

Marquette University
e-Publications@Marquette

Chemistry Faculty Research and Publications

Chemistry, Department of

1-1-2006

Thermal and Flame Properties of Polyethylene and Polypropylene Nanocomposites Based on an Oligomerically–Modified Clay

Jinguo Zhang
Marquette University

David D. Jiang
Marquette University

Charles A. Wilkie
Marquette University, charles.wilkie@marquette.edu

Accepted version. *Polymer Degradation and Stability*, Vol. 91, No. 2 (February 2006): 298-304. DOI.
© 2005 Elsevier Ltd. Used with permission.

Marquette University

e-Publications@Marquette

Chemistry Faculty Research and Publications/College of Arts and Sciences

This paper is NOT THE PUBLISHED VERSION; but the author's final, peer-reviewed manuscript. The published version may be accessed by following the link in the citation below.

Polymer Degradation and Stability, Vol. 91, No. 2 (February 2006): 298-304. [DOI](#). This article is © Elsevier and permission has been granted for this version to appear in [e-Publications@Marquette](#). Elsevier does not grant permission for this article to be further copied/distributed or hosted elsewhere without the express permission from Elsevier.

Thermal and Flame Properties of Polyethylene and Polypropylene Nanocomposites Based on An Oligomerically-Modified Clay

Jinguo Zhang

Department of Chemistry, Marquette University, Milwaukee, WI

David D. Jiang

Department of Chemistry, Marquette University, Milwaukee, WI

Charles A. Wilkie

Department of Chemistry, Marquette University, Milwaukee, WI

Abstract

An oligomerically-modified clay was made using a surfactant which is the ammonium salt of an oligomer. The newly modified clay contains 37.5% inorganic clay and 62.5% oligomer. Polyethylene and polypropylene nanocomposites were made by melt blending the polymer with the oligomerically-modified clay in a Brabender mixer at various clay loadings. The structure of the nanocomposites was characterized by X-ray diffraction and transmission electron microscopy. Mechanical testing showed that the polyethylene nanocomposites had an enhanced Young's modulus and slightly decreased elongation, while the changes for polypropylene nanocomposites are small compared with the virgin

polymers. The thermal stability and flame properties were evaluated using thermogravimetric analysis and cone calorimetry, respectively. The plasticising effect of the oligomer was suppressed because of the increased inorganic content. The maximum reduction in peak heat release rate is about 40%.

Keywords

Fire retardancy, Nanocomposites, Oligomerically modified

1. Introduction

Since the great advantages of polyamide-6-clay nanocomposites were first observed [\[1\]](#), much work has been carried out on polymer–clay nanocomposites [\[2\]](#). It is a challenge to make polyethylene (PE) and polypropylene (PP) because of their non-polarity. Much research has focused on the use of maleic anhydride grafted PE or PP as a compatibiliser [\[3\]](#), [\[4\]](#), [\[5\]](#) through melt blending with organically-modified clay while others have used new catalysts through in situ polymerisation [\[6\]](#). Recent work from this laboratory has shown that both polyethylene and polypropylene nanocomposites could be formed by direct melt blending polymer with an oligomerically-modified clay [\[7\]](#), [\[8\]](#), [\[9\]](#), [\[10\]](#). Typically, the oligomerically-modified clays contain 25% inorganic clay and 75% oligomer but a variation in the oligomer content can lead to more advantageous behaviour on some properties.

With 5% inorganic clay loading, the best result of reduction in peak heat released rate (PHRR) for PE and PP nanocomposites is 60%. The clay used in that case, known as triclays, was prepared from an oligomeric surfactant, which is an ammonium salt of the terpolymer from vinylbenzyl chloride (VBC), styrene (St) and lauryl acrylate. The disadvantage of using this oligomeric surfactant containing lauryl acrylate is its ability to plasticise the polymer. When 5% inorganic clay is introduced into the system, 15% oligomer will be introduced into the system at the same time. The Young's modulus and tensile strength of the nanocomposites usually decrease, which is opposite to that of nanocomposites based on the typical organically-modified clay.

