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Synergy Between Nanocomposite Formation and Low Levels of Bromine on Fire Retardancy in Polystyrenes

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Abstract

An organically-modified clay has been prepared using ammonium salts which contain an oligomeric material consisting of vinylbenzyl chloride, styrene and dibromostyrene. The presence of dibromostyrene enhances the flame retardancy of polystyrene nanocomposites compared to both the virgin polymer and polystyrene nanocomposites prepared from non-halogen-containing organically-modified clays. The nanocomposites were prepared both by bulk polymerization and melt blending and they were evaluated by X-ray diffraction, transmission electron microscopy, thermogravimetric analysis and cone calorimetry measurements. Bulk polymerization produced nanocomposites with reduced peak heat release rate, reduced total heat release and

improved thermal stability. It is noteworthy that all these improvements were obtained with clay loading as low as 3% and bromine content less than 4%.

Keywords

Polystyrene, Nanocomposites, Fire retardancy, Thermal stability

1. Introduction

A significant amount of work has been done on polymer–clay nanocomposites, due to improvements in both physical and mechanical properties offered by nanocomposite formation compared to the virgin polymer [1, 2, 3, 4, 5]. These improvements are obtained at clay loadings as low as 3%. From the point of view of fire retardancy, the most significant advantage offered by nanocomposites formation is the reduction in the peak heat release rate (PHRR) from cone calorimetric measurements. In addition to the large reductions in PHRR, nanocomposite formation is typically also associated with small reductions in time to ignition (t_{ign}), which may not be significant, and no change in the total heat released (THR). This means nanocomposite formation results in the formation of compounds that are easy to ignite and also, like the virgin polymer, everything eventually will burn. On the other hand, additives, mainly halogenated [6] but also non-halogenated, have been effective in lowering both the PHRR and THR; however, the time to ignition is not changed compared to the virgin polymer [7, 8, 9, 10]. The disadvantages of using additives are that very high quantities have to be used and also for halogenated compounds the degradation products may have environmental concerns associated with them.

Nanocomposites can be exfoliated or intercalated, depending on how the polymer inserts between the clay layers; and work from these laboratories has shown that there is no difference between intercalation and exfoliation in fire retardancy for polystyrene nanocomposites, as long as the clay is nano-dispersed [11]. Much work has been done with montmorillonite but other clays, such as hectorite [12] and magadiite [13], have also been studied. These pristine clays are hydrophilic in nature and thus have to be modified by reaction with organic salts to make the gallery space compatible with the polymer. Ammonium salts are generally used, but other salts, including phosphonium [8, 14] and stibonium [15], have also been prepared.

In this study an organically-modified clay which contains an oligomeric unit containing bromine has been prepared and nanocomposites of styrene were made. The aim is to introduce a low amount of bromine chemically attached to the clay and evaluate its effectiveness as a fire retardant.

2. Experimental

The majority of the chemicals used in this study including vinylbenzyl chloride (VBC), styrene (ST), benzoyl peroxide (BPO), *N,N*-dimethylhexadecylamine, trimethyl amine (40% in H₂O), triethyl amine and initiator removal agent were obtained from Aldrich Chemical Co. Pristine sodium montmorillonite was provided by Southern Clay Products, Inc. and dibromostyrene (DBS) was provided by Great Lakes Chemical Company.

2.1. Instrumentation

X-ray diffraction (XRD) measurements were performed using a Rigaku powder diffractometer with a Cu tube source ($\lambda = 1.54 \text{ \AA}$); the generator tension is 50 kV and the current is 20 mA. Scans were taken from $2\theta = 1.0\text{--}10$, step size = 0.1 and scan time per step of 10 s using the high-resolution mode. Bright field transmission electron microscopy (TEM) images of the composites were obtained at 60 kV with a Zeiss 10c electron microscope. The samples were ultramicrotomed with a diamond knife on a Rigchert-Jung Ultra-Cut E microtome at room temperature to give ~ 70 nm thick section. The sections were transferred from the knife-edge to 600 hexagonal mesh Cu grids. Thermogravimetric analysis, TGA, was performed on a SDT 2960 simultaneous TGA–DTA (TA Instruments) unit under a flowing nitrogen atmosphere at a scan rate of 20 °C per minute from 20 °C to 600 °C. All TGA experiments have been done in triplicate; the reproducibility of temperature is ± 3 °C while amount of nonvolatile residue is reproducible to ± 2 °C. Cone calorimeter measurements at 35 kW/m² were performed

using an Atlas Cone 2 according to ASTM E 1354-92; the spark was continuous until the sample ignited. All samples were run in triplicate and the average value is reported; results from cone calorimeter are generally considered to be reproducible to $\pm 10\%$ [16]. Midwest Microlab, LLC, performed bromine analysis.

