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Additional XPS Studies on the Degradation of Poly(Methyl Methacryalte) and Polystyrene Nanocomposites

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Abstract

XPS studies have been undertaken on exfoliated nanocomposites of polystyrene and poly(methyl methacrylate). One can clearly see that carbon is lost and that oxygen, silicon and aluminum accumulate at the surface of the degrading polymer. The concentration of aluminum at the surface is very low at the beginning of the experiment but makes a large jump at the same temperature at which carbon is lost and oxygen begins to accumulate at the

surface. It appears that the ratio of silicon to aluminum changes as the polymer is lost. A brief discussion is given to explain the origin of oxygen at the surface.

Keywords

1. Introduction

Polymer–clay nanocomposites are one of the new and exciting areas in chemistry and materials science. The initial discovery, by Toyota scientists, was that a polyamide-6 clay nanocomposite, containing 5% clay, shows an increase of 40% in tensile strength, 68% in tensile modulus, 60% in flexural strength and 126% in flexural modulus, while the heat distortion temperature increases from 65 to 152 °C and the impact strength is lowered by only 10% [1]. The current feeling is that nanocomposites may be useful in four areas: increasing the heat distortion temperature, enhancing fire retardancy, enhancing the flexural modulus, and decreasing the permeability of polymers.

Nanocomposites may be described as intercalated, if the registry between the clay layers is maintained as the polymer inserts, or exfoliated, also known as delaminated, if this registry is lost. In some cases, true nano-dispersion of the clay is not obtained and then the system is described as either an immiscible nanocomposite or a microcomposite. The general feeling is that exfoliation is important for permeability and flexural modulus but that it is not important for fire retardancy. There is no uniform agreement on the matter of fire retardancy; some scientists feel that intercalated systems show better fire retardancy while others feel that there is no difference.

Two mechanisms have been suggested to explain the enhanced fire retardancy of nanocomposites: a barrier mechanism [2] and radical trapping due to the presence of iron, or other paramagnetic impurities, in the clays [3]. It is believed that the multi-layered carbonaceous-silicate structure can act as an insulator and as a barrier to mass transport [2]. The radical trapping process seems to be only important at low clay concentration; as the fraction of clay increases, the barrier mechanism becomes more important.

In previous work from these laboratories, we have examined by X-ray photoelectron spectroscopy (XPS) polystyrene (PS) [4], poly(methyl methacrylate) (PMMA) [5] and poly(vinyl chloride) (PVC) [6]nanocomposites. For the first two polymers, which degrade without the production of char, one can see that carbon is lost and oxygen, presumably from the clay, accumulates at the surface. This seems to be evidence to support the barrier properties of the clay. It is of great interest to note that the silicon:aluminum ratio changes, depending on the organic treatment that has been applied to the clay. In the case of PVC, one can see that the presence of the clay does retard the chain-stripping process by which PVC undergoes degradation. Since PVC is a char-forming polymer, the accumulation of carbon, and not oxygen from the clay, is observed at the surface.

In this work, we have used XPS to investigate additional nanocomposites of PS and PMMA. The objective is to understand the effect of the organic treatment on the clay and the role it plays in the variation of the silicon:aluminum ratio at the surface at elevated temperatures.

2. Experimental

The preparation and characterization of the PS and PMMA nanocomposites have been previously described [7], [8], [9]. The organo-clays were prepared by ion exchange between the sodium clay (generously supplied by Southern Clay Products) and the various ammonium salts (prepared in these laboratories) that enable the preparation of the clay in question. Two different clays have been examined, the ammonium salt on one of these contains two styryl units and two methyl groups (this material is referred to herein as the divinyl clay and is shown as DV), while the other contains an oligomeric styrene unit of molecular weight near 5000 along with two methyl groups and one hexadecyl unit (this is referred to as the COPS clay). The structures of

