

6-1-2005

Effects of Surfactants on the Thermal and Fire Properties of Poly(Methyl Methacrylate)/Clay Nanocomposites

Panchatapa Jash
Marquette University

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

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. 88, No. 3 (June 2005): 401-406. [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.

Effects Of Surfactants On The Thermal And Fire Properties Of Poly(Methyl Methacrylate)/Clay Nanocomposites

Panchatapa Jash

Department of Chemistry, Marquette University, Milwaukee, WI

Charles A. Wilkie

Department of Chemistry, Marquette University, Milwaukee, WI

Abstract

Nanocomposites of poly(methyl methacrylate) (PMMA) with layered silicates and with polyhedral oligosilsesquioxanes (POSS) were prepared by bulk polymerization. The thermal and fire stabilities of the various organically-modified clay and POSS nanocomposites were evaluated using both thermogravimetric analysis (TGA) and cone calorimetry. Thermogravimetric analysis is not a good criteria for evaluating nanocomposite formation but cone calorimetry can be. For montmorillonite systems, when more than 4% clay is present, the expected reduction in peak heat release rate is observed. For hectorite, a minimum of 6% clay concentration is required to achieve the same reduction in peak heat release rate. POSS has the potential to reduce the peak heat release rate but one must be careful in selecting the POSS material to be evaluated.

Keywords

Poly(methyl methacrylate), Nanocomposites, Fire retardancy, Cone calorimetry

1. Introduction

Since the pioneering work on polymer layered silicate nanocomposites by Toyota researchers ^{[1], [2], [3]}, much research has been carried out in this field for the past two decades. With the addition of a very small amount of an organically-modified clay, these nanocomposites show a significant increase in many properties, including mechanical properties (tensile modulus and strength, flexural modulus and strength), thermal stability, flame retardancy and barrier properties. Montmorillonite (MMT) is the common natural clay, which is most often used; since it is hydrophilic, it is necessary to exchange the inorganic Na^+ or Ca^{+2} with organic cations to render the gallery space more organophilic to permit the entry of organic polymers into this space. This is usually accomplished by ion exchange of MMT using quaternary ammonium or, occasionally, phosphonium ions ^{[4], [5], [6]}. This organic modification has two benefits: (1) the increase in the interlayer spacing creates more room for the polymer to enter this space and (2) this space is now less hydrophilic and thus is more receptive to the entry of the organic polymer. The 'onium' salt must have at least one chain which is 12 or more carbons in length in order to make the gallery space organophilic enough to permit the entry of the polymer; the organophilicity improves the wetting characteristic of the clay surface with polymers or monomers.

Three different types of nanocomposites may be produced: an immiscible system in which the clay is not nano-dispersed and is acting as an filler; an intercalated system in which the clay is nano-dispersed throughout the entire polymer and the registry between the clay layers is maintained; and an delaminated system (also known as exfoliated) in which again nano-dispersion is achieved and the registry between the clay layers is lost. Nanocomposites may be produced either by an in situ polymerization of the monomer in the presence of the clay or by melt blending of the polymer with the clay. In general, one long carbon chain is sufficient for in situ polymerization but more may be required for a melt blending operation.

While montmorillonite is the most commonly used clay, other clays are also available which may also be useful for nanocomposite formation, especially hectorite must be considered. Previously, Sandi et al. ^[7] have prepared and characterized polymer–hectorite nanocomposites, focusing on the layered structure changes, mechanical properties and the preparation method. In earlier work from this laboratory ^[8], it has been shown that hectorite–polystyrene nanocomposites show a different fire behavior than does montmorillonite–polystyrene systems. In particular, a greater amount of hectorite is required in order to show the same reduction in peak heat release rate that is seen with montmorillonite.