In this paper, we describe an oligomerically-modified clay based on previous work [\[10\]](#), but containing a higher amount of inorganic clay. The modified clay is melt blended with PE and PP in a Brabender mixer. The PE nanocomposites show enhanced Young's modulus and slightly decreased elongation, while the change for PP nanocomposites are small compared with virgin PP.

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) were acquired from the Aldrich Chemical Company; vinylbenzyl chloride (VBC), styrene (St), lauryl acrylate and 2,2'-azobisisobutyronitrile (AIBN) were also from Aldrich. Sodium montmorillonite was provided by Southern Clay Products, Inc.

2.2. Synthesis of VBC, St and lauryl acrylate copolymer and its ammonium salt

The procedure is the same as has been reported [\[10\]](#) except that the amount of vinylbenzyl chloride is doubled. A solution was prepared containing 115.2 g (0.48 mol) portion of lauryl acrylate, 50.0 g (0.48 mol) styrene and 18.4 g (0.12 mol) vinylbenzyl chloride in 400 ml THF in a 1000 ml 3 neck round bottom flask, equipped with a magnetic stirrer and a condenser. The solution was first stirred for 10 min then gently refluxed under nitrogen for 10 min. To this solution was added 9.8 g (60 mmol)

AIBN in one portion. The system was kept at a gentle reflux for 12 h. The copolymer was precipitated with a large amount of methanol. A 160 g portion of a colourless copolymer was collected after filtration. ¹H NMR: (CDCl₃, ppm) 7.1(br, 17H), 6.7(br, 12H), 4.5(br, 2H), 3.8(br, 10H), 2.2(br, 11H), 1.9(br, 22H), 1.6(br, 10H), 1.3(br, 90H), 0.9(t, 15H).

For the synthesis of the ammonium salt of the copolymer, a large excess amount of triethylamine was added to a solution of 160 g copolymer in 500 ml THF in a 1000 ml round bottom flask. The solution was stirred at room temperature for 2 h then kept at gentle reflux for another 10 h under nitrogen. The solvent was evaporated at 70 °C under vacuum and 170 g copolymer was collected. A new broad peak in the NMR spectrum at 3.4 ppm 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.

2.3. Preparation of triclays II

A 30.0 g portion of sodium montmorillonite in 600 ml THF/H₂O (50:50) was stirred overnight to obtain a well-dispersed suspension while 50.0 g of the copolymer salt was dissolved in 250 ml THF. A 200 ml portion of the salt solution was slowly added to the dispersed clay and the system was vigorously stirred for 12 h, then the remaining portion of the salt solution was added drop-wise with stirring. A precipitate quickly settled to the bottom of the flask after stirring was stopped, and the supernatant liquid was poured off, then another 500 ml portion of THF/H₂O (50:50) was added and stirring was continued for an additional 2 h. Finally, the precipitate was collected and dried in a vacuum oven at 80 °C for 24 h and 80 g of oligomerically-modified clay, triclays II, was obtained.

2.4. Preparation of polymer–clay nanocomposites

All nanocomposites were prepared using melt blending in a Brabender Plasticorder at 60 rpm and 185 °C for 5 min; the calculated amount of polymer and triclays II was put into the Brabender mixer at the same time. After 5 min of blending, the mixture was removed from the chamber and allowed to cool to room temperature. The composition of the nanocomposites is given in [Table 1](#).

Table 1. Composition of polymer clay nanocomposites

No.	PE or PP	Triclays II	Inorganic clay loading (%)
1	97	3	1.1
2	92	8	3.0
3	88	12	4.5

2.5. Instrumentation

X-ray diffraction (XRD) measurements were performed on a Rigaku Geiger Flex, 2-circle powder diffractometer equipped with Cu-K α generator ($\lambda = 1.5404 \text{ \AA}$) at 1 kW, scanning from 1 to 10° at 0.1 step; generator tension was 50 kV at a current of 20 mA. All the samples were compression molded into 20 mm \times 15 mm \times 1 mm plaques for XRD measurements. Bright field transmission electron microscopy (TEM) images were 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 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 an SDT 2960 unit under nitrogen at a scan rate of 20 °C per minute from room temperature to 600 °C at 15 mg scale. Temperatures are reproducible to ± 3 °C while the fraction of non-volatile is repeatable to $\pm 2\%$. Cone calorimetry was performed on an Atlas CONE-2 according to ASTM E 1354 at an incident flux of 35 kW/m² 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 moulding the composites into 100 mm × 100 mm × 3 mm square plaques. Typical results from cone calorimetry are reproducible to within about ±10%. These uncertainties are based on many runs in which thousands of samples have been combusted [11]. 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 5 determinations.

