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Jianwei Hao

*Beijing Institute of Technology*

Menachem Lewin

*Polytechnic University - Brooklyn*

Charles A. Wilkie

*Marquette University, charles.wilkie@marquette.edu*

Jiangqi Wang

*Beijing Institute of Technology*

Marquette University

e-Publications@Marquette

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# Additional Evidence for The Migration of Clay Upon Heating of Clay–Polypropylene Nanocomposites from X-Ray Photoelectron Spectroscopy (XPS)

Jianwei Hao

Beijing Institute of Technology, School of Materials Science and Engineering, National Lab of Flame Retardant Materials, Beijing, China

Menachem Lewin

Polytechnic University, Brooklyn, NY

Charles A. Wilkie

Department of Chemistry, Marquette University, Milwaukee, WI

Jianqi Wang

Beijing Institute of Technology, School of Materials Science and Engineering, National Lab of Flame Retardant Materials, Beijing, China

## Abstract

The explanation for reduction in the peak heat release rate of polymer–clay nanocomposites which is normally accepted is that clay accumulates at the surface, forming a thermal shield which is also a barrier to mass transport. The process by which this clay arrives at the surface has never been described in print but the common assumption is that pyrolysis is required for clay accumulation to occur. In this work, X-ray photoelectron spectroscopy, a tool much more sensitive in surface analysis than conventional techniques, is used to probe the surface of polypropylene–clay nanocomposites that have been annealed at relatively low temperatures, well below that required for pyrolysis. The composition of the surface changes with time and temperature of annealing, which provide a strong indication that the clay at the surface undergoes chemical change at fairly low temperatures.

## Keywords

Migration of clay; Clay–PP nanocomposites; X-ray photoelectron spectroscopy (XPS); Silicon: aluminum ratio

## 1. Introduction

It has been postulated that when the thermal degradation of a polymer–clay nanocomposite occurs, a clay-containing barrier is formed gradually from the residue of the clay particles.<sup>1,2,3</sup> It was, however, pointed out by Lewin<sup>4</sup> that this hypothesis would require the existence of the nanocomposite structure up to the combustion temperature, so that its gradual decomposition and the release of the clay from the structure would occur upon gasification. This is unlikely, since the surfactant in the organoclay begins its decomposition already at 200 °C, so that the nanocomposite structure collapses well before pyrolysis occurs. It was, therefore, proposed that the clay migrates to the surface, accumulates there, and forms the barrier before pyrolysis. When gasification commences, the clay-containing barrier is already in place, and brings about the decrease in the rate of heat release. Evidence for the migration and accumulation of the clay on the surface at temperatures as low as 200 °C has recently appeared from FTIR-ATR measurements of the concentration of silicates on the surface of heated and annealed samples.<sup>5</sup> Previous work has shown that the greatest accumulation of oxygen for non-charring polymers occurs accompanied with the greatest loss of carbon.<sup>3</sup> The work reported herein has been undertaken to confirm the infrared evidence that this clay migration occurs using X-ray photoelectron spectroscopy, specifically by looking at the aluminium and silicon on the surface of the nanocomposite.

## 2. Experimental

### 2.1. Materials

Nanoblend™ 1001, a masterbatch which contains 60% polypropylene and its compatibiliser and 40% organically modified clay, was obtained from PolyOne Corporation. Polypropylene was supplied by Equistar Chemicals, Houston, Texas, as Petrothene PP 31KK01, with a melt flow index of 5 g/10 min. These ingredients were combined to give a mineral content of 5% in a Brabender mixer at a speed of 40 rpm at 190 °C for 5 min. The nanocomposites were then milled in a ScienceWare micro-mill with a water-cooled milling compartment. The milling time varied but never exceeded 10 min. After preparation, the material was heated for various time under either air or nitrogen; the samples that were evaluated are shown in Table 1.

Table 1. Annealing conditions for the samples evaluated by XPS

Identification	Annealing conditions
S1	Untreated
S2	Heated at 200 °C for 2 h in air
S3	Heated at 300 °C for 2 h in air
S4	Heated at 250 °C for 0.25 h in nitrogen
S5	Heated at 250 °C for 0.5 h in nitrogen
S6	Heated at 250 °C for 1 h in nitrogen
S7	Heated at 250 °C for 1.5 h in nitrogen
S8	Heated at 250 °C for 2 h in nitrogen
S9	Heated at 250 °C for 3 h in nitrogen
S10	Heated at 250 °C for 5 h in nitrogen
S11	Original masterbatch, 40% organically modified clay

All samples contain 5% inorganic clay except S11, the original masterbatch, which is 40% organically modified clay.

## 2.2. XPS experiments

The Si2p and Al2p spectra of the various annealed nanocomposites were recorded on a PHI 5300 ESCA System (Perkin–Elmer) at 250 W (12.5 kV and 20 mA) under a vacuum better than  $10^{-6}$  Pa ( $10^{-8}$  Torr). The binding energies that were obtained are referenced to that from adventitious carbon, 285.0 eV and the pass energy was set at 35.7 eV. In order to eliminate contamination, all samples were heated at 90 °C for 20 min prior to testing. It should be noted that it was not one single sample that was annealed at each condition, rather each condition was a separate sample; there will certainly be inhomogeneity in these samples.

