerization and melt blending, and melt blending is favored in industry. To obtain a nanocomposite, the inorganic clay must be modified with some organic surfactant, usually an 'onium' salt, which replaces the inorganic cation and makes the gallery space of the clay sufficiently organophilic to permit the entry of a monomer or polymer. This has been used quite successfully for polymers, such as polystyrene [2], polyamide [3], etc.

Polyethylene (PE) and polypropylene (PP) are the most widely used polyolefin polymers, but, because of their non-polar backbones, it is a challenge to make nanocomposites of PE and PP by melt blending with organically modified clay. In most instances, maleic anhydride grafted PE or PP was used as a compatibilizer [4], [5] to permit the formation of the nanocomposite. Previous work from this laboratory has also shown that the presence of maleic anhydride as an additive during melt blending can assist in the formation of PE and PP nanocomposites [6], [7]. Recent work from this laboratory has introduced oligomerically modified clays, which show great promise for nanocomposite formation [8], [9], [10]. A very recent paper by Bartholmai and Schartel has asked the question if nanocomposites are a solution or an illusion for fire retardancy [11].

In this work, a new surfactant containing an oligomeric group was prepared and nanocomposites of PP and PE were prepared by melt blending, in the absence of a compatibilizer. Nanocomposite formation is completely characterized and thermogravimetry and cone calorimetry was used to evaluate the thermal and fire properties of these systems.

2. Experimental

2.1. Materials

Low-density polyethylene (melt index 190 °C/2.16 kg, 7 g/10 min) and isotactic polypropylene (melt index 230 °C/2.16 kg 4 g/10 min), as well as vinylbenzyl chloride, lauryl acrylate and 2,2'-azobisisobutyronitrile (AIBN) were acquired from the Aldrich Chemical Company. The sodium montmorillonite was provided by Southern Clay Products, Inc.

2.2. Synthesis of vinylbenzyl chloride and lauryl acrylate copolymer

A 173 g (0.720 mol) portion of lauryl acrylate, 9.2 g (60 mmol) vinylbenzyl chloride and 400 ml THF were placed in a 1000 ml round bottom flask and the solution was stirred for 10 min, then gently refluxed under nitrogen for 10 min. To this solution was added 9.84 g (50 mmol) AIBN and the solution was kept at reflux for 12 h. The solution was then cooled and poured into a large excess of methanol to precipitate the polymer; 146 g of a colorless copolymer was collected after filtration. The number average molecular weight is 4100 with a polymer dispersity index of 1.2. ^{1}H NMR: (CDCl$_3$, ppm) 7.2 (br, 2H), 7.0 (br, 2H), 4.5 (br, 2H), 4.0 (br, 30H), 2.3 (br, 16H), 1.9 (br, 32H), 1.6 (br, 30H), 1.3 (br, 270H), 0.9 (t, 45H).

2.3. Synthesis of the ammonium salt of the copolymer

To a solution of 146 g copolymer in 250 ml THF in a 500 ml round bottom flask was added a large excess of triethylamine and the solution was stirred at room temperature for 12 h. Then the solvent was evaporated at 70 °C under vacuum; the recovery of the copolymer salt was 150 g. There is a new broad peak in the NMR spectrum at 3.4 ppm, which may be assigned as the methylene group attached to the nitrogen of the ammonium salt. The methyl group adjacent to the methylene is in the 1.3 ppm region.

2.4. Preparation of the lauryl clay

A 50 g portion of sodium montmorillonite was well dispersed in 1000 ml THF/H_2O (50:50) while 150 g of the copolymer salt was dissolved in 500 ml THF. A 400 ml portion of the salt solution was slowly added to the dispersed clay and the system was vigorously stirred for about 8 h, then the remaining portion of the salt solution was added drop-wise with stirring. After stirring was stopped, a precipitate settled to the bottom of the flask and the supernatant liquid was poured off, then another 500 ml portion of THF/H_2O (50:50) was added to the slurry and stirred for an additional 2 h. Finally, the precipitate was collected and dried in a vacuum oven at 80 °C for 24 h and 200 g of oligmerically modified clay, herein called lauryl clay, was obtained.

