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An XPS Study of the Thermal Degradation and Flame Retardant Mechanism of Polystyrene-Clay Nanocomposites

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Abstract

X-ray photoelectron spectroscopy, XPS, has been used to examine several polystyrene-clay nanocomposites. The accumulation of oxygen, from the almuniosilicate, on the surface of the polymer was observed, along with the loss of carbon. This confirms that the barrier properties of the clay provide a mechanism by which nanocomposite formation can enhance the fire retardancy of the polymers. No difference is detected depending upon the extent of exfoliation or intercalation of the nanocomposite.

Keywords

1. Introduction

Organic-inorganic nanocomposites, comprised of an organically-modified clay dispersed in a polymer have attracted considerable attention. The mechanical properties of these materials are typically enhanced [1]. For instance, a polyamide–6 clay nanocomposite, with 5% clay, increases 40% in tensile strength, 60% in flexural strength, 126% in flexural modulus, 68% in tensile modulus, and the heat distortion temperature increases from 65 to 152 °C, whilst the impact strength is lowered by only 10% [2].

The typical nanocomposite is prepared either by a blending process or by bulk polymerization. In either case the normal sodium cations, found in montmorillonite, a classic aluminosilicate material, must be replaced by cations which are organophilic enough to permit the introduction of an organic polymer. This usually requires the use of an ammonium or phosphonium salt that contains at least one alkyl chain which is 14 or 16 carbons in length; the other substituents on the 'onium' salt may be freely chosen in order to enhance some particular property of the nanocomposite [3].

Nanocomposites may exist in either an intercalated form, in which registry is maintained between the aluminosilicate layers, or in an exfoliated form, in which such registry is lost. Previous investigations have shown that the largest increases in mechanical properties are obtained in exfoliated, also known as delaminated materials; there is some evidence that the intercalated materials show the best performance in fire studies [4].

The mechanism which has been proposed to explain the fire retardant action is the concentration of the aluminosilicate on the surface of the degrading polymer where it may function both as a barrier to mass transport from the bulk of the underlying polymer and a barrier to separate the flame from the underlying polymer [5]. A recent suggestion has been made that the presence of iron, substituted for the aluminum or silicon atoms in the clay, can act as a radical trap and thus slow the rate of combustion [6].

In this study, the results of an XPS investigation on a series of polystyrene-clay nanocomposites is reported. The 'onium' ions have been carefully chosen so that both intercalated and exfoliated materials can be compared.

## 2. Experimental

2.1. Materials

Most of the chemicals used in this study were acquired from the Aldrich Chemical Company, including styrene, triphenylphosphine, inhibitor removal columns, etc. TCI America supplied the *n*-hexadecyl chloride. Clays were kindly provided by Southern Clay Products, Inc. Two materials were used in this study, a sodium-containing clay and one which had received an organic modification in which the sodium was replaced by an ammonium cation on which the four substituents were one methyl group, M, one tallow group, T, (containing 70% C_{18}, 25% C_{16}, 4% C_{14} and 1% C_{12}) and two hydroxyethyl groups, Et. Thus this clay is identified as MT2Et.

2.2. Preparation of the ammonium salts

The preparation of three of the clays used in this study, *N,N*-dimethyl-*n*-hexadecyl-(4-hydroxymethylbenzyl) ammonium chloride, OH16, *N,N*-dimethyl-*n*-hexadecyl-(4-vinylbenzyl) ammonium chloride, VB16, and *n*-hexadecyl triphenylphosphonium chloride, P16, has been described previously [7].

Tris-[2-(dimethyloctadecylammonium chloride) isopropyl]phosphate, NP, was prepared by the reaction of dimethyloctadecylamine, DMOA, and tri(2-chloroisopropyl) phosphate, TCIPP, in a 3:1 ratio. The reaction is shown in Scheme 1. 6.6 g (22.1 mmol) of DMOA (10% excess) and 2.2 g (6.7 mmol) of TCIPP, were dissolved in