In addition to clays, polyhedral oligosilsesquioxanes, POSS, have been shown to have an effect on the fire stability of polymers. There has been much less work in fire retardancy with POSS than with clays, one US patent ^[9] and one paper ^[10]. POSS significantly reduces the PHRR for a polyether–block–polyamide system (50–70% reduction), for polypropylene (a 40% reduction) and a styrene–butadiene–styrene (SBS) triblock polymer (40–60% reduction) ^[9]. The decrease in the time to ignition, which is common for clay-based systems, is observed for some polymers, but not for all polymers, with POSS. For the combination of POSS with polyurethane fabrics ^[10], the reduction in PHRR is about 55%. It appears that POSS materials should be more widely studied as fire retardant systems, since the reduction in PHRR is quite large and the time to ignition shows a more useful behavior.

In this study we examine nanocomposites of poly(methyl methacrylate), PMMA, with montmorillonite and hectorite with the same organic modifications as well as one POSS material. Nanocomposite formation is

evaluated by X-ray diffraction while thermogravimetric analysis and cone calorimetry are used to evaluate thermal and fire stability, respectively. This study was stimulated by the observation that the time to ignition is usually reduced for most polymer nanocomposites, but PMMA nanocomposites do not show this change.

2. Experimental

2.1. Materials

Most of the materials used in this study, including monomeric methyl methacrylate (MMA), 2,2'-azobisisobutyronitrile (AIBN), hexadecyltributylphosphonium bromide (phos1), tetraphenylphosphonium bromide (phos2), were acquired from the Aldrich Chemical Company. Various organically-modified clays were supplied by Southern Clay Products, Inc, while hectorite was provided by Elementis Specialities. The surfactants that were used to produce the organically-modified hectorites and montmorillonites were kindly provided by Akzo Nobel, the organically-modified clays include dimethyl,dihydrogenatedtallow ammonium, 6A and 15A (they differ in the amount of surfactant that has been added); dimethyl,hydrogenatedtallow,2-ethylhexyl ammonium, 25A; methyl,tallow,bis-2-hydroxyethyl ammonium, 30B; and methyl,dihydrogenatedtallow ammonium, 93A. The POSS material that has been studied, trisylanol phenyl POSS, was kindly provided by Hybrid Plastics, Inc.

2.2. Modification of the clay

The organically-modified clays were obtained by treatment of montmorillonite or hectorite with the onium salt, using the method described by Zhu et al. ^{[11], [12]} and Wang et al. ^[8].

2.3. Synthesis of PMMA/clay nanocomposites

In a 400 ml beaker were placed 4.0 g of organically-modified clay, 100 g of methyl methacrylate and 1.0 g of 2,2'-azobis-isobutyronitrile (AIBN), as the radical initiator. The mixture was stirred at room temperature under a nitrogen atmosphere until the solution become somewhat homogeneous. This was followed by heating in an oil-bath at 60 °C until the mixture solidified. It was then cooled to room temperature and placed in a vacuum oven which was maintained in a nitrogen atmosphere and heated for 24 h at 60 °C and then at 80 °C for an additional 24 h. Finally the beaker was heated to 100 °C under vacuum to remove excess monomer.

2.4. Instrumentation

X-ray diffraction (XRD) patterns were obtained using Rigaku Geiger Flex, 2-circle powder diffractometer equipped with CuK α generator ($\lambda = 1.5404 \text{ \AA}$). Generator tension is 50 kV and the current is 20 mA. TGA was performed on a TA Instruments model SDT 2960 Simultaneous DTA–TGA unit under a 40 mL/min flowing nitrogen atmosphere at a scan rate of 20 °C/min. The same measurements, under the identical conditions, were also carried out in air. In order to better understand the degradation pathway, some samples were heated at a rate of 1 °C/minute under a flowing nitrogen atmosphere. All measurements were carried out at least twice and showed good reproducibility; temperatures are considered accurate to $\pm 4 \text{ °C}$ while the quantity of non-volatile substance that remains at 600 °C, the highest temperature used in this study, was $\pm 3\%$. Cone calorimetry was performed on the Atlas CONE2 according to ASTM E 1354-92 at an incident flux of 35 kW/m² using a cone shaped heater. Exhaust flow is set at 24 l/s and the spark is continuous until the sample ignited. Cone samples are prepared by compression molding the sample (about 30 g) in to square plaques. Typical results from cone calorimetry are reproducible to about $\pm 10\%$; these uncertainties are based on many runs in which thousands of samples have been combusted ^[13].