2.5. Preparation of the polymer–clay nanocomposites

All nanocomposites in this work were prepared by melt blending in a Brabender Plasticorder at 60 rpm and 185 °C for 3 min, the calculated amount of polymer and lauryl clay were charged to the Brabender at the same time. After 3 min blending, the mixture was removed from the chamber and allowed to cool to room temperate. Table 1 gives the composition of the nanocomposites.

Table 1. Composition of polymer clay nanocomposites

No.	PE or PP	Lauryl clay	Inorganic clay loading (%)
1	96	4	1
2	88	12	3
3	80	20	5

2.6. Instrumentation

X-ray diffraction (XRD) was performed on a Rigaku Geiger Flex, 2-circle powder diffractometer equipped with Cu Kα generator (λ = 1.5404 Å) at 50 kV and 20 mA, scanning from 1 to 10° at 0.1 step. All the samples were compression molded into 20 mm × 15 mm × 1 mm plaques for XRD measurements. Bright field transmission electron microscopy (TEM) image was obtained at 120 kV, at low-dose conditions, with a Phillips 400T electron microscopy. The sample was ultramicrotomed with a diamond knife on a Leica Ultracut UCT microtome at room temperature to give 70-nm-thick section. The section was transferred from water to carbon-coated Cu grids of 200 mesh. The contrast between the layered silicate and the polymer phase was sufficient for imaging, so no heavy metal staining of sections prior to imaging was required. Thermogravimetric analysis (TGA) was carried out on a Cahn TG131 unit under a flowing nitrogen atmosphere at a scan rate of 20 °C/min from room temperature to 600 °C. Temperatures are reproducible to ±3 °C while the fraction of non-volatile is repeatable to ±3%. Cone calorimetry was performed on an Atlas CONE-2 according to ASTM E 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 the composites into 100 mm × 100 mm × 3 mm square plaques. Typical results from cone calorimetry are reproducible to within about ±10%, based on many runs in which thousands of samples have been

combusted [12]. Tensile properties were measured using MTS Alliance RT/5 tensile test machine at a crosshead speed of 25.4 mm/min. The reported values are based on the average of five determinations. Molecular weights were determined using a DAWN EOS MALLS (Wyatt Technologies) coupled with a W-410 RID (Waters Corporation) using Waters Ultrastyragel columns HR4, HR3, HR1 in series; the mobile phase was THF.

3. Results and discussion

3.1. XRD measurement of lauryl clay and its nanocomposites

The XRD pattern of the lauryl clay is shown in Fig. 1. It suggests that this oligomerically modified clay is highly ordered. Three peaks are visible in the 2ϑ range from 1 to 10°. The first peak is assigned as the [0 0 1] plane of the clay crystal and is located at 2.3°, which gives a d-spacing of 3.8 nm.
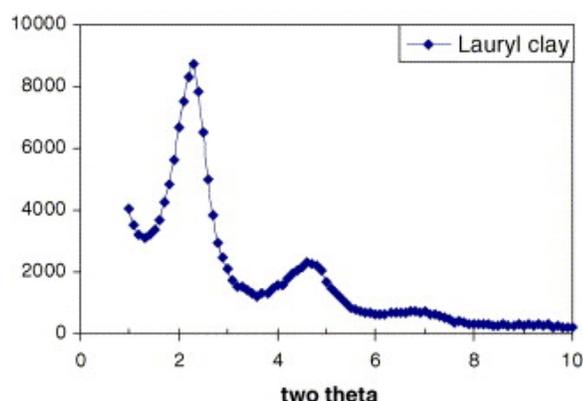

Fig. 1. X-ray diffraction pattern of lauryl clay.