100 ml of dichloromethane in a 100 ml round bottom flask equipped with a stirrer and a nitrogen inlet and outlet and refluxed at 70 °C for 24 h. After evaporation of the solvent and recrystallization, 5.3 g of white powder with a melting point of 77–81 °C resulted. Elemental analysis(%): N, 3.48 (3.44 theo); C, 65.69 (67.9 theo); H, 13.15 (12.16 theo).
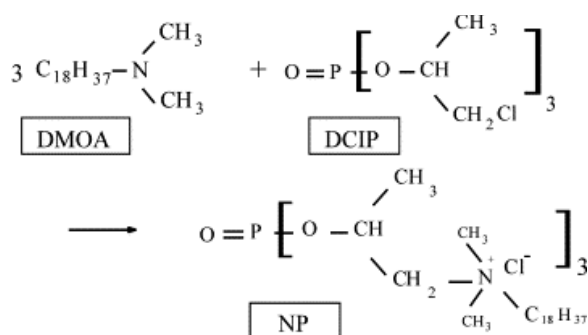
Scheme 1.

2.3. Preparation of the nanocomposites

The preparation of the VB16, OH16 and P16 nanocomposites of styrene by the bulk polymerization technique have been previously described [8]. The NP-polystyrene nanocomposite were prepared by an identical procedure. These nanocomposites all contained 3% clay.

Finally melt blending was used to prepare mixtures of polystyrene and NP, the MT2Et clay and the sodium clay. These samples were processed in a two-roll mill at 160 °C for 20 min, followed by heating under vacuum at 150 °C for 24 h. Each of these systems contained 5 wt.% clay. There is neither XRD or TEM available on these samples so they are here described as mixtures, rather than nanocomposites, because their exact structure is not known. A description of the sample formulations and identification is shown in Table 1.

Table 1. List of sample formulations and preparation methods

Sample	Description	Comment
PS	Polystyrene	Aldrich Chemical Company, USA
PS-VB 16	PS:VB16=100:3	In-situ polymerization
PS-OH 16	PS:OH16=100:3	In-situ polymerization
PS-P16	PS:P16=100:3	In-situ polymerization
PS-NP	PS: OLS-NP=100:3	In-situ polymerization
MT2Et	PS:OLS-MT2Et=100:5	Melt blending
Na	PS:OLS Na=100:5	Melt blending (virgin clay)

Details of the pseudo in situ XPS technique have been previously described. All samples were prepared by casting a thin film onto aluminum foil [9].

3. Results and discussion

Characterization of the VB16, OH16, P16, and MTEt$_2$ nanocomposites of polystyrene has previously been published [7], [8]. The polystyrene-VB16 nanocomposite is completely exfoliated while the polystyrene-OH16 and polystyrene-P16 materials are mixtures of intercalation and exfoliation and the MT2Et material is completely intercalated. We have hypothesized that the presence of a double bond on the ammonium cation of the clay permits some amount of the monomer to attach to the clay and that this encourages exfoliation. More recently, nanocomposites of poly(methyl methacrylate) with VB16 and another clay which also contains a double bond at

the end of the cation, dimethyl-n-hexadecyl-allyl, have been reported and these show a mixture of intercalation and exfoliation [10]. In the case of the phosphonium clay, it is believed that the much larger size of the cation encourages exfoliation, since the aluminosilicate layers are already widely spaced. XRD characterization of the polystyrene-NP material synthesized via in-situ polymerization shows that the *d*-spacing is 35.6 Å; this is believed to be an intercalated nanocomposite. In the case of the material which was prepared by bulk polymerization, it is difficult to imagine how this could not be intercalated, since every previous preparation that has been carried out by bulk polymerization in our laboratories has resulted in an intercalated system.