3. Results and discussion

The purpose of this study is to evaluate the fire properties, particularly the time to ignition, of a collection of methyl methacrylate nanocomposites, to determine the effects of different surfactants and different clays on

the thermal stability and fire properties of the polymer. Because there has been little comparison of clays with POSS materials, a POSS–PMMA system is also included in this study. If the evaluation of cone calorimetric parameters is to make sense, one must first of all understand if a nanocomposite has been formed; X-ray diffraction is used for this purpose. It is also of utility to have information from thermogravimetric analysis to compare with the cone calorimetric data.

3.1. X-ray diffraction analysis

The d-spacing observed for virgin sodium montmorillonite (MMT) is 1.2 nm, which always increases upon organic modification. The d-spacings for the various organically-modified clays are shown in [Table 1](#) while the actual XRD traces are shown in [Fig. 1](#). Phos1 contains a long chain, tributylhexadecylphosphonium, while phos2 has no long chain, tetraphenylphosphonium. It is clear that an expansion of the clay layers occurs for phos1 but not for phos2; the latter is a microcomposite while the former is a nanocomposite. The d-spacing is, in general, larger for MMT than for hectorite, which may suggest better nanocomposite formation with MMT. The XRD traces in all cases show peaks, which suggest that intercalated systems are produced.

Table 1. d-Spacing (001) of PMMA/organically-modified clay nanocomposites

PMMA hybrid with	Spacing (nm)	PMMA hybrid with	Spacing (nm)
6A/MMT	3.2	6A/hectorite	2.6
15A/MMT	3.2	15A/hectorite	2.6
25A/MMT	3.2	25A/hectorite	3.2
30B/MMT	3.7	30B/hectorite	2.2
93A/MMT	3.0		
Phos1	3.3	Phos2	2.0

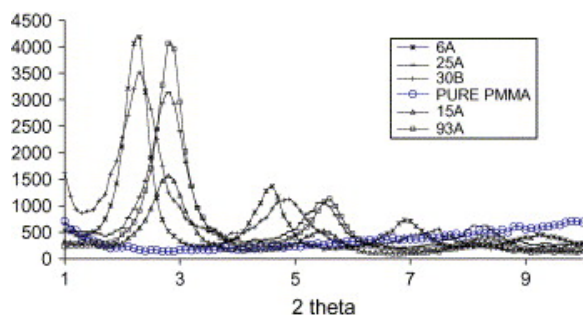


Fig. 1. XRD traces for the PMMA/MMT nanocomposites, 6% clay.

3.2. Thermogravimetric analysis

The TGA results on PMMA and its nanocomposites, shown in [Table 2](#), provide information on the degradation pathway of these materials; representative TGA curves for one surfactant are shown in [Fig. 2](#). The data that are presented include the temperature at which 10% degradation occurs, a measure of the onset temperature of the degradation, the temperature for 50% degradation, the mid-point in the degradation process, and the fraction that is not volatilized at 600 °C, denoted as char. The general conclusions that may be drawn, which are in agreement with previous work on PMMA nanocomposite systems ^[14], are that the onset temperature is relatively unaffected by nanocomposite formation while the temperature at which 50% degradation occurs is increased by 30–50 °C. In some cases the fraction of non-volatile is lower than expected but, in general, it appears to track rather well with the amount of clay that is present. It must be stated that there appears to be no difference between montmorillonite and hectorite-based nanocomposites. On the other hand, phosphorus-based surfactants do seem to give somewhat higher thermal stability than is seen for nitrogen-based

surfactants. This has also been shown in previous work on polystyrene nanocomposites ^[15]. There is little difference between the microcomposite phos2, and the nanocomposite, phos1, indicating that TGA is not a useful way to evaluate nanocomposite formation.