With polypropylene and polyethylene, loadings of 4, 12 and 20% lauryl clay, which correspond to 1, 3 and 5% inorganic clay were investigated (the TGA results that justify this statement will be shown later in this paper). The XRD traces of PE and PP nanocomposites are shown in Fig. 2, Fig. 3, respectively, while the corresponding numerical data is reported in Table 1. For PE nanocomposites, 1% inorganic clay gives a very weak signal while 3 and 5% inorganic clay give stronger signals, and the 0 0 1 reflection is slightly shifted to a lower 2ϑ value. For polypropylene, strong reflections are seen at all clay amounts and the position is the same as observed for the PE systems and the lauryl clay. Since the d-spacing is essentially unchanged, either there is no entry of the polyolefin between the clay layers or else the layers are already sufficiently expanded by the presence of the acrylate polymer to enable intercalation of the polyolefin. The use of TEM is required to answer this question.
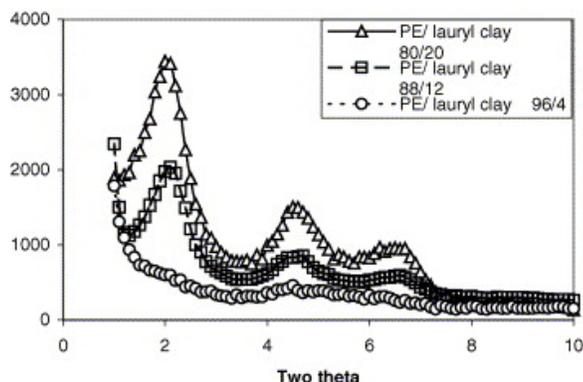

Fig. 2. X-ray diffraction traces of polyethylene/lauryl clay nanocomposites.
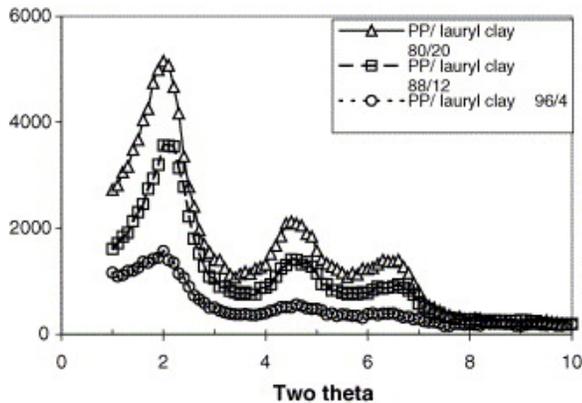
Fig. 3. X-ray diffraction traces of polypropylene/lauryl clay nanocomposites.

3.2. TEM images of PE and PP nanocomposites

TEM images were obtained on both polyethylene and polypropylene nanocomposites at 5% inorganic clay loading and these are shown in Fig. 4, Fig. 5, respectively. From the lower magnifications images (on the left in each figure) one can clearly see the presence of some clay tactoids as well some regions where the nano-dispersion is excellent; the quality of the nano-dispersion appears to be higher in the polypropylene system than in the polyethylene system. In the images at higher magnification, one can see both intercalated and delaminated regions. These systems should probably be described as mixed immiscible/intercalated/delaminated systems. This is in agreement with the results of XRD.
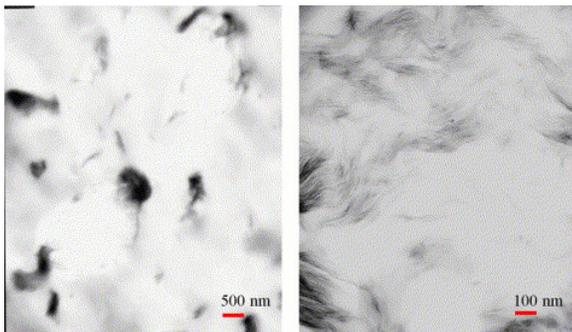

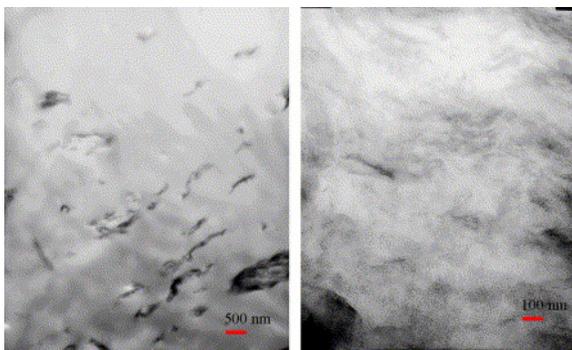Fig. 4. TEM images of polyethylene/lauryl clay nanocomposite at 5% inorganic clay loading.