2.2. Preparation of the ter-polymer

In a 250 ml beaker were placed the appropriate weight percentages of styrene, dibromostyrene and vinylbenzyl chloride to make a 100 g sample (Table 1). To the mixture was added 10% BPO and the mixture was stirred at room temperature for several hours, then the samples were placed in an oil bath at 40 °C overnight and the temperature was increased to 60 °C for 8 h and then placed in vacuum oven at 80 °C for 6 h. Table 1 shows the polymer compositions prepared. (In some cases, high molecular weight polymers were prepared using 1% BPO as initiator. Clays made from these polymers have *h* accompanying the clay name for example; *hter-3-clay* means clay is made from higher MW polymer.)

Table 1. Clay identification

| Clay name | %Dibromostyrene, DBS | %Styrene | %Vinylbenzyl chloride, VBC | Modifier |
|---------------|----------------------|----------|----------------------------|---|
| Ter-1-clay | 10 | 85 | 5 | Oligomeric trimethyl ammonium salt |
| Ter-2-clay | 20 | 75 | 5 | Oligomeric trimethyl ammonium salt |
| Ter-3-clay | 50 | 45 | 5 | Oligomeric trimethyl ammonium salt |
| Ter-4-clay | 70 | 25 | 5 | Oligomeric trimethyl ammonium salt |
| Di-clay | 95 | – | 5 | Oligomeric trimethyl ammonium salt |
| Et-ter-3-clay | 50 | 45 | 5 | Oligomeric triethyl ammonium salt |
| LC-ter-3-clay | 50 | 45 | 5 | Oligomeric dimethyl hexadecyl ammonium salt |
| hter-3-clay | 50 | 45 | 5 | Oligomeric trimethyl ammonium salt |

2.3. Molecular weight measurements

The approximate molecular weights of the ter-polymers were determined by viscosity measurements and the molecular weight was found to be in the range of $26,000 \pm 4000$ and $35,000 \pm 3000$ for the low and high MWs, respectively. The Mark-Houwink constants of styrene were used, so these are quite approximate values.

2.4. Preparation of the ammonium salt

In a 500 ml flask, 30 g (9 mmol) of ter-polymer was dissolved in 200 ml THF, then a 1.80 g (11.6 mmol) portion of *N,N*-dimethylhexadecyl amine was added. The mixture was stirred at room temperature for several hours; a white precipitate formed and was filtered. The same procedure was used to prepare the trimethyl and triethyl ammonium salts.

2.5. Preparation of the organically-modified clay

A 20.0 g portion of Na-MMT clay was dispersed in 1000 ml distilled water for at least 24 h or until a homogenous mixture was formed. A 6.50 g portion of the ammonium salt prepared as above was dissolved in the minimum amount of THF and the mixture was added dropwise to the Na-MMT suspension. The mixture was stirred at 45 °C overnight, then the slurry was filtered and the precipitate was repeatedly washed with distilled water and then air-dried. The organically-modified clay (21.2 g) were obtained. (The same procedure was used to prepare modified clay with both triethyl and *N,N*-dimethyl hexadecyl ammonium salts, but the cation exchange was carried out at room temperature.) Clay modified with the triethyl ammonium salt have *Et* while those modified with *N,N*-dimethylhexadecyl ammonium salt have *LC* before the name of the chain (Table 1).