Table 2. TGA parameters on the various PMMA nanocomposites

Composition	T_{10} (°C)	T_{50} (°C)	% Char
PMMA	271	309	0
<i>Montmorillonite</i>			
2% 6A	290	346	0
4% 6A	286	347	1
4% 6A (air)	292	357	3
6% 6A	288	367	1
2% 15A	286	344	0
4% 15A	287	355	1
4% 15A (air)	285	354	4
6% 15A	282	362	1
2% 30B	291	350	3
4% 30B	295	361	3
4% 30B (air)	294	359	3
6% 30B	298	358	1
2% 93A	292	362	4
4% 93A	295	367	4
4% 93A (air)	297	368	5
4% phos1	293	376	4
4% phos2	285	368	5
<i>Hectorite</i>			
4% 6A clay	285	365	3
4% 15A clay	290	376	6
4% 30B clay	291	377	5
<i>POSS</i>			
0.1%	247	340	0
1%	291	357	0
3%	283	366	0
6%	290	368	6

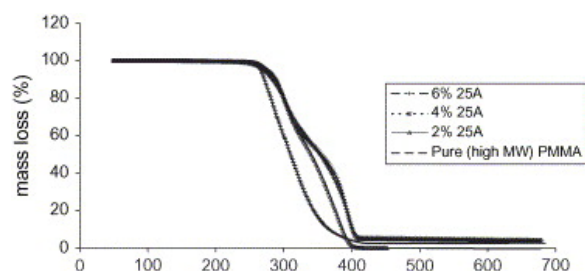


Fig. 2. TGA curves for PMMA and its nanocomposites at varying amounts of clay in nitrogen.

The comparison between the thermal stability of PMMA/POSS and virgin PMMA is also available from [Table 2](#). It is clearly shown that the increase in the amount of POSS lowers the thermal stability from virgin PMMA for 0.1–6% POSS. It is interesting to note that only about 33% of the POSS has undergone degradation at 600 °C, but the nanocomposites do not reflect this thermal stability.

It is significant to note that there is no difference in the TGA data for reaction carried out in nitrogen vs an air atmosphere. This is sometimes used as a criterion of nanocomposite formation [16]. In order to better understand the degradation process, the degradation was studied at a very slow ramp rate of 1 °C/minute. This is based upon the work of Kashiwagi et al. [17] who found that there are three separate steps in the thermal degradation of PMMA and they have attributed these to the degradation of weak links in the polymer chain, degradation arising from end chain unsaturation, and the third and the largest step is ascribed to random scission. The initial step is absent or reduced for PMMA nanocomposites, probably due to the templating effect; an idea which originated in the pioneering work of Blumstein and Billmeyer on the synthesis of methacrylate polymers in the presence of clays [18].

3.3. Cone calorimetry

Cone calorimetry provides information on the fire properties of polymers and nanocomposites; the data collected include the time to ignition (t_{ign}), the heat release rate curve and especially its peak value (PHRR), the time to reach PHRR (t_{PHRR}), the total heat release (THR), which is a measure of the fraction of the material which actually burns during the combustion, the mass loss rate (MLR), and the specific extinction area (SEA), a measure of the quantity of smoke that is evolved during the combustion. We [19], [20] and others [13], have shown that microcomposites show essentially no change in PHRR while nanocomposites, whether intercalated or exfoliated, show significant reductions, which are dependent upon the identity of the polymer. Zhu et al. [21] have carried out cone calorimetric studies on both PMMA and PS nanocomposites and they have found that the time to ignition is decreased for PS but is unchanged for PMMA; the major reason for this study is to expand the number of PMMA nanocomposites that have been studied to see if this is a universal observation.

The cone calorimetric results are shown in Table 3 and the heat release rate curves are shown in Fig. 3, Fig. 4, Fig. 5, Fig. 6. The first parameter to be examined is the time to ignition. It is interesting to note that again, as seen for other PMMA nanocomposites, the type to ignition is essentially unchanged for PMMA and its MMT, hectorite and POSS nanocomposites. The peak heat release rate shows significant reductions, in the range of 20–30%, when the clay loading is 4–6% but there is no reduction at either 0.1 or 2% clay loading, unlike what has been observed for polystyrene nanocomposites [22]. For hectorite, 6% loading is required to achieve a decrease in the peak heat release rate. The time to peak heat release rate is constant, as are the total heat released and the smoke produced while the mass loss rate shows the expected reduction. For POSS systems, none of the cone parameters are improved. It is possible that some other POSS material may give more interesting cone results but the material that has been used herein does not show efficacy with PMMA.