Fig. 5. TEM images of polypropylene/lauryl clay nanocomposite at 5% inorganic clay loading.

3.3. Thermogravimetric analysis

TGA curves for the lauryl clay alone, shown in Fig. 6, and for the polyethylene and polypropylene nanocomposites, shown in Fig. 7, Fig. 8, respectively, have been obtained. From these TGA curves, we have extracted the pertinent information, which includes the onset temperature of the degradation,

usually taken in this laboratory as the temperature at which 10% degradation occurs, $T_{0.1}$, the mid-point temperature of the degradation, another measure of thermal stability, $T_{0.5}$, and the fraction of non-volatile that remains at 600 °C, denoted as char; this data is displayed in Table 2. From the TGA curve of the clay alone one can see that 75% of the clay volatiles by 600 °C, indicating the inorganic content of the clay and this controlled the amount that was added to prepare the nanocomposites. The lauryl clay shows excellent thermal stability, the temperature must rise to 384 °C to give 10% mass loss. At 340 °C, the mass loss is only 1.5%; if one compares this to the typical organically modified clay, for example, one which contains one long chain and three methyl groups, this exhibits 12% mass loss at 335 °C and 20% mass loss at 390 °C. The lauryl clay has enhanced thermal stability compared to the common systems (Table 3).
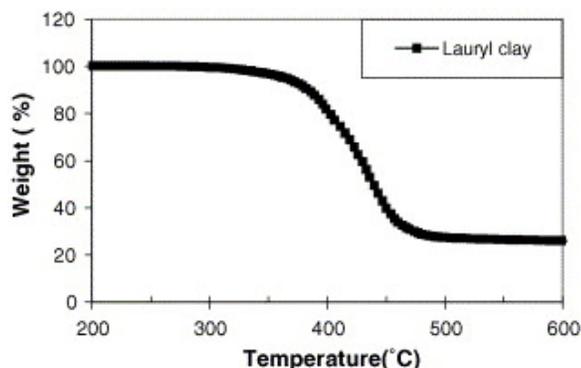

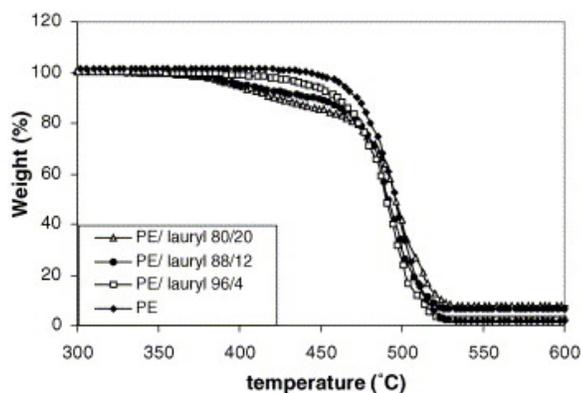Fig. 6. TGA curve for lauryl clay.

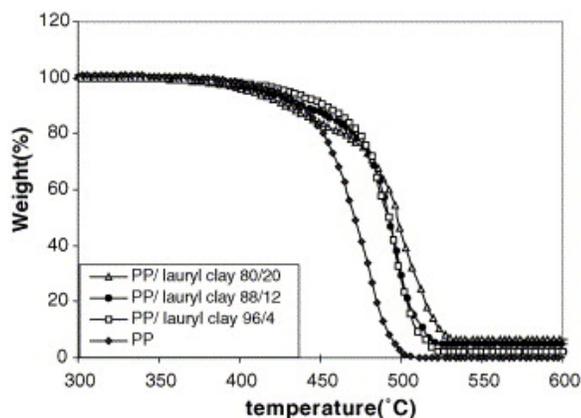Fig. 7. TGA curves for polyethylene/lauryl clay nanocomposites.

Fig. 8. TGA curves for polypropylene/lauryl clay nanocomposites.