2.6. Preparation of PS-ter/di-clay nanocomposites by bulk polymerization

In a 250 ml beaker were placed 3.6 g organically-modified clay, 1.2 g benzoyl peroxide (BPO) as radical initiator, and 116.4 g monomeric styrene. The mixture was stirred at room temperature until a homogenous suspension was formed, followed by placing in an oil bath at 40 °C overnight, then the temperature was increased to 70 °C

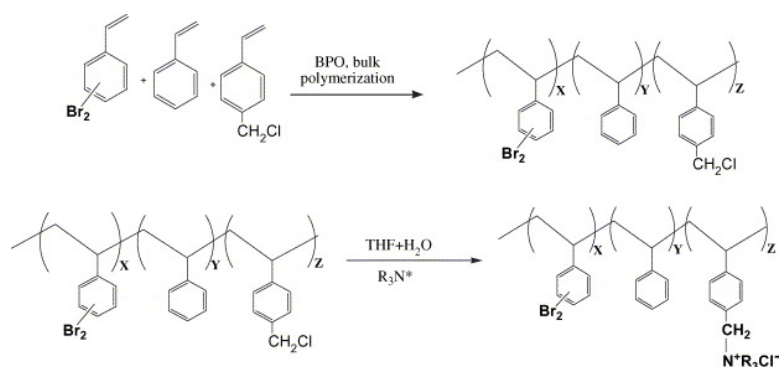
for 24 h. The unreacted monomer was then removed under vacuum for 6 h at 80 °C to obtain the nanocomposite.

2.7. Preparation of PS–ter/di-clay nanocomposites by melt blending

The nanocomposites were prepared by melt blending in a Brabender Plasticorder at high speed (60 rpm) at 190 °C for 20 min. The composition of each nanocomposite is calculated from the amount of clay and polymer charged to the Brabender.

3. Results and discussion

This work was inspired by previous work by Su et al. ^[17] in which oligomerically-substituted ammonium salts were prepared and used to make the organically-modified clays. In that work, intercalated PS nanocomposites were prepared, in which the nanocomposites had a d-spacing of about 8.1 nm from XRD measurements; this led to improved thermal stability and a reduced peak heat release rate. However, like other nanocomposites, the total heat released was not changed compared to the virgin polymer and the time to ignition was also lowered. Since it is well-known that bromine is a useful element in fire retardancy ^[18], it was decided to produce an oligomeric unit which also contained bromine. The route that was used for the preparation of this unit is shown below as Scheme 1.



Scheme 1. Preparation of the brominated ammonium salt.

The proportions of reactants were chosen so as to try to permit only one, or at most two, benzyl chloride units per chain.

If one assumes that all of the dibromostyrene is consumed in the reaction, one may calculate the amount of bromine in the ter–polymer, then using thermogravimetric analysis data, which are presented later in this paper, one can calculate the percentage of bromine in the clays. Since there is only a very small difference in mass of the various amines that are used compared to the mass of the oligomer, there is expected to be essentially no difference amongst the various surfactants. The expected bromine content for each of the clays is shown in Table 2. This calculation assumes that all of the monomers have completely reacted; in order to validate this assumption, elemental analysis was performed on three of the polystyrene nanocomposites, these results are reported in Table 3. There is no obvious explanation for the discrepancies between the theoretical and experimental values, in one case the experimental value is higher while in the others it is lower. The difference between the expected and experimental values is not so large and the expected values are used in discussion of the results, knowing that there is some error in the bromine content.

Table 2. Percentage of bromine expected in the various clays

| Clay | %Br |
|------------|-----|
| Ter-1-clay | 4 |
| Ter-2-clay | 12 |
| Ter-3-clay | 24 |

| | |
|------------|----|
| Ter-4-clay | 32 |
| Di-clay | 44 |

Table 3. Elemental analysis

| Nanocomposite composition | %Br theoretical | %Br experimental |
|---------------------------|-----------------|------------------|
| PS + 10% ter-1-clay | 0.36 | 0.52 |
| PS + 10% ter-3-clay | 1.63 | 1.36 |
| PS + 10% di-clay | 3.80 | 2.72 |

The main objective in this work is to evaluate the effectiveness of these bromine-containing clays in fire retardance of polymers. However, before one can evaluate fire retardancy, one must first show that nanocomposite formation has occurred and also identify the type of nanocomposite. This is accomplished using the combination of X-ray diffraction (XRD) and transmission electron microscopy (TEM).