Table 3. Cone calorimetric parameters for various PMMA nanocomposites

Composition	t_{ign} (s)	PHRR (kW/m ²) (% reduction)	t_{PHRR} (s)	THR (MJ/m ²)	MLR (g/s m ²)	SEA, m ² /kg
PMMA	21 ± 0	790 ± 1	81	76 ± 3	20.3	270
<i>Montmorillonite</i>						
0.1% 6A	23 ± 1	853 ± 17	103	75 ± 1	21.2	129
2% 6A	24 ± 4	725 ± 41(8)	81	71 ± 6	16.8	228
4% 6A	20 ± 0	634 ± 8(20)	77	72 ± 1	15.4	267
6% 6A	20 ± 3	579 ± 21(27)	77	68 ± 5	13.4	218
0.1% 15A	25 ± 2	865 ± 2	94	76 ± 1	20.8	214
2% 15A	21 ± 3	771 ± 61(2)	75	72 ± 3	18.0	215
4% 15A	21 ± 1	635 ± 3(20)	68	67 ± 3	16.0	239
6% 15A	18 ± 1	548 ± 12(30)	70	68 ± 1	16.0	212
0.1% 25A	15 ± 3	862 ± 25	101	76 ± 1	20.1	250
2% 25A	19 ± 1	748 ± 21(15)	75	73 ± 3	17.8	188
4% 25A	19 ± 1	623 ± 40(21)	68	67 ± 3	15.0	225

6% 25A	20 ± 1	548 ± 12(30)	80	68 ± 1	13.6	276
0.1% 30B	16 ± 1	929 ± 47	95	77 ± 1	21.5	267
2% 30B	16 ± 0	730 ± 50(9)	76	71 ± 0	17.5	212
4% 30B	21 ± 1	627 ± 24(18)	71	71 ± 1	15.5	236
6% 30B	34 ± 3	536 ± 27(32)	75	66 ± 1	13.3	239
0.1% 93A	26 ± 0	911 ± 57	106	80 ± 2	19.8	284
2% 93A	20 ± 2	793 ± 28	69	67 ± 1	20.2	192
4% 93A	25 ± 1	626 ± 27(21)	85	71 ± 5	16.1	215
6% 93A	21 ± 3	600 ± 22(24)	72	69 ± 2	14.4	252
4% Phos1	24 ± 4	592 ± 10(25)	111	69 ± 3	18.4	469
4% phos2	23 ± 2	794 ± 13	92	71 ± 0	15.7	322
<i>Hectorite</i>						
4% 6A	19 ± 1	747 ± 27	96	72 ± 4	16.8	299
6% 6A	22 ± 1	656 ± 1(17)	100	75 ± 4	15.8	330
4% 15A	20 ± 2	771 ± 27	101	75 ± 2	17.2	323
6% 15A	25 ± 5	657 ± 33(17)	105	80 ± 4	14.8	291
4% 25A	18 ± 0	717 ± 55	87	73 ± 2	16.8	315
6% 25A	23 ± 0	693 ± 26(12)	92	77 ± 6	16.0	304
4% 30B	23 ± 2	707 ± 121	98	74 ± 1	14.8	365
6% 30B	21 ± 2	724 ± 11(8)	89	74 ± 8	17.0	372
<i>POSS</i>						
0.1%	19 ± 3	758 ± 35	87	72	19.2	259
1%	17 ± 2	789 ± 35	103	74	19.0	300
3%	17 ± 2	825 ± 40	95	68	20.0	440
6%	20 ± 2	765 ± 20	101	71	18.8	400

t_{ign} , time to ignition; PHRR, peak heat release rate; t_{PHRR} , time to PHRR; THR, total heat released; MLR, mass loss rate; SEA, average specific extinction area.