Table 2. XRD data for polyethylene and polypropylene/lauryl clay nanocomposites

	Lauryl clay	2ϑ	d-spacing (nm)
PE			
80	20	2.0	4.4
88	12	2.1	4.2
96	4	–	–
PP			
80	20	2.0	4.4
88	12	2.1	4.2
96	4	2.0	4.4

Table 3. TGA data, in nitrogen, for polyethylene and polypropylene/lauryl clay nanocomposites

	Lauryl clay	$T_{0.1}$ (°C)	$T_{0.5}$ (°C)	Char@600 °C (%)
PE				
0	100	384	438	25
100	0	476	496	0
96	4	460	491	2
88	12	444	492	6
80	20	420	495	8
PP				
100	0	437	470	0
96	4	453	493	2
88	12	438	493	5
80	20	430	498	6

It is not surprising that the polyethylene nanocomposites show an earlier onset temperature than does the virgin polymer, since lauryl clay begins to degrade earlier than does polyethylene. The mid-point of the degradation is not lowered by nanocomposite formation, even though the mid-point for lauryl clay is lower than that of polyethylene. This is in agreement with previous work on PE nanocomposites which has shown that nanocomposite formation has almost no effect on the TGA curves [6], [13]. There also may be a slight increase in the amount of non-volatile material, compared to that expected from the clay alone.

In the case of polypropylene, the onset temperature jumps by 25 °C at 4% clay, which corresponds to 1% inorganic clay, and then falls back at higher temperatures while the mid-point temperature remains elevated at any clay loading. We cannot offer an explanation for this observation at this time, but similar behavior has been seen previously [13]. Since the vast majority of work that has been carried out on PP has utilized PP-g-MA, there is little that one can use for comparison.

3.4. Flammability properties of nanocomposites

The fire properties of materials were evaluated by cone calorimetery, from which one may obtain the time to ignition, t_{ign}, the heat release rate and especially its peak value (PHRR), the mass loss rate

(MLR) whose change usually corresponds to the changes in the heat release rate, the total heat released (THR), a measure of the amount of material that is combusted, and the specific extinction area (SEA), a measure of the amount of smoke produced. The peak heat release rate is frequently considered to be one of the most important, if not the most important, parameter that can be obtained from the cone calorimeter. Part of its importance arrives from observation due to Gilman, who showed that there is a significant reduction in this parameter for nanocomposites but little change, if any, for microcomposites [12]. Similar observations have been obtained for other polymers in these laboratories [14], [15].

The cone calorimetric results for the various PE and PP nanocomposites are shown in Table 4, while the heat release rate curves for the pure polymer and its nanocomposites are presented in Fig. 9, Fig. 10. The PHRR of PE and its nanocomposites show around a 10% reduction, compared with the pure polyolefins, when there is less than 5% inorganic clay present. When the loading of inorganic clay reaches 5%, both PE and PP nanocomposites show about 40% reduction in PHRR. This figure may be compared with those that have been previously reported for these polymers. The maximum reduction in PHRR that has been previously observed in this laboratory is 35% for a nanocomposite formed by melt blending PE with Cloisite 6A [6] while for PP, values of 35% was obtained when an oligomerically modified clay containing styrene was used [8] and the value was 59% for an oligomerically modified clay that contained caprolactone [16]. The value obtained for the lauryl clay nanocomposites is indicative of good dispersion, in agreement with the XRD and TEM results.

Table 4. Cone calorimeter data for polyethylene and polypropylene and their nanocomposites at 35 kW/m^2

	Lauryl clay	t_{ign}[a] (s)	PHRR[a] (kW/m^2) (% reduction)	SEA[a] (m^2/kg)	MLR[a] (g/sm^2)	THR[a] (MJ/m^2)
PE						
100	0	71 ± 5	1835 ± 41	379 ± 27	26 ± 2	94 ± 5
96	4	72 ± 7	1699 ± 99 (7)	402 ± 46	25 ± 2	91 ± 3
88	12	70 ± 4	1657 ± 94 (10)	448 ± 32	25 ± 1	95 ± 2
80	20	56 ± 5	1031 ± 48 (44)	555 ± 17	22 ± 2	89 ± 2
PP						
100	0	52 ± 1	1659 ± 59	460 ± 40	25 ± 1	96 ± 8
96	4	54 ± 3	1498 ± 21 (10)	498 ± 6	24 ± 1	92 ± 3
88	12	50 ± 3	1467 ± 103 (12)	521 ± 5	24 ± 1	91 ± 1
80	20	49 ± 5	989 ± 24 (40)	627 ± 33	19 ± 1	90 ± 1