3. Results and discussion

The clay used in this study, triclax II, is sodium montmorillonite modified with an oligomeric surfactant, which is an ammonium salt of a random copolymer. The reactive site of the copolymer is from vinylbenzyl chloride. Comparing the surfactant used in this study with that previously used, triclax, the amount of vinylbenzyl chloride used to synthesize the new surfactant is doubled. Triclax contains 25% inorganic clay and 75% oligomer surfactant [10], while triclax II contains 37.5% inorganic clay, as will be shown from the TGA analysis.

3.1. Characterization of the clay and its nanocomposites by XRD

The XRD pattern of the triclax II is shown in Fig. 1; this is the same pattern that was seen for triclax [10]. The [001] reflection of the clay is located at 2.4°, which gives a d-spacing of 3.7 nm. In this study, 1.1%, 3.0% and 4.5% inorganic clay loadings were investigated. Because this clay contains 37.5% inorganic clay, the corresponding amounts of oligomerically-modified clay that were used are 3%, 8%, and 12%. The XRD traces of PE and PP nanocomposites are shown in Fig. 2, Fig. 3, respectively. All the nanocomposites exhibit a strong reflection at 2.4°, which is the same as that of the clay. The same lack of change in the d-spacing has been observed with triclax [10]; either no polymer inserts between the clay layers and an immiscible system is obtained or the d-spacing is already sufficiently large to permit the entry of the polymer without increasing the d-spacing. Transmission electron microscopy (TEM) is necessary to answer this question.

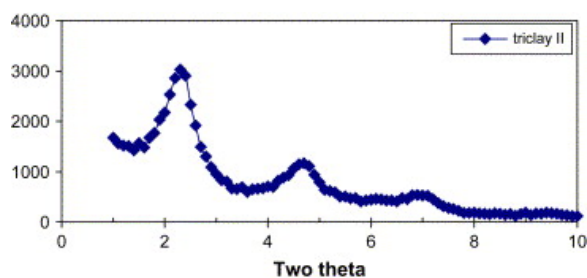


Fig. 1. X-ray diffraction pattern of the oligomerically-modified clay.

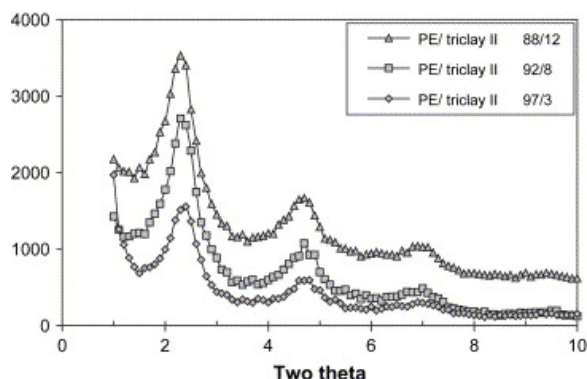


Fig. 2. X-ray diffraction traces of polyethylene-clay nanocomposites.

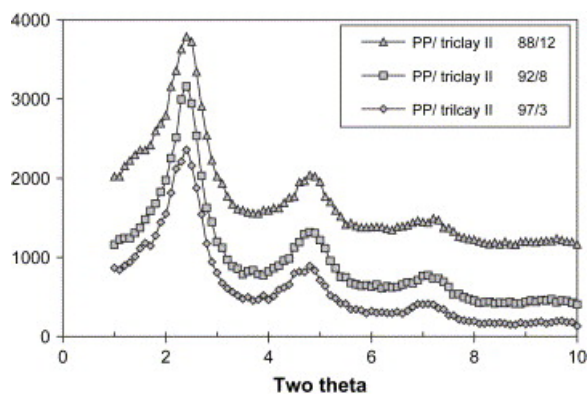


Fig. 3. X-ray diffraction traces of polypropylene–clay nanocomposites.