## 3. Results

X-ray photoelectron spectra have been collected for silicon (Si2p) and aluminium (Al2p) and the results are summarised in Table 2.

Table 2. XPS average binding energies (BE) and signal intensity (cps eV) for silicon and aluminium for the various samples

Sample	Si2p		Al2p		Si:Al
	BE (eV)	cps eV	BE (eV)	cps eV	
S1: control	102.6	1290	74.7	340	3.4
S2: 200 °C, 2 h, air	102.6	1212	75.1	220	3.8
S3: 300 °C, 2 h air	102.5	240	74.1	38	4.3
S4: 250 °C, 0.25 h, N <sub>2</sub>	102.8	3490	75.0	670	4.6
S5: 250 °C, 0.5 h, N <sub>2</sub>	102.8	3910	74.8	710	4.9
S6: 250 °C, 1 h, N <sub>2</sub>	102.5	660	74.5	92	6.4
S7: 250 °C, 1.5 h, N <sub>2</sub>	102.7	364	75.1	36	6.9
S8: 250 °C, 2 h, N <sub>2</sub>	102.8	1360	75.0	140	8.6
S9: 250 °C, 3 h, N <sub>2</sub>	102.7	530	75.3	38	9.6
S10: 250 °C, 5 h, N <sub>2</sub>	102.7	2140	n.d.	n.d.	–
S11: masterbatch	102.7	3350	74.7	847	3.5

n.d.: Not detectable.

There is some inherent error in the determination of the absolute number of counts for an individual element, especially since each sample is different, so it is preferable to use a ratio. These samples are the same as those used in the previous study<sup>9</sup> in which an infrared method was used to study this system. In that study, the absorbance due to the Si–O vibration showed a maximum at 200 °C and decreased at higher temperatures and with longer times at these higher temperatures. The decrease in intensity was attributed to the thermal degradation of the surfactant. Thus, due to the inhomogeneity of the samples and the degradation of the surfactant with time, one cannot actually follow accumulation of the clay at the surface by annealing. For this reason, the ratio of silicon to aluminium is used to examine changes in amount and type and the data are plotted in Fig. 1, which shows the sample number as the abscissa (refer to Table 1 for each sample's characteristics) and the ratio as the ordinate. Considering first of all the samples that were annealed in nitrogen, it is clear that there is a smooth increase in the Si:Al ratio as the time of annealing increases, this is shown in Fig. 2. A similar result may occur upon annealing in air but the data are very limited and one cannot make any confident statement on the behaviour in air.

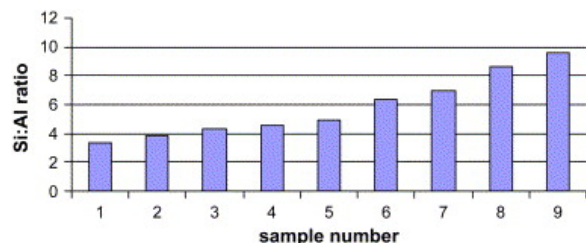


Fig. 1. The Si:Al ratio for each sample analyzed by XPS. Sample 10 is not shown because the aluminium signal is too small to be detected in that sample.

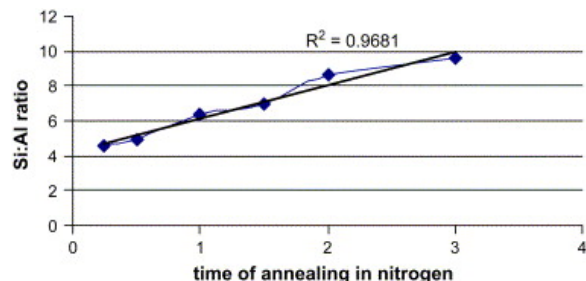


Fig. 2. The Si:Al ratio as a function of the time of annealing in nitrogen.

Additional data are available from the position of the peak for silicon. Specifically, the binding energy in a silicate is 102.6 eV while that in SiO<sub>2</sub> is 103.4 eV.<sup>6</sup> The two peaks can be reasonably resolved using curve-fitting techniques with background subtraction performed using the Shirley method.<sup>7</sup> The values that have been obtained are shown in Table 3. A plot of the ratio of silicate to silicon dioxide versus the time of annealing in nitrogen is given in Fig. 3 and it is quite clear that there is a clear correspondence between these; apparently, the longer the sample is annealed, the more conversion occurs from silicate to SiO<sub>2</sub> in the surface layer.