these cations is shown in Fig. 1. These will provide the modified clay. In the case of the DV clay, the nanocomposites were prepared by bulk polymerization, using azobisisobutyronitrile (AIBN) as the initiator. The COPS nanocomposites were prepared by melt blending the clay and the polymer in a Brabender mixer at 175 °C. The XPS experiments were carried out as previously described [10], [11]. The spectra were obtained using a Perkin-Elmer PHI 5300 ESCA system at 250 W (12.5 kV at 20 mA) under a vacuum better than 10^{-6} Pascal (10^{-8} torr). The spectrometer was calibrated using the binding energy of adventitious carbon as 285.0 eV. The samples were prepared by solvent casting a thin film from a dichloromethane solution onto aluminum foil. The d-spacing of the nanocomposite before and after dissolution was determined and no change in d-spacing was found. The pseudo-in situ technique was utilized. In this technique the sample is heated outside of the XPS chamber under an argon atmosphere and then the sample is placed in the XPS chamber for analysis.
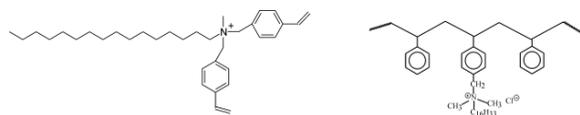
Fig. 1. Structures of the ammonium cations used to make the clays: DV is on the left and COPS on the right.

3. Results and discussion

3.1. The changes in carbon and oxygen in the surface vs temperature

In previous work, we have shown that carbon is lost from the surface of both PS and PMMA nanocomposites and oxygen accumulates and that these results are invariant for both intercalated and exfoliated nanocomposites. Nanocomposites of both PS and PMMA have been examined using organoclays that produce fully exfoliated systems. The exfoliation has been shown by both TEM [7], [8], [9] and NMR spectroscopy [12]. Looking first at changes in the amount of carbon at the surface, shown in Fig. 2, one sees that virgin PS loses a small amount of carbon initially; this is usual for polymers and represents the loss of adventitious carbon present at the surface. There is essentially no change in the carbon intensity with temperature. This must be contrasted to the results for the nanocomposites. In general, one sees an immediate jump in carbon intensity, indicative of carbon accumulation at the surface. An accumulation of carbon must imply a loss of some other element, and this must be hydrogen for these systems, since there are no other elements present. There is a quite small jump in carbon intensity for PMMA and a larger jump for all of the PS systems. It is apparent from this that the nature of the clay has a significant effect on the thermal degradation of the polymer. The thermal degradation of PS proceeds by random scission [13], [14], [15], [16], [17], [18], and the typical products are a mixture of monomer and oligomer. In a TGA/FTIR study of the degradation of nanocomposites [19], we have seen that monomer production is decreased and the formation of oligomer is enhanced for COPS/PS nanocomposites.
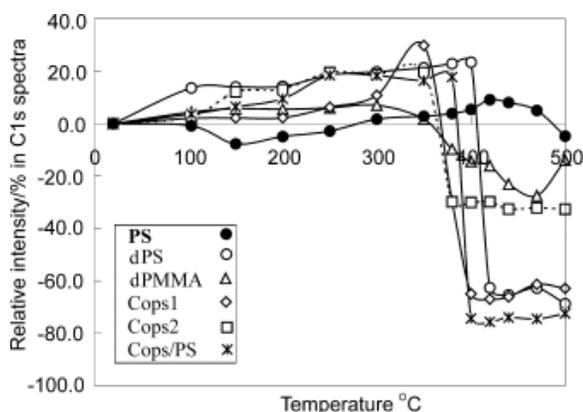
Fig. 2. Relative intensity/% in the C1s spectra as a function of temperature.

PMMA is, of course, of lower thermal stability than PS and, as expected, one sees the loss of carbon begins at lower temperature for PMMA than for PS. In the plot of carbon intensity versus temperature for virgin

PMMA (not shown here but available in Ref. [5]) the intensity of carbon increases with temperature and this is ascribed to a loose cross-linking process. One may suggest that the radicals that are formed couple to reform oligomeric materials and thus maintain carbon. Since carbon is accumulating, this means that something else, normally hydrogen-rich species, is lost. The nanocomposite reported in this paper shows very similar behavior to those previously reported.