3.2. Characterization of the nanocomposites by TEM

TEM images were obtained for both polyethylene and polypropylene nanocomposites at 4.5% inorganic clay loads and these images are shown in [Fig. 4](#), [Fig. 5](#), respectively. In the low magnification images, one can see that reasonably good dispersion of the clay in the polymer has been obtained. In the high magnification images, an intercalated structure can be deduced for both PE and PP nanocomposites. Thus, these are best described as intercalated nanocomposites.

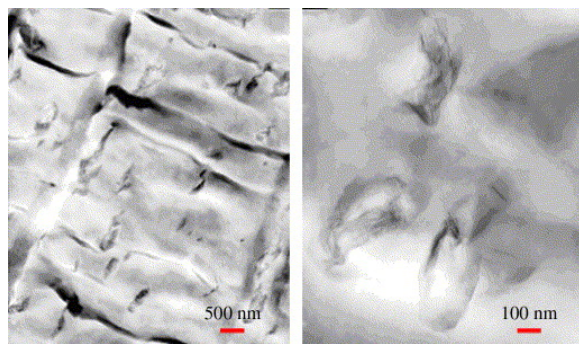


Fig. 4. TEM images of PE–clay nanocomposite at 4.5% inorganic clay loading.

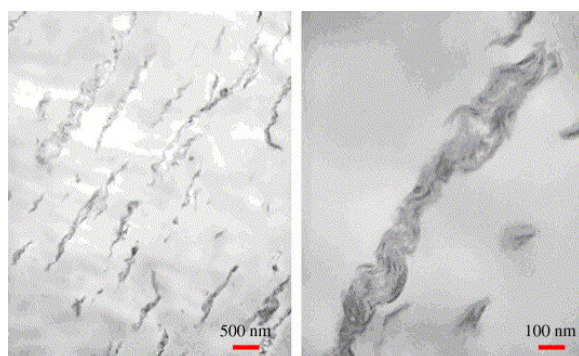


Fig. 5. TEM images of PP–clay nanocomposite at 4.5% inorganic clay loading.

3.3. TGA characterization of nanocomposites

TGA data for clay and its nanocomposites are collected in [Table 2](#) and shown graphically in [Fig. 6](#) for the clay alone, and [Fig. 7](#), [Fig. 8](#) for the PE and PP nanocomposites, respectively. The parameters listed are the onset temperature of the degradation, usually taken as the temperature at which 10% degradation occurs, $T_{0.1}$, the mid-point of the degradation, $T_{0.5}$, another indication of thermal stability and the non-volatile residue found at 600 °C, denoted as char. The non-volatile fraction for modified

clay is 37.5% at 600 °C, indicating the inorganic content. The 10% mass loss temperature of the clay is 350 °C and 50% mass loss temperature is 418 °C indicating that triclay II has a similar thermal stability as triclay [\[10\]](#); the decreased organic content does not have an effect on the thermal stability.

Table 2. TGA data, in nitrogen, for polyethylene and polypropylene–clay nanocomposites

	Triclay II	T _{0.1} (°C)	T _{0.5} (°C)	Char at 600 °C (%)
<i>PE</i>				
100	0	436	475	0
97	3	463	488	2
92	8	456	492	4
88	12	431	492	5
<i>PP</i>				
100	0	400	449	0
97	3	431	467	2
92	8	441	472	3
88	12	441	472	5
0	100	350	418	37.5

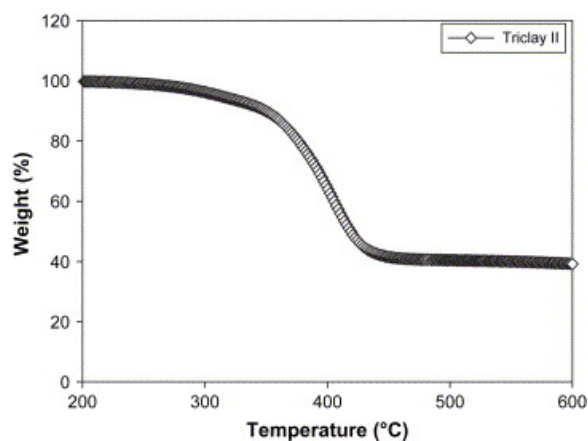


Fig. 6. TGA curve for the clay in nitrogen.