Table 3. XPS data for silicon (Si2p) on the various samples

Samples	Si2p				Ratio
	Peak 1		Peak 2		
	BE <sub>1</sub> (eV)	A <sub>1</sub> /cps eV	BE <sub>2</sub> (eV)	A <sub>2</sub> /cps eV	A <sub>1</sub> /A <sub>2</sub>
S1: control	102.1	1030	103.6	200	5.2

S2: 200 °C, 2 h, air	102.2	990	103.3	220	4.5
S3: 300 °C, 2 h, air	102.1	210	103.6	50	4.2
S4: 250 °C, 0.25 h, N <sub>2</sub>	102.2	2350	102.9	1110	2.1
S5: 250 °C, 0.5 h, N <sub>2</sub>	102.1	2550	102.9	1370	1.9
S6: 250 °C, 1 h, N <sub>2</sub>	101.9	420	102.7	240	1.8
S7: 250 °C, 1.5 h, N <sub>2</sub>	101.9	220	102.7	140	1.6
S8: 250 °C, 2 h, N <sub>2</sub>	101.9	780	102.6	550	1.4
S9: 250 °C, 3 h, N <sub>2</sub>	101.9	270	102.8	220	1.2
S10: 250 °C, 5 h, N <sub>2</sub>	101.9	1020	102.8	1080	0.9
S11: masterbatch	102.1	2720	103.0	670	4.1

$A_1$  and  $A_2$  are the intensities of each peak.

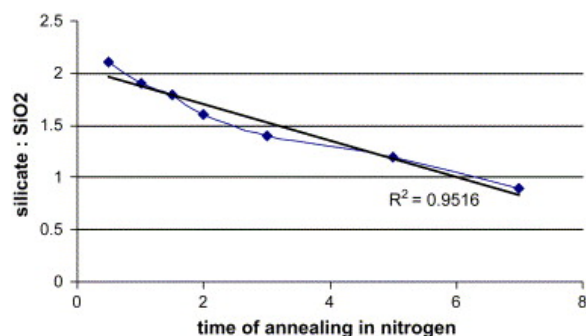


Fig. 3. Relationship between the time of annealing and the ratio of silicate to SiO<sub>2</sub>.

## 4. Discussion

There are two rather surprising observations that can be made from the XPS data for silicon and aluminium at the surface: (1) the ratio of silicon to aluminium increases as the time of annealing increases and (2) as the time of annealing increases, silicates are converted into silicon dioxide. In both cases, there is a clear dependence of the ratios of silicon to aluminium and silicates to silicon dioxide on the time of annealing in nitrogen. These observations may be explained as follows.

First of all, it must be remembered that XPS is a surface technique so that only the surface layer of the material is probed; it is typically considered that the technique is able to probe up to 100 Å deep into the sample. It was observed that the silicon:aluminium ratio was the same for both the masterbatch, containing 40% organically modified clay, and a sample in which this masterbatch had been blended with additional polypropylene to reduce the content to 5% inorganic clay. As the time of annealing increases the ratio also increases, which can mean either that surface silicon increases or surface aluminium decreases. The following hypothesis is offered. The edges of the clay contain hydroxyl groups both in the tetrahedral silicate unit and in the octahedral aluminium region and these hydroxyl groups are likely to shield the emission of photoelectrons from the underlying silicon and aluminium atoms. If these are lost, silicon and aluminium are then exposed and can be seen at the surface. The observation that silicate is converted to SiO<sub>2</sub> is in complete accord with the loss of hydroxyls from the silicate layer. This will convert two Si–OH units into one Si–O–Si unit, which is much more SiO<sub>2</sub>-like and should have the binding energy of this moiety. Apparently, this reaction does not occur as readily in the octahedral aluminium layer so the aluminium remains protected by the hydroxyls and its surface concentration does not increase. Lagaly<sup>8</sup> has depicted the edge chemistry of a clay platelet and envision reactions

between the edge hydroxyls and an ionic polymer which may serve as a prototype for the process described herein.

There are a few additional items that must be considered to fully understand this explanation. First of all, it is suggested that the edges of the clay are what is seen in the XPS experiment. In XPS, data acquisition arises from the photoelectrons from the area irradiated by the X-ray photons. The signal intensity is averaged over a large area (ca. 5 mm × 5 mm in this case) of the sample at a sampling depth of ca. 100 Å. Since exfoliated polypropylene nanocomposites have yet to be reported, intercalation is expected. X-ray diffraction data have been reported in a previous paper<sup>9</sup> and this shows the formation of intercalated systems. It is thought that the greater part of the XPS signal is from an intercalated system, even though the clay platelets are randomly distributed throughout the polymer matrix. If one were examining the surface of the clay, rather than the edge, one would expect to see a large concentration of silicon and a much smaller, if visible, concentration of aluminium, since the silicate layers are attached to the aluminate and cover it completely. Since aluminium is seen in the control and only disappears upon relatively long annealing time, it is much more reasonable to assume that the edges are viewed. An alternative explanation for these observations invokes some very complicated rearrangement of both the tetrahedral silicate layers and the octahedral aluminate layer, a rearrangement for which no precedent has been shown. One cannot completely eliminate the notion of this rearrangement but the simpler explanation that has been suggested above fits the observed data and provides a tentative explanation. It is obvious that further work must be carried out to confirm this proposed explanation for the increase in the silicon:aluminium ratio and the conversion of silicate to SiO<sub>2</sub> and this work is planned.

## 5. Conclusions

This work appears to verify the assertion that the migration of the clay to the surface does not require polymer degradation but the process can occur at relatively low temperatures. Equally as important, this work shows how and why the silicon:aluminium ratio changes as the polymer–clay nanocomposite is annealed.

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