It is noteworthy that the loss of carbon begins at the highest temperature for the divinyl–PS nanocomposite. If one compares COPS1 (a copolymer which contains 5% vinylbenzyl chloride) and COPS2 (which contains 10% vinylbenzyl chloride), it is interesting to observe that the carbon intensity falls much lower for COPS1 than for COPS2; these are simply the organically-modified clays. The loss of carbon begins at about the same temperature for both systems. According to our calculations, COPS1 contains about one benzyl chloride per styrene oligomer unit, thus when this is treated with an amine, the stoichiometry will be one amine to one oligomer, producing only one ammonium salt. When the fraction of benzyl chloride units is increased, one oligomer can form more than one ammonium salt. The reason for the difference in the final carbon intensity is that COPS1 contains more carbon than does COPS2, since COPS2 can form two ammonium salts and thus occupy two cation positions. It must be noted that all of the benzyl chloride units have quaternized an amine, since there is no chlorine found in these samples by XPS.

The results for the accumulation of oxygen, shown in Fig. 3, nicely parallel those from the loss of carbon. The loss of carbon from the PMMA nanocomposite begins at the lowest temperature and the accumulation of oxygen also begins at the lowest temperature for this system. The accumulation of oxygen at the surface is never large for PMMA, and the loss of carbon is also not large. There is a nice parallel between carbon and oxygen for PMMA nanocomposites.
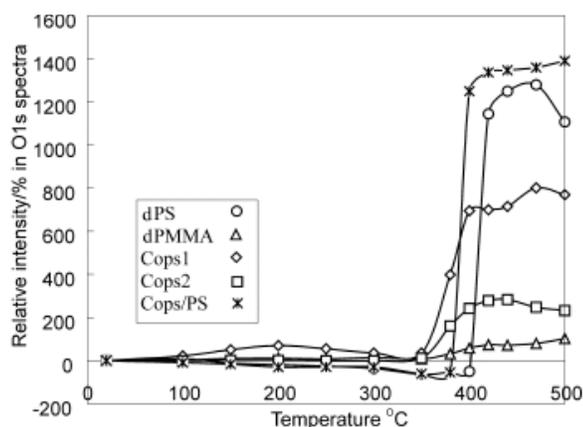
Fig. 3. Relative intensity/% in the O1s spectra as a function of temperature.

The greatest accumulation of oxygen occurs for dPS and COPS/PS, the same systems which show the greatest loss of carbon. There is an exact parallel between the loss of carbon and the accumulation of oxygen at the surface for all systems. It is clear that in non-charring polymers, the clay does accumulate at the surface and provides an impermanent barrier to mass transport and it may also act as an insulator to prevent additional degradation. The only data that has been presented to assert this is the accumulation of oxygen, which, it is reasoned, must come from the clay. It is far more beneficial to show the accumulation of the other clay components, aluminum and silicon, to confirm this assertion.

3.2. The changes in Si/Al ratios in the surface vs temperature

The intensity of both aluminum and silicon at the surface were followed using the 2p orbitals of each of these. In general the intensity of silicon is greater at the surface. The plot from dPS is shown in Fig. 4 and one can see that there is minimal intensity due to silicon starting at ambient temperatures up to 400 °C; at 420 °C intensity due to aluminum appears and at that same temperature the silicon intensity shows a large increase. If one refers to Fig. 2, Fig. 3, this is the same temperature at which carbon is lost and oxygen begins to accumulate.