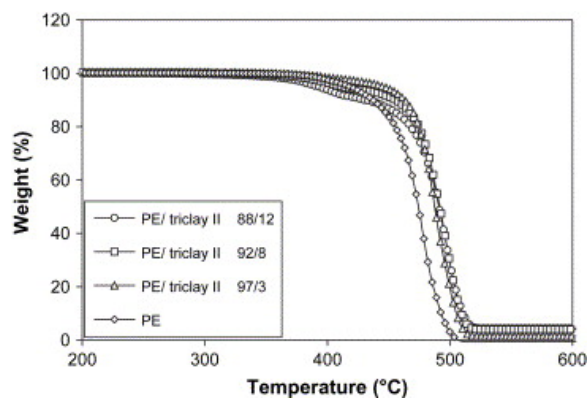


Fig. 7. TGA curves for PE–clay nanocomposites in nitrogen.

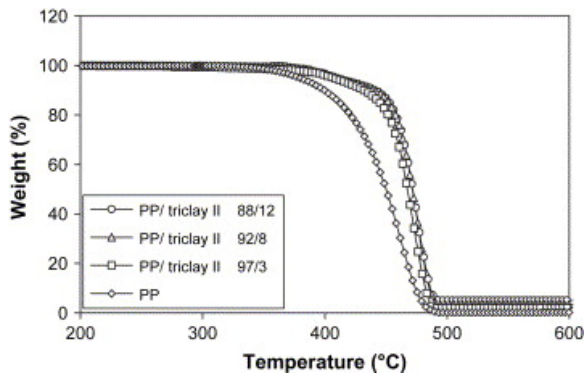


Fig. 8. TGA curves for PP–clay nanocomposites in nitrogen.

The onset temperature of polyethylene is around 90 °C higher than that of triclay II, so one might expect an earlier onset temperature for the polyethylene nanocomposites than in the virgin polymer. The nanocomposites contain 3% and 8% triclay II actually show an onset temperature which is 20 °C higher than that in polyethylene. When the loading of triclay II reaches 12%, the onset temperature is 5 °C lower than that of PE itself, which means the oligomer begins to have an influence on the degradation at this level. The mid-point of the degradation, $T_{0.5}$, of all the PE nanocomposites is about 25 °C higher than that of virgin PE even though the mid-point for the clay is 57 °C lower than that of PE. The amount of char that is formed at 600 °C corresponds rather well to the inorganic clay loading in the system.

PP nanocomposites show enhanced thermal stabilities in all case. The onset temperature increases by 31 °C at 3% clay loading, while the mid-point temperature increases by 28 °C. At higher clay loadings, 8% and 12%, the onset temperature of the nanocomposites is 41 °C higher than that of PP and the increase for the mid-point temperature is 23 °C, which should be again assigned to the nanocomposite effect.

3.4. Cone calorimetry

The fire properties of materials can be evaluated using cone calorimeter. The most important parameters from cone calorimetry are the heat release rate, and especially its peak value, (PHRR); the time to ignition (t_{ign}); the mass loss rate, MLR, which usually tracks very well with the peak heat release rate; the specific extinction area (SEA), a measure of the amount of smoke produced; and the total heat released (THR).

The heat release rate curves for the virgin polymers and their nanocomposites are shown graphically in [Fig. 9](#), [Fig. 10](#) and the corresponding data are given in [Table 3](#). PE and PP nanocomposites have similar behaviour at the same clay loading. The peak heat release rates of the nanocomposites that contains 3% clay (1.1% inorganic clay) show a small reduction compared with the virgin polymers. When the loading of clay reaches 8% (3% inorganic clay), both PE and PP nanocomposites show about 30% reduction in PHRR. At a clay loading of 12% (4.5% inorganic clay), the reduction in PHRR is around 40%. The reduction in the mass loss rate is roughly proportional to the reduction in the peak heat release rate. The reduction in the PHRR is less for triclay II than for the previously examined triclay [\[10\]](#). Since there is a correlation between reduction in the PHRR and the quality of nano-dispersion [\[11\]](#), [\[12\]](#), [\[13\]](#), this is an indication that better nano-dispersion has been obtained with the clay with a higher organic content, which should not be a surprise since an increased organic content must make for better compatibility. The TEM images also show better nano-dispersion for triclay [\[10\]](#) than for