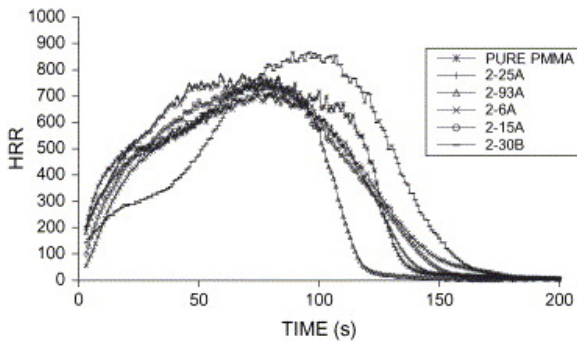


Fig. 3. Heat release rate curves for PMMA/MMT nanocomposites at 2% clay loading.

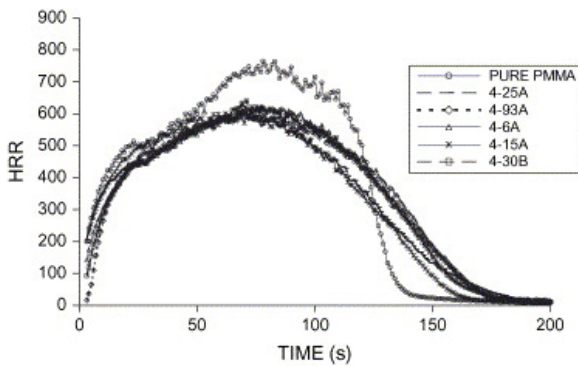


Fig. 4. Heat release rate curves for PMMA/MMT nanocomposites at 4% clay loading.

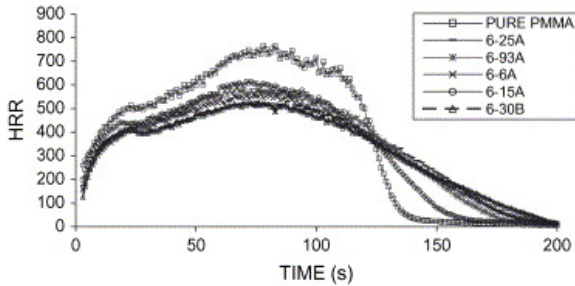


Fig. 5. Heat release rate curves for PMMA/MMT nanocomposites at 6% clay loading.

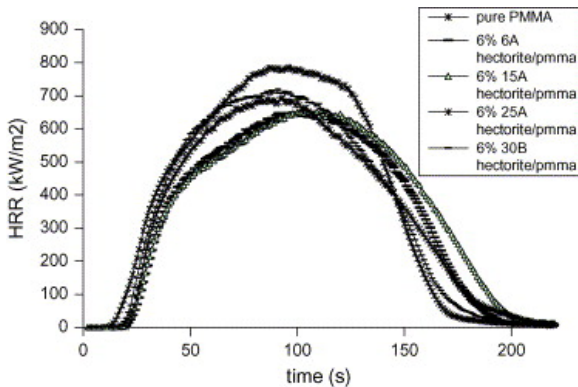


Fig. 6. Heat release rate curves for PMMA/hectorite nanocomposites at 6% clay loading.

Here we offer a speculative explanation for these changes in cone calorimetric parameters. In previous work [23], [24], [25] we have shown that the presence of clay causes a change in the degradation pathway of a polymer and this may be generalized to say that for those polymers for which there are multiple degradation pathways, i.e., those that degrade to give both monomer and oligomer, the presence of clay influences the degradation pathway, favoring one over the other. The favored pathway seems to be that which leads to transient cross-linking of the fraction that does not immediately volatilize. In the case of PMMA, which degrades to give only monomer [26], since there is no change in the degradation pathway and only monomer is produced, we hypothesize that this change in the degradation pathway is connected to the early time to ignition. This is obviously a speculative suggestion that must be further evaluated.