The advantage that XPS offers to the investigation is that one can probe the surface of the system and detect subtle changes in composition. In this study, the carbon 1s and the oxygen 1s spectrum of the nanocomposites have been examined. If the aluminosilicate is well-dispersed within the polymer, and it concentrates on the surface upon heating, one would expect to see the concentration of oxygen increase and that of carbon decrease. This result can be rationalized as follows: (1) as the polymer is lost by thermal degradation and the aluminosilicate becomes the dominant material at the surface and (2) at a temperature of 200–250 °C the montmorillonite begins to decompose into its components, SiO_2 and Al_2O_3; SiO_2, with much lower surface energy than Al_2O_3[11], dominates at the surface. It is assumed that the Si:Al ratio will be comparable to that found in the PER/APP/MMT system, as measured by XPS at high temperatures [12]. Fig. 1 shows the relative intensity in the O1s spectrum for the mixture of polystyrene and the MT2Et clay that was prepared by melt blending at 5% clay, MT2Et, a mixture of polystyrene and the sodium clay, Na, also at 5% clay, and virgin polystyrene, PS. The relative intensity of oxygen for virgin PS begins to increase above 450 °C, probably due to reaction with adventitious oxygen. The sodium clay-containing system, on the other hand, begins to accumulate oxygen, at a low level, about 100 °C and a significant increase as seen above 400 °C. The small amount that is initially observed is probably due to the clay or its components. The increase at higher temperatures is again likely due to adventitious oxygen. The MT2Et material shows a large increase in the relative surface concentration of oxygen somewhat below 400 °C, a temperature at which thermal degradation and volatilization of polystyrene is occurring.
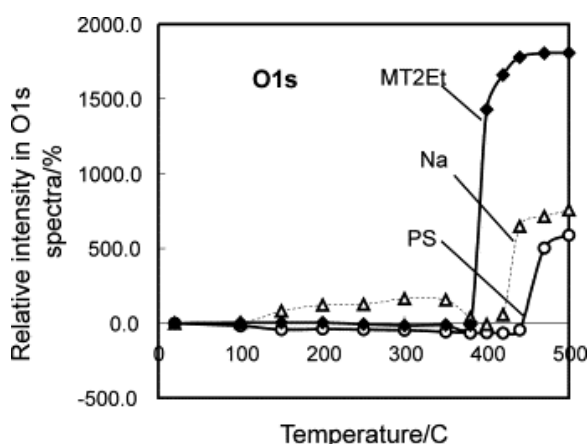

Fig. 1. Relative intensity in the O1s spectrum for PS, the sodium clay blend, and the MT2Et nanocomposite.

Fig. 2 shows the relative intensity of oxygen for the other nanocomposites examined in this study. Aside from a small hump in the curve for the P16 nanocomposite, accumulation of oxygen begins at the decomposition temperature of polystyrene, indicating that the polymer must degrade in order to permit the two components to migrate to the surface. There is some difference in the relative intensity of oxygen for each of the nanocomposites but this is not considered significant, i.e. the state of the nanocomposite, intercalated, exfoliated, or a mixture of these, does not appear to affect the barrier properties of the aluminosilicate as far as the flame retardant mechanism is concerned.
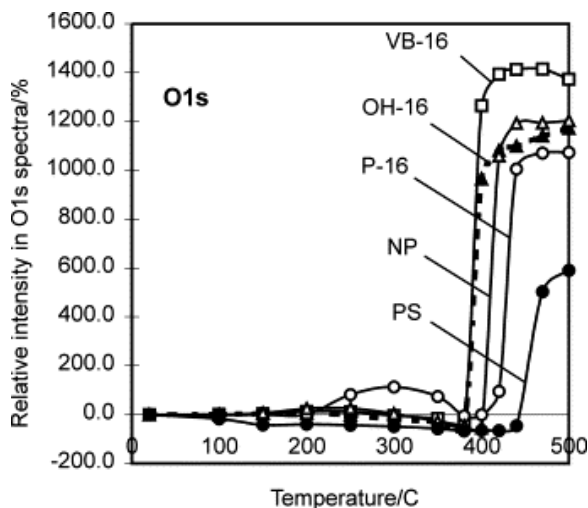
Fig. 2. Relative intensity in the O1s spectrum for PS and the nanocomposites.

The hump in the curve for P16 is similar to that seen in the blend of the sodium salt, but it begins at somewhat higher temperature. This may be an indication that some amount of clay is not nano-dispersed; the XRD of the P16 nanocomposite does show a small peak at the same d-spacing as the virgin clay.