the clay used in this study. There is no change in the total heat released for any of these nanocomposites compared with the virgin polymers, which is the usual observation for nanocomposites. The change in the time to ignition (t_{ign}) for the PE nanocomposites is small, while there is essentially no change for PP nanocomposites. The amount of smoke gradually increases as the clay loading increases, which has been observed in previous work. There is an obvious explanation for the difference between the two versions of triclay. The clay used in this study, triclay II, was prepared using a much higher content of vinylbenzyl chloride, which means that there will be many more ammonium cations on the clay and thus the opportunity for the pinning of the clay layers together is greatly increased. It is clear from the TEM and the data from cone calorimetry that pinning is much more likely to occur with the clay under study herein and this is the likely explanation for the poorer nano-dispersion in this case.

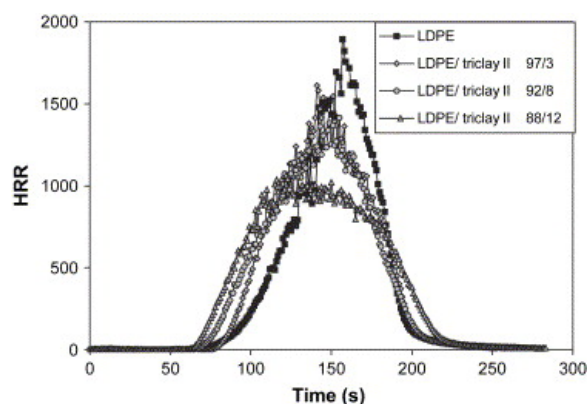


Fig. 9. Comparison of the heat release rate (HRR) plots for pure PE and its clay nanocomposites at 35 kW/m² heat flux.

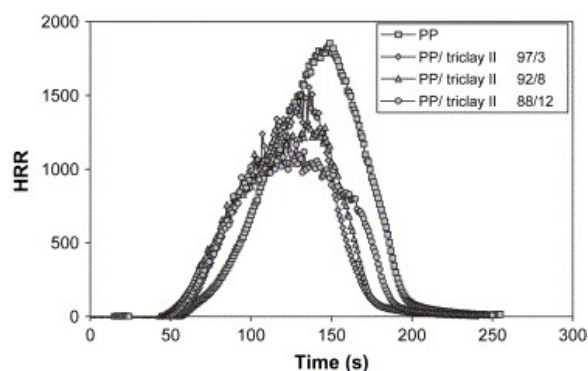


Fig. 10. Comparison of the heat release rate (HRR) plots for pure PP and its clay nanocomposites at 35 kW/m² heat flux.

Table 3. Cone calorimetric data for polyethylene, polypropylene and their nanocomposites

	Triclay II	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 ± 3	1892 ± 95	357 ± 16	29 ± 0	99 ± 2
97	3	75 ± 3	1614 ± 146 (15)	446 ± 41	26 ± 3	99 ± 5
92	8	72 ± 4	1415 ± 44 (25)	463 ± 22	24 ± 0	100 ± 1
88	12	64 ± 3	1044 ± 58 (45)	554 ± 5	20 ± 1	99 ± 1
PP						

100	0	52 ± 0	1897 ± 44	56 ± 13	25 ± 1	101 ± 1
97	3	48 ± 3	1577 ± 92 (17)	588 ± 25	25 ± 0	95 ± 3
92	8	49 ± 4	1309 ± 8 (31)	607 ± 28	23 ± 1	97 ± 2
88	12	52 ± 5	1160 ± 51 (40)	644 ± 31	21 ± 2	93 ± 1

^at_{ign}, Time to ignition; PHRR, peak heat release rate; % reduction = [PHRR (virgin) – PHRR (nano)]/PHRR (virgin); SEA, specific extinction area; MLR, mass loss rate; THR, total heat released.