3.1. X-ray diffraction

XRD offers the opportunity to determine the distance between the clay layers. In general, if a peak is observed one states that an intercalated nanocomposite has been obtained. On the other hand, if no peak is seen, either an exfoliated system, in which registry between the layers has been lost, or a disordered immiscible system has been produced. In this case, no peaks were observed but, due to the presence of bromine, a third possibility is presented, that bromine absorbs much of the X-ray radiation so that no peak can be seen. This seemed to be a real possibility in this case, especially since the results from cone calorimetry show a large reduction in PHRR which is usually associated with excellent nano-dispersion ^{[16], [19]}, and this required that transmission electron microscopy, TEM, be used to fully identify the sample.

3.2. Transmission electron microscopy

The TEM result is shown in [Fig. 1](#). From the low resolution image, one can see that the nano-dispersion is acceptable. The high-resolution image (right) shows that an intercalated nanocomposite was formed since the clay registry was maintained and the clay layers were separated.

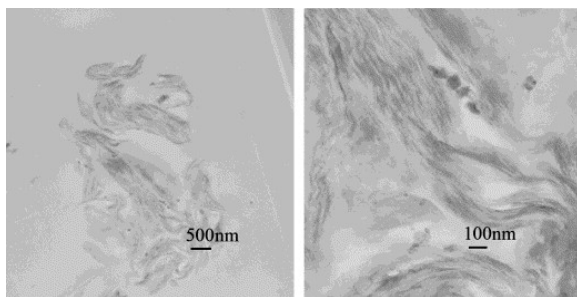


Fig. 1. TEM image for the polystyrene nanocomposite prepared using 10% ter-3-clay.

3.3. Thermogravimetric analysis (TGA) of nanocomposites

There are several variables in this study, including the role of the various amines that are used to form the ammonium salt, the bromine content and the mode used in the preparation. Of interest is the onset temperature of the degradation, the temperature at which 50% degradation occurs and the residue that remains at 600 °C, denoted as char. We will first of all consider only the clays and the effect of the various amines; the results are shown in [Fig. 2](#), [Fig. 3](#) for the oligomeric trimethylammonium-modified clay and the oligomeric triethylammonium-modified clay, respectively; the bromine content does not have an effect on the TGA results ([Table 4](#)). An average of 30% char was obtained, which indicates the approximate percentage of the inorganic clay present in the clay.

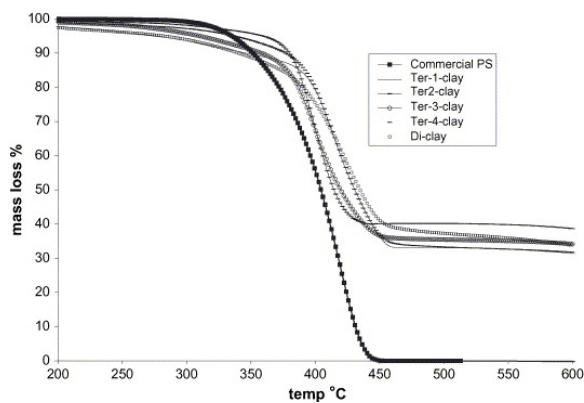


Fig. 2. TGA curves for different oligomeric trimethyl ammonium clays.

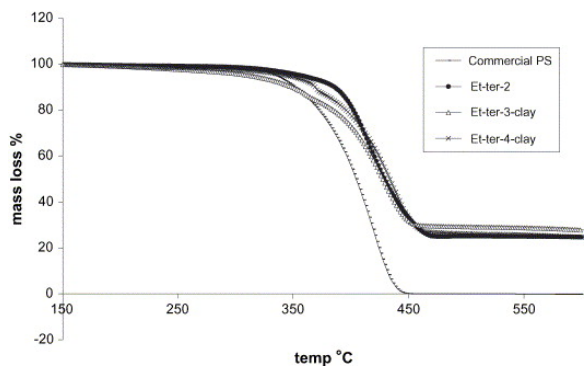


Fig. 3. TGA curves for different clays using the oligomeric triethyl ammonium clay.