This is a nice confirmation that it is indeed clay that accumulates at the surface. The silicon:aluminum ratio stays constant at 1.5 – 1.8 at temperature above ca 400 °C. A change in the Si:Al ratio would imply some change in the structure of the clay, which has been seen previously [5].
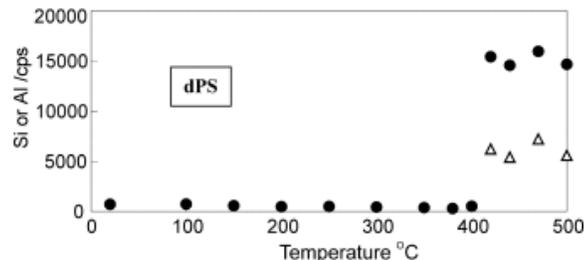
Fig. 4. Silicon (solid circles) and aluminum (open triangles) intensity/cps for dPS as a function of temperature. Si:Al=1.5–1.8 at temperature above ca 400 °C.

A very similar result is seen for dPMMA, shown in Fig. 5; in this case the change occurs at about 350 °C, which is once again in accord with the C1s and the O2p spectra. It is interesting to note that the Si:Al ratio is in the 2.2–2.6 range for PMMA at temperature above ca 350 °C, significantly larger than is seen for dPS. It is most likely that this means either that each polymer may interact in a different way with the clay and this interaction controls what can migrate to the surface, or that the earlier degradation for dPMMA compared to dPS and the earlier evanesence of polymer controls what can appear at the surface. As for the interaction in dPMMA, the surface is obviously more silicon-rich, which may imply that the alumina component interacts with the polymer as well. It should not be surprising that a change in polarity of the clay can cause a change in how the polymer and the clay may interact.
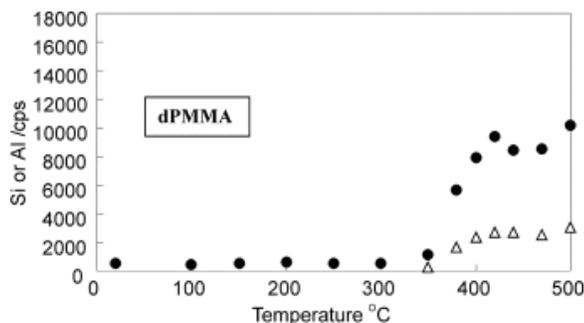
Fig. 5. Silicon (solid circles) and aluminum (triangles) intensity/cps for dPMMA as a function of temperature. Si:Al=2.2–2.6 at temperature above ca 350 °C.