Similar results are available from the carbon data. Fig. 3 shows the relative intensity of carbon for polystyrene, PS, the mixture of polystyrene with the sodium clay, Na, and the nanocomposite prepared from MT2Et. For virgin PS some carbon is lost initially; this is commonly seen for untreated polymers in XPS and is attributed to the loss of loosely bound adventitious carbon on the surface. In the case of both the nanocomposite and the sodium clay, there is essentially no change until the decomposition temperature of the polymer is reached. There is greater loss of carbon from the nanocomposite than the blend with the sodium salt, since loss of carbon must correlate with the gain of oxygen.
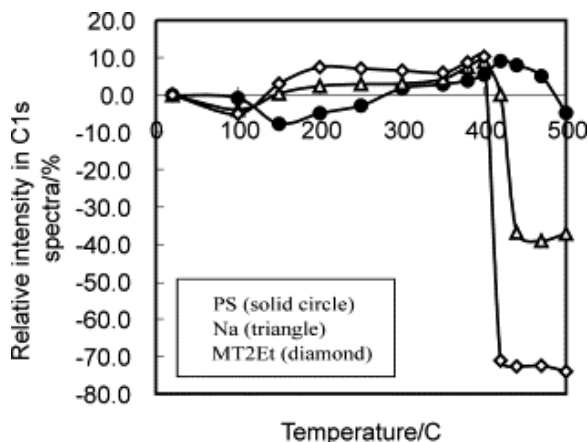

Fig. 3. Relative intensity in C1s spectra as a function of temperature for PS, the Na clay blend, and the MT2Et nanocomposite.

Similar results are shown for VB16, OH16 and P16 in Fig. 4. Again the observation is that the loss of carbon correlates rather well with the gain of oxygen at the surface. An additional parameter is available from the carbon 1s spectrum, the plasmon loss. This is a measure of the degree of organization of carbon during the combustion process. The data are shown in Fig. 5 for the VB16, OH16 and P16 nanocomposites, and they are remarkable similar, even though both VB16 and OH16 grow faster than P16 along with temperature increase. The latter may indicate the rate of change in nature of charring with temperature variation. The plasmon loss does increase slightly as a function of temperature but it never approaches the value for graphite, and, in fact, it

shows a decrease at the highest temperatures. This indicates that a graphite-like char is not accumulating on the surface of the polymer.
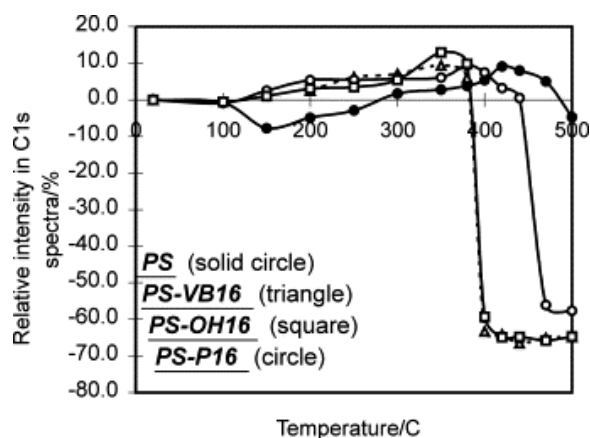

Fig. 4. Relative intensity in C1s spectra as a function of temperature for PS and the nanocomposites.
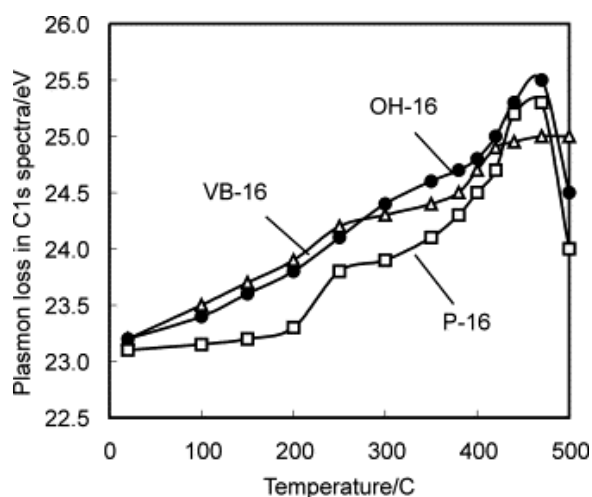

Fig. 5. Plasmon loss in C1s spectra as a function of temperature for the VB-16, OH-16 and P-16 nanocomposites.

4. Conclusions

The XPS data confirm that the aluminosilicate does accumulate on the surface of the polymer and, presumably, this can act as a barrier to both mass transport and to protect the underlying polymer from the flame. There is no difference amongst exfoliated, intercalated, or mixed intercalated-exfoliated nanocomposites as far as the flame retardant mechanism is concerned, but there is a difference between the nanocomposite and blends with the sodium clay.

Acknowledgements

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