4. Conclusions

One can prepare PMMA nanocomposites using both montmorillonite and hectorite-based clays with a wide variety of organic modifications and obtain virtually the same fire properties as measured with the cone calorimeter. The nature of the surfactant, polar or non-polar, does not have a significant influence on these cone

parameters. A speculative explanation is offered for the different reduction in peak heat release rate that is observed with a wide variety of polymers.

References

- [1] A. Usuki, M. Kawasumi, Y. Kojima, A. Okada, T. Kurauchi, O. Kamigaito. *J Mater Res*, 8 (1993), p. 1174
- [2] A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, et al.. *J Mater Res*, 8 (1993), p. 1180
- [3] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, et al. *J Mater Res*, 8 (1993), p. 1185
- [4] E.P. Giannelis, R. Krishnamoorti, E. Manias. *Adv Polym Sci*, 138 (1999), p. 107
- [5] G. Lagaly. *Appl Clay Sci*, 15 (1999), p. 1
- [6] J. Gilman. *Appl Clay Sci*, 15 (1999), p. 31
- [7] G. Sandi, K.A. Carrado, H. Joachin, W. Lu, J. Prakash. *J Power Sources*, 492 (2003), pp. 119-121
- [8] Wang D, Jang BN, Su S, Zhang J, Zheng X, Chigwada GS, et al. In: LeBras M, Bourbigot S, Duquesne S, Jama C, Wilkie C, editors. *Fire retardancy of polymers: the use of mineral fillers in micro and nano-composites*; 2005, in press.
- [9] Lichtenhan JD, Gilman JW. *Pre-ceramic additives as fire retardants for plastics*. US patent 6,362,279 B2, issued Mar. 26, 2002.
- [10] E. Devaux, M. Rochery, S. Bourbigot. *Fire Mater*, 26 (2002), p. 155
- [11] J. Zhu, A.B. Morgan, F.J. Lamelas, C.A. Wilkie. *Chem Mater*, 13 (2001), p. 3774
- [12] J. Zhu, P. Start, K.A. Mauritz, C.A. Wilkie. *J Polym Sci A Polym Chem*, 40 (2002), p. 1498
- [13] J.W. Gilman, T. Kashiwagi, M. Nyden, J.E.T. Brown, C.L. Jackson, S. Lomakin. S. Al-Maliaka, A. Golovoy, C.A. Wilkie (Eds.), *Chemistry and technology of polymer additives*, Blackwell Scientific, London (1998), pp. 249-265
- [14] S. Kumar, P.J. Jyoti, U. Natarajan. *J Appl Polym Sci*, 89 (2003), p. 1186
- [15] J. Zhu, F.M. Uhl, A.B. Morgan, C.A. Wilkie. *Chem Mater*, 13 (2001), pp. 4649-4654
- [16] Camino G. Private communication; 2003.
- [17] T. Kashiwagi, A. Inaba, J.E. Brown, K. Hatada, T. Kitayama, E. Masuda. *Macromolecules*, 19 (1986), p. 2160
- [18] A. Blumstein, F.W. Billmeyer Jr. *J Polym Sci Part A*, 2 (1966), p. 465
- [19] D. Wang, C.A. Wilkie. *Polym Degrad Stab*, 80 (2001), p. 171
- [20] J. Zhang, C.A. Wilkie. *Polym Degrad Stab*, 80 (2003), p. 163
- [21] J. Zhu, P. Start, K.A. Mauritz, C.A. Wilkie. *Polym Degrad Stab*, 77 (2002), p. 253
- [22] J. Zhu, C.A. Wilkie. *Polym Int*, 49 (2000), p. 1158
- [23] S. Su, C.A. Wilkie. *Polym Degrad Stab*, 83 (2004), p. 347
- [24] Jang BN, Wilkie CA. *Polymer*, in press.
- [25] Costache M, Wilkie CA, in preparation.
- [26] C.F. Cullis, M.M. Hirschler *The combustion of organic polymers*. Oxford Science Publications (1981)