In the case of COPS1, the copolymer that contains 5% vinylbenzyl chloride, and COPS2, which contains 10% vinylbenzyl chloride, one can see aluminum, as well as silicon, from ambient temperature up to the highest values to which we have gone. The data for COPS1 is shown in Fig. 6, while that for COPS2 is shown in Fig. 7. In both cases the jump in silicon and aluminum intensity occurs at the same temperature at which carbon decreases and oxygen begins to accumulate. In Fig. 8, we present the change in the silicon:aluminum ratio for COPS1, while Fig. 9 shows the analogous data for COPS2. It is easily seen from Fig. 8, Fig. 9 that the Si:Al ratio must change and it drops somewhat slowly from ambient temperature up to 350 °C, where the major change in carbon, oxygen and silicon and aluminum intensities occur. At this temperature there is a significant drop, indicating that the surface contains more aluminum above this temperature than it does below it. At temperatures above ca 350 °C the ratio stays nearly constant, ca 2.2 and 3.5 for COPS1 and COPS2, respectively; COPS1 and COPS2 have a higher Si:Al ratio than either dPS or dPMMA. In dPS and dPMMA, no aluminum intensity is observed at room temperature, so one cannot calculate a Si:Al ratio at room temperature. Much larger values of the Si:Al ratio for COPS1 and COPS2 than what was seen at high temperatures for either dPS or dPMMA mean that much more silicon is at the surface in the COPS compounds than from the simple divinyl clay.
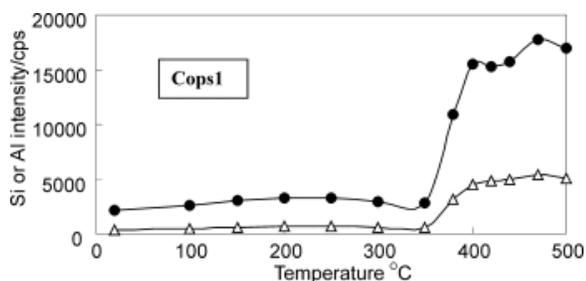
Fig. 6. Silicon (solid circles) or aluminum (triangles) intensity/cps for COPS1 as a function of temperature.
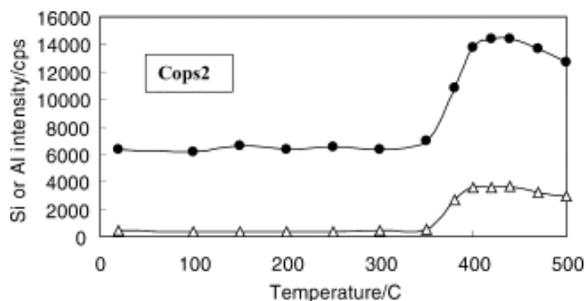
Fig. 7. Silicon (solid circles) or aluminum (triangles) intensity/cps for COPS2 as a function of temperature.
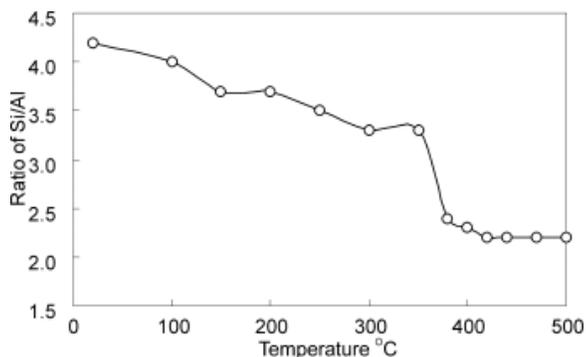
Fig. 8. Ratio of Si:Al for COPS1 as a function of temperature.
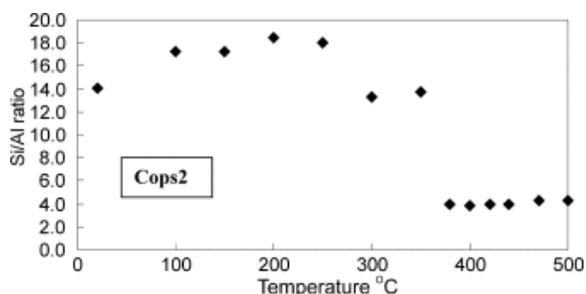
Fig. 9. Ratio of Si:Al for COPS2 as a function of temperature.

The Si:Al ratio for COPS2 is much larger at ambient temperature than that of COPS1, again this may be attributable to the higher benzyl concentration leading to one oligomer spanning two or more clays layers. This can 'pin' the clay layers. In Fig. 8, Fig. 9 the ratio appears to change in two steps, at about 300 °C and again at about 380 °C. The first step is well before carbon is lost or oxygen is accumulated and may be attributed to the beginning of the degradation of the organic moiety on the clay, meaning that the clay is no longer 'pinned' and it may now assume its normal configuration.

The final example is the COPS/PS nanocomposite, shown in Fig. 10. Once again no intensity due to aluminum can be observed until almost 400 °C and at that same temperature the silicon intensity also jumps. The temperature at the jump is about the same as that at which carbon is lost and oxygen begins to accumulate.
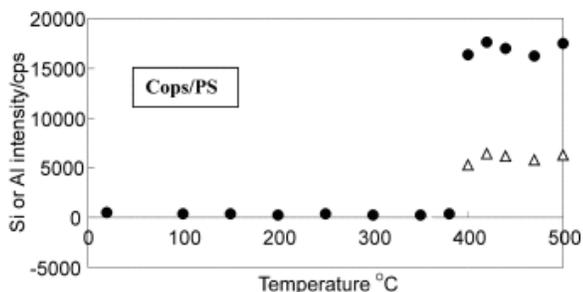
Fig. 10. Si or Al intensity/cps for cops/PS vs temperature Si:Al=1.9–2.1 at temperature above ca 380 °C.