Table 4. TGA data for the different clays

| Sample | T_{10} | T_{50} | %Char |
|---------------------|----------|----------|-------|
| PS | 361 | 413 | 0 |
| Di-clay | 339 | 434 | 34 |
| PS + 1% di-clay | 357 | 413 | 0 |
| PS + 3% di-clay | 373 | 422 | 1 |
| PS + 10% di-clay | 336 | 426 | 4 |
| Ter-1-clay | 353 | 428 | 33 |
| PS + 1% ter-1-clay | 386 | 424 | 0 |
| PS + 3% ter-1-clay | 383 | 430 | 0 |
| PS + 5% ter-1-clay | 393 | 434 | 1 |
| PS + 10% ter-1-clay | 397 | 431 | 1 |
| Ter-3-clay | 356 | 422 | 36 |
| PS + 1% ter-3-clay | 343 | 416 | 0 |
| PS + 3% ter-3-clay | 384 | 430 | 3 |
| PS + 10% ter-3-clay | 325 | 431 | 4 |
| Et ter-3-clay | 345 | 428 | 28 |
| LC ter-3-clay | 344 | 422 | 30 |

Nanocomposites have been prepared from all of these clays at varying levels of clay, and hence of bromine. The TGA curves are shown in Fig. 4 for the ter-1-clay (4%Br), Fig. 5 for the ter-3-clay (23%Br) and Fig. 6 compares the methyl and ethyl amines at two levels of bromine (ter-2-clay is 12%Br while ter-4-clay is 32%Br). The thermal stability of the nanocomposites increased as the amount of clay for all the organically-modified clays was increased, as shown by the improvement in the onset temperature of degradation, T_{10} , and 50% degradation temperature, T_{50} . Considering nanocomposites with 10% clay of all the materials from ter-1-clay (10%DBS) to the

di-clay (95%DBS), even though the bromine content varies from a low of 0.4% to a high of 4%, there is essentially no difference in the thermal stability in inert atmosphere.

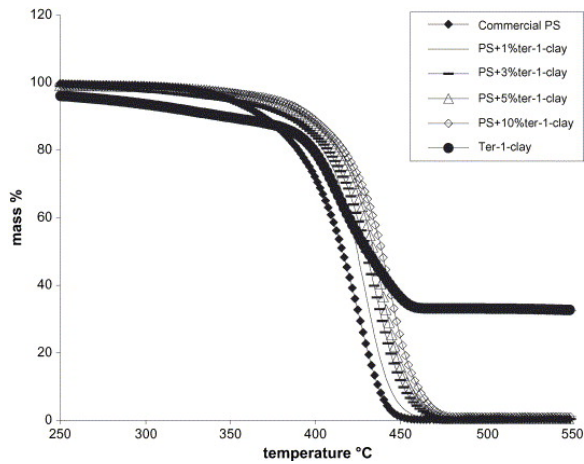


Fig. 4. TGA curves for polystyrene nanocomposites using the ter-1-clay (4%Br).

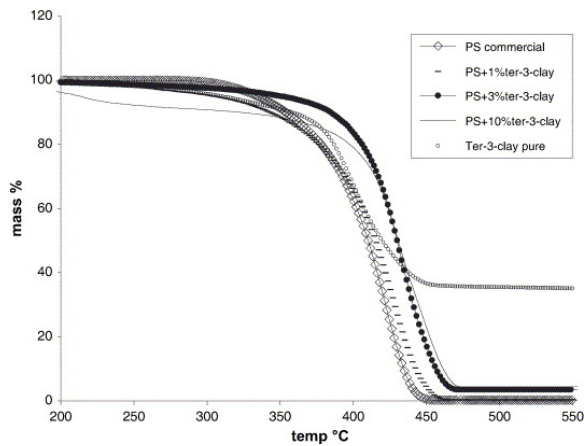


Fig. 5. TGA curves for polystyrene nanocomposites using the ter-3-clay (23%Br).