3.5. Mechanical properties

The mechanical properties of the nanocomposites, such as tensile strength, Young's modulus and elongation at break, have been evaluated and the data are presented in [Table 4](#). In both PE and PP nanocomposites, the tensile strength is slightly decreased compared with the virgin polymers, while Young's modulus is slightly increased. From previous work with the higher organic content clay, a plasticising effect was observed, leading to a decrease in all aspects of the mechanical properties. Here, the increased inorganic content causes a diminishing of this plasticisation. The elongation at break for PE nanocomposites drops from 418% to 250% when clay loading increases to 12%, while the change for PP nanocomposites is negligible.

Table 4. Tensile properties of PE, PP and their nanocomposites

	Triclay II	Tensile strength (MPa)	Modulus (MPa)	Elongation (%)
<i>PE</i>				
100	0	12	162	418
97	3	10	194	352
92	8	8	215	268
88	12	9	210	250
<i>PP</i>				
100	0	35	875	655
97	3	30	864	523
92	8	28	842	478
88	12	30	894	584

4. Conclusions

Clay is modified by cationic exchange with an oligomeric surfactant, which contains a long alkyl group and a benzene ring. In order to suppress the plasticising effect that has been previously observed, the inorganic content in this oligomerically-modified clay is increased to 37.5%. The modified clay was directly melt blended with polyethylene and polypropylene, which led to enhanced thermal stability for the nanocomposites compared with the virgin polymers. The increased Young's modulus for the nanocomposites indicates that the increased inorganic clay content has a significant effect on the mechanical properties. On the other hand, these nanocomposites do not show the same level of nano-dispersion, which leads to a smaller reduction in the peak heat release rate. The poorer nano-dispersion is no doubt due to the increased content of vinylbenzyl chloride, which leads to an increased content on ammonium salts and hence to the pinning of the clays layers. The balance of properties is an important aspect of nanocomposite research and if one changes the surfactant it may have an advantageous effect on some property and a disadvantageous effect on other properties.

References

- [1] A. Usuki, M. Kawasumi, Y. Kojima, A. Okada, T. Kurauchi, O. Kamigaito. *J Mater Res*, 8 (1993), pp. 1174-1178
- [2] M. Alexandre, P. Dubois. *Mater Sci Eng*, R28 (2000), pp. 1-63
- [3] C.M. Koo, H.T. Ham, S.O. Kim, K.H. Wang, I.J. Chung. *Macromolecules*, 35 (2002), pp. 5116-5122
- [4] G. Liang, J. Xu, S. Bao, W. Xu. *J Appl Polym Sci*, 91 (2004), pp. 3974-3980
- [5] P. Svoboda, C. Zeng, H. Wang, L.J. Lee, D.L. Tomasko. *J Appl Polym Sci*, 85 (2002), pp. 1562-1570
- [6] L. Wei, T. Tang, B. Huang. *J Polym Sci Part A Polym Chem*, 42 (2004), pp. 941-949
- [7] S. Su, D.D. Jiang, C.A. Wilkie. *Polym Degrad Stab*, 84 (2004), pp. 269-277
- [8] S. Su, D.D. Jiang, C.A. Wilkie. *Polym Degrad Stab*, 84 (2004), pp. 279-288
- [9] S. Su, D.D. Jiang, C.A. Wilkie. *Polym Degrad Stab*, 83 (2004), pp. 333-346
- [10] Zhang J, Jiang DD, Wilkie CA. *Thermochim Acta*, in press.
- [11] J.W. Gilman, T. Kashiwagi, M. Nyden, J.E.T. Brown, C.L. Jackson, S. Lomakin, et al. S. Al-Maliaka, A. Golovoy, C.A. Wilkie (Eds.), *Chemistry and technology of polymer additives*, Blackwell Scientific, London (1998), pp. 249-265
- [12] S. Su, D.D. Jiang, C.A. Wilkie. *J Vinyl Addit Tech*, 10 (2004), pp. 44-51
- [13] S. Su, D.D. Jiang, C.A. Wilkie. *Polym Degrad Stab*, 83 (2004), pp. 321-331