The ratio of Si to Al in a given <u>aluminosilicate</u> material, i.e., clay, depends on several factors, such as, the organic modification applied to the clay, the temperature, the interaction between the clay and the polymer, the surface dynamics of the components' migration from the bulk, adventitious contamination of the outer surface, <u>sample preparation</u> for the XPS experiments, etc.

All figures show higher signal intensities for Si2p than Al2p as seen in <u>Fig. 6</u>, <u>Fig. 7</u>, <u>Fig. 8</u>, <u>Fig. 9</u> for COPS1 and COPS2, within experimental error. Sometimes no Al signal can be monitored at all as shown in <u>Fig. 4</u>, <u>Fig. 5</u>, <u>Fig. 10</u> for dPS, dPMMA and COPS/PS. This can be attributable in general to the fact that the Si:Al ratio of the virgin clays have values of the Si:Al ratio larger than 2.0 in the bulk at room temperature, particularly for clays, such as COPS1 and COPS2, which contain larger amounts of silicon and aluminum. Therefore, the normal intensity for silicon is at least twice that of aluminum.

In organically-modified clays and/or polymer–clay nanocomposites, the situation appears to be far more complicated than expected when examined by XPS. At least two processes may occur: (i) thermal degradation of organically-modified clay: between 200 and 300 °C the cations of clays undergo a <u>Hofmann elimination</u>, with the evolution of an <u>olefin</u> and the formation of a trisubstituted <u>ammonium ion</u>; and (ii) thermal decomposition of aluminosilicate: when the aluminosilicate is heated above ca 250 °C, the aluminosilicate commences degradation and gradually splits into silica-like and alumina-like species at higher temperatures, ca 400 °C [20]. The ratio of silicon to aluminum maintains values of 2.2–2.4 and 2.5–3.0 for COPS 1 and 2, respectively, at temperatures above that at which degradation can be seen from the carbon and oxygen data.

In COPS1 and COPS 2 the Si:Al ratios of 4.2 and 14.0 for COPS1 and COPS2 determined at room temperature drop gradually to 2.2–2.3 and 3.5–4.0 between 400 and 500 °C, respectively. The reason for the abnormal values of the Si:Al ratio is likely explained by:

(i) unavoidable surface contamination: surface contamination of adventitious carbon and oxygen is unavoidable in XPS experiments; it always causes an error in quantitation of the surface. In addition, the signal of Al2p may be further weakened as a result of its lower kinetic energy compared to Si2p, while escaping from the bulk toward the detector through the contamination layer. Sometimes, the experimental error caused by contamination in the surface may be so crucial that the Si:Al ratio determined at room temperature can be very high.

(ii) <u>dealumination</u> may occur in the organoclays: it was reported [21] that the ammonium ion-exchanged Y-zeolite evolves <u>ammonia</u> and water upon heating at 370–770 °C and higher temperatures, with a change from $NH_4Y \rightarrow HY \rightarrow$ dehydroxylated <u>zeolite</u>, the latter is not stable and the <u>aluminum ions</u> are easily dislodged from the framework. The ratio of silicon to aluminum would then go up, if dealuminiation occurs at the surface.

In our previous work [5], [20] concave curves of the Si:Al ratio vs temperature were observed. Analysis of these figures may depend on the following assumptions, i.e. for the moiety on the left side of the minima, the surface dynamics may play a dominant role in the 300–400 °C temperature region. More polar components, e.g. aluminum-containing species, migrate to the surface because the atmosphere around the surface at this stage contains more <u>polar molecules</u> like amines and water. The moiety on the right side of the minima behaves in the

opposite fashion, since the atmosphere around the surface is air. Less polar silica-like species migrate toward the surface more easily in this temperature regime.