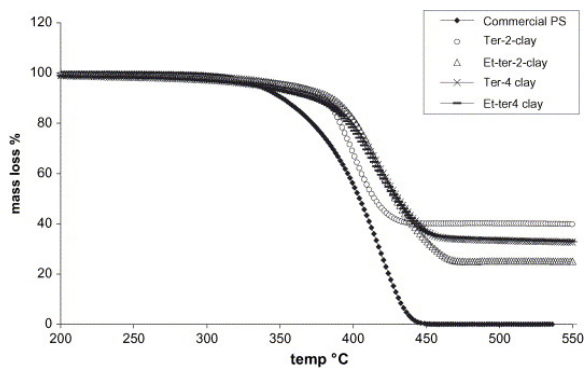


Fig. 6. TGA curves of polystyrene nanocomposites using different amines (ter-2-clay contains 12%Br, ter-4-clay contains 32%Br).

3.4. Cone calorimetric characterization of nanocomposites

It has been shown that nanocomposite formation results in good reduction in peak heat release rate, PHRR. However, compared to the virgin polymer, the time to ignition, t_{ign} , is usually lowered while the total heat released, THR, is unchanged. The decrease in t_{ign} suggests that it is easier to combust the nanocomposite than the virgin polymer while the constancy in THR means that like the virgin polymer, the nanocomposite is

completely combusted. The goal is to see if any improvements in the time to ignition and total heat release, while maintaining the reduction in peak heat release rates, can be achieved by the incorporation of a small amount of bromine chemically attached to the clay cation.

In all the different clay compositions, the total amount of bromine present in the nanocomposites is less than 4%. The data for the polystyrene nanocomposites as a function of bromine content are shown in [Table 5](#) for the oligomeric trimethyl ammonium substituted clays while the data for the other clays, ethyl and long chain, are shown in [Table 6](#); the actual heat release rate curves are provided in [Fig. 7](#), [Fig. 8](#), [Fig. 9](#), [Fig. 10](#), [Fig. 11](#), [Fig. 12](#), [Fig. 13](#). To demonstrate that the reduction in PHRR is due to nanocomposite formation and not the presence of bromine, blends of polystyrene with decabromodiphenyl oxide, a very common bromine-containing fire retardant, are compared and one can see that there is no effect on the PHRR, thus we may conclude that nanocomposite formation effects the PHRR and the presence of bromine is important in the reduction of the total heat released. In work with polypropylene systems, it has also been observed that the addition of decabromodiphenyl oxide does not have an effect on the PHRR ^[20].

Table 5. Cone calorimetric data for polystyrene nanocomposites using oligomeric trimethylammonium-modified montmorillonite

| Sample | t_{ign} (s) | PHRR (kW/m ²) (% reduction) | t_{PHRR} (s) | THR (MJ/m ²) | AMLR (g/stm ²) | ASEA (m ² /kg) |
|-----------------------------|---------------|---|----------------|--------------------------|----------------------------|---------------------------|
| PS | 68 ± 2 | 1399 ± 59 | 114 ± 3 | 108 ± 2 | 20 ± 0 | 1479 ± 167 |
| PS + 3%Br (DBDPO) | 66 ± 3 | 1352 ± 16 | 132 ± 2 | 78 ± 2 | 26 ± 1 | 1362 ± 189 |
| PS + 7%Br (DBDPO) | 69 ± 1 | 1404 ± 28 | 143 ± 4 | 80 ± 2 | 26 ± 1 | 1610 ± 63 |
| Ter-1-clay | | | | | | |
| PS + 1% ter-1-clay (0.2%Br) | 45 ± 1 | 1530 ± 80 | 107 ± 7 | 110 ± 8 | 19 ± 2 | 1340 ± 130 |
| PS + 3% ter-1-clay (0.6%Br) | 40 ± 0 | 1586 ± 69 | 105 ± 2 | 119 ± 4 | 21 ± 1 | 1082 ± 105 |
| PS + 5% ter-1-clay (1%Br) | 51 ± 0 | 1472 ± 17 | 114 ± 0 | 111 ± 8 | 21 ± 1 | 1335 ± 117 |
| PS + 10% ter-1-clay (2%Br) | 41 ± 1 | 1051 ± 86 (25) | 100 ± 1 | 101 ± 4 | 19 ± 1 | 1613 ± 161 |
| Ter-2-clay | | | | | | |
| PS + 3% ter-2-clay (0.2%Br) | 23 ± 1 | 970 ± 23 (31) | 107 ± 9 | 86 ± 3 | 20 ± 1 | 1385 ± 63 |
| PS + 5% ter-2-clay (0.6%Br) | 42 ± 4 | 968 ± 31 (31) | 128 ± 12 | 94 ± 5 | 18 ± 1 | 1427 ± 90 |
| PS + 10% ter-2-clay (2%Br) | 39 ± 7 | 820 ± 30 (41) | 121 ± 10 | 85 ± 4 | 16 ± 1 | 1427 ± 25 |
| Ter-3-clay | | | | | | |
| PS + 1% ter-3-clay (0.2%Br) | 35 ± 1 | 1341 ± 115 (4) | 95 ± 6 | 109 ± 4 | 19 ± 2 | 1410 ± 119 |
| PS + 3% ter-3-clay (0.6%Br) | 39 ± 8 | 1197 ± 57 (15) | 86 ± 4 | 111 ± 8 | 19 ± 2 | 1569 ± 157 |
| PS + 10% ter-3-clay (2%Br) | 27 ± 5 | 713 ± 68 (49) | 89 ± 7 | 87 ± 7 | 14 ± 2 | 1705 ± 107 |
| PS + 3% ter-4-clay (1%Br) | 28 ± 4 | 1325 ± 55 (5) | 114 ± 5 | 101 ± 1 | 21 ± 1 | 1323 ± 86 |
| PS + 5% ter-4-clay (2%Br) | 25 ± 2 | 1072 ± 26 (23) | 113 ± 7 | 95 ± 3 | 19 ± 1 | 1509 ± 82 |