[a]t_{ign}: time to ignition; PHRR, peak heat release rate; SEA, specific extinction area; MLR, mass loss rate; THR, total heat released.
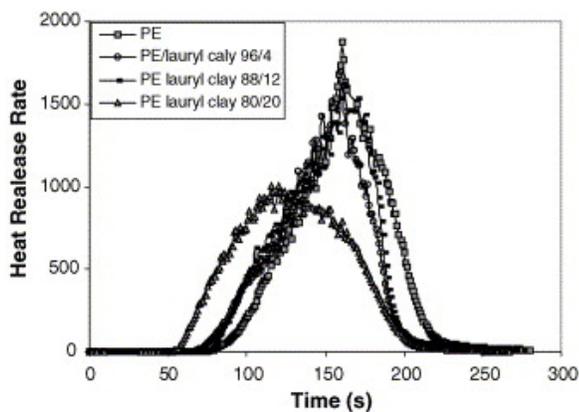
Fig. 9. Heat release rate curves for polyethylene and polyethylene/lauryl clay nanocomposites at 35 kW/m²heat flux.
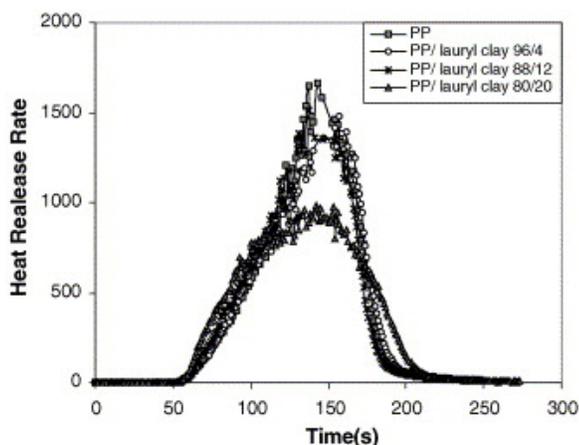

Fig. 10. Heat release rate curves for polypropylene and polypropylene/lauryl clay nanocomposites at 35 kW/m² heat flux.

The time to ignition is slightly decreased for the PE nanocomposite at 5% inorganic clay loading while there is no change in time to ignition for the polypropylene system. As is normal, the total heat released is unaffected by the presence of the clay, meaning that the entire polymer will eventually burn, but at a slower rate and this is reflected in the lower mass loss rate. Finally the amount of smoke stays relatively constant for the nanocomposites compared to the virgin polymers.

3.5. Mechanical properties

The mechanical properties of the nanocomposites have been evaluated and are compared to those of the virgin polymers in Table 5. The mechanical properties have been evaluated at all three levels of clay, but, since it is only at 20% organic clay loading (corresponding to 5% inorganic clay) that one observes changes in fire behavior, this is the level at which the comparison between virgin polymer and nanocomposite is most appropriate. For polyethylene, the tensile strength and the elongation are significantly decreased but the decrease is much less for the polypropylene system, leading to the possibility that this may be a useful system for polypropylene.

Table 5. Mechanical properties of polyethylene and polypropylene and their nanocomposites

	Lauryl clay	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
PE				
100	0	12	138	402

96	4	10	144	368
88	12	7	130	192
80	20	6	112	137
PP				
100	0	32	773	580
96	4	31	712	554
88	12	27	711	485
80	20	22	637	430

4. Conclusions

An oligmerically modified clay, containing 75% surfactant, can be directly melt blended in a Brabender mixer with polyolefins, such as polyethylene and polypropylene, and give nanocomposites without resort to other compatibilizers. There must be a minimum of 5% inorganic clay present to lead to useful reductions in the fire properties but there is an impact on the mechanical properties but this is less for polypropylene than for polyethylene.

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