Based upon an observation of the C1s, O1s, Si2p and Al2p spectra, the carbon loss and oxygen gain show pronounced changes at similar temperatures to that at which changes in both the silicon and aluminum spectra are seen. One may conclude that either the silica-like and alumina-like species migrate from the bulk toward the surface as the temperature increases, or, alternatively, the emergence of silica-like and alumina-like species at the surface may be simply a consequence of the loss of carbon. In other words, the clays migrate to the surface because the carbon is lost and only clay is available. It is also possible that both processes occur.

4. Conclusions

The thermal degradation of polymer–clay nanocomposites results in the migration, for whatever reason, of the clay to the surface, or, possibly as a consequence of carbon loss, thus forming an impermanent barrier which can prevent mass transport and insulate the underlying polymer from the thermal energy. The process by which the aluminosilicate migrates to the surface is not known but it leads to a change in the intensities of both aluminum and silicon on the surface and they are not effected equally. Apparently the process involves some type of rearrangement of the aluminosilicate, perhaps to increase compatibility between the polymer and the clay.

References

[1] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, O. Kamigaito. *J. Mater. Res*., 8 (1993), pp. 1185-1189

[2] J.W. Gilman, T. Kashiwagi. T.J. Pinnavaia, G.W. Beall (Eds.), *Polymer-clay nanocomposites*, Wiley, New York (2000), pp. 193-205

[3] J. Zhu, F.M. Uhl, A.B. Morgan, C.A. Wilkie. *Chem. Mater*., 12 (2001), pp. 4649-4654

[4] J. Wang, J. Du, J. Zhu, C.A. Wilkie. *Polym. Degrad. Stab*, 77 (2002), pp. 249-252

[5] J. Du, J. Zhu, C.A. Wilkie, J. Wang. *Polym. Degrad. Stab*, 77 (2002), pp. 377-381

[6] J. Du, D. Wang, C.A. Wilkie, J. Wang. *Polym. Degrad. Stab*, 79 (2003), pp. 319-324

[7] S. Su, C.A. Wilkie. *J. Polym. Sci: Part A: Polym. Chem*., 41 (2003), pp. 3837-3843

[8] Su S, Jiang D, Wilkei CA [submitted for publication].

[9] Su S, Jiang D, Wilkie CA [submitted for publication].

[10] J. Hao, S. Wu, C.A. Wilkie, J. Wang. *Polym. Degrad. Stab*, 66 (1999), pp. 81-89

[11] J. Hao, C.A. Wilkie, J. Wang. *Polym. Degrad. Stab*, 71 (2001), pp. 305-315

[12] Bourbigot S, Gilman JW, Vanderhart DL, Awad WH, Davis RD, Morgan AB, Wilkie CA. *J. Polym. Sci: Polym. Phys*. [in press].

[13] O. Chiantiore, G. Camino, L. Costa, N. Grassie. *Polym. Degrad. Stab*, 3 (1981), p. 209

[14] L. Costa, G. Camino, A. Guyot, M. Bert, A. Chiotis. *Polym. Degrad. Stab*, 4 (1982), p. 245

[15] A. Guyot. *Polym. Degrad. Stab*, 15 (1986), p. 219

[16] I.C. McNeill, M. Zulfiqar, T. Kousar. *Polym. Degrad. Stab*, 28 (1990), p. 131

[17] G. Audiso, F. Bertini. *Anal. Appl. Pyrolysis*, 24 (1992), p. 61

[18] M. Suzuki, C.A. Wilkie. *Polym. Degrad. Stab*, 47 (1995), p. 217

[19] Su S, Wilkie CA [submitted for publication].

[20] Wang J, Wei P, Hao J. In *Fire and polymers ACS Symposium Series* 797. ACS; 2001. p. 150–160.

[21] K. Tanabe, M. Misono, Y. Ono, H. Hattori ***New solid acids and bases.*** Elsevier (1989)