| | | | | | | |
|----------------------------|--------|-----------------|---------|---------|--------|------------|
| PS + 10% ter-4-clay (3%Br) | 24 ± 4 | 896 ± 29 (36) | 110 ± 6 | 83 ± 4 | 18 ± 0 | 1641 ± 57 |
| Di-clay | | | | | | |
| PS + 1% di-clay (0.4%Br) | 50 ± 1 | 1200 ± 176 (14) | 110 ± 8 | 100 ± 5 | 21 ± 5 | 1263 ± 126 |
| PS + 3% di-clay (1%Br) | 46 ± 3 | 1436 ± 74 | 97 ± 8 | 95 ± 5 | 21 ± 5 | 1330 ± 133 |
| PS + 10% di-clay (4%Br) | 20 ± 5 | 737 ± 5 (49) | 30 ± 6 | 73 ± 3 | 17 ± 2 | 1675 ± 52 |

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

Table 6. Effects of the various amines on the cone calorimetric properties of the polystyrene nanocomposites

| Sample | t _{ign} (s) | PHRR (kW/m ²) (% reduction) | t _{PHRR} (s) | THR (MJ/m ²) | MLR (g/stm ²) | ASEA (m ² /kg) |
|--------------------------------|----------------------|---|-----------------------|--------------------------|---------------------------|---------------------------|
| PS | 68 ± 2 | 1399 ± 59 | 114 ± 3 | 102 ± 3 | 20 ± 0 | 1479 ± 167 |
| PS + 3%Br (DBDPO) | 66 ± 3 | 1352 ± 16 | 132 ± 2 | 80 ± 2 | 26 ± 1 | 1362 ± 189 |
| PS + 3% Et ter-3-clay (0.2%Br) | 29 ± 3 | 1195 ± 68 | 105 ± 3 | 75 ± 3 | 20 ± 2 | 1131 ± 137 |
| PS + 5% Et ter-3-clay (0.6%Br) | 38 ± 6 | 1305 ± 93 | 113 ± 8 | 83 ± 2 | 21 ± 2 | 1242 ± 73 |
| PS + 10% Et ter-3-clay (2%Br) | 40 ± 7 | 1045 ± 70 (25) | 131 ± 11 | 84 ± 2 | 21 ± 1 | 1280 ± 91 |
| PS + 1% LC ter-3-clay (0.2%Br) | 45 ± 4 | 1377 ± 32 | 126 ± 10 | 93 ± 4 | 21 ± 1 | 1231 ± 42 |
| PS + 3% LC ter-3-clay (0.6%Br) | 44 ± 1 | 1426 ± 102 | 125 ± 4 | 97 ± 4 | 22 ± 1 | 1365 ± 136 |
| PS + 10% LC ter-3-clay (2%Br) | 23 ± 4 | 961 ± 7 (31) | 76 ± 3 | 66 ± 5 | 18 ± 1 | 1510 ± 39 |
| PS + 3% Et ter-2-clay (0.2%Br) | 46 ± 5 | 1525 ± 102 | 120 ± 13 | 102 ± 9 | 22 ± 3 | 1366 ± 70 |
| PS + 5% Et ter-2-clay (0.6%Br) | 38 ± 4 | 1550 ± 91 | 122 ± 11 | 106 ± 10 | 20 ± 2 | 1360 ± 132 |
| PS + 10% Et ter-2-clay (2%Br) | 21 ± 2 | 1046 ± 57 (25) | 102 ± 4 | 72 ± 4 | 20 ± 2 | 1349 ± 84 |

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

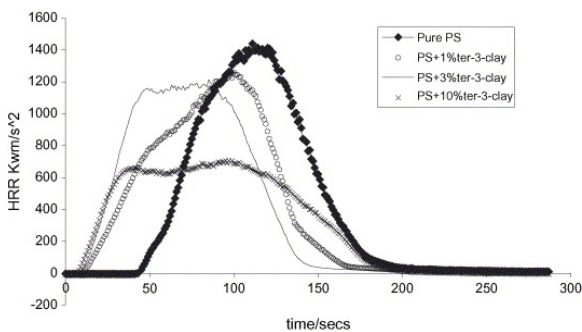


Fig. 7. Heat release rate curves using oligomeric trimethyl ammonium ter-3-clay.

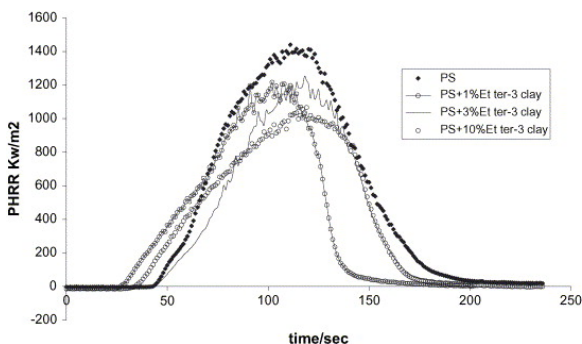


Fig. 8. Heat release rate curves for the polystyrene nanocomposites prepared using the oligomeric triethyl ammonium ter-3-clay.

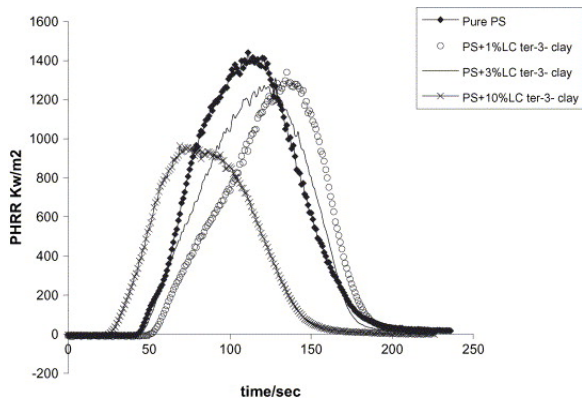


Fig. 9. Heat release rate curves for the polystyrene nanocomposites prepared using the oligomeric-long chain ammonium ter-3-clay.

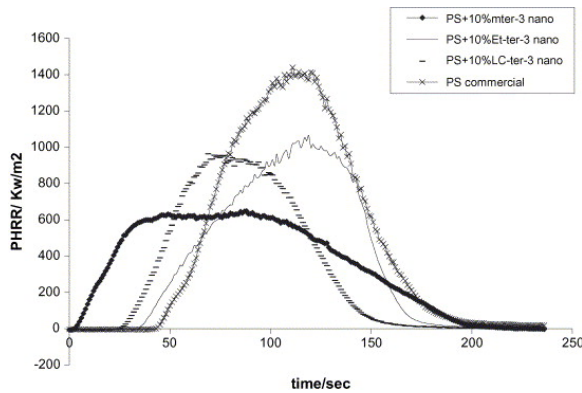


Fig. 10. Comparison of the heat release rate curves for polystyrene nanocomposites prepared using the three different ter-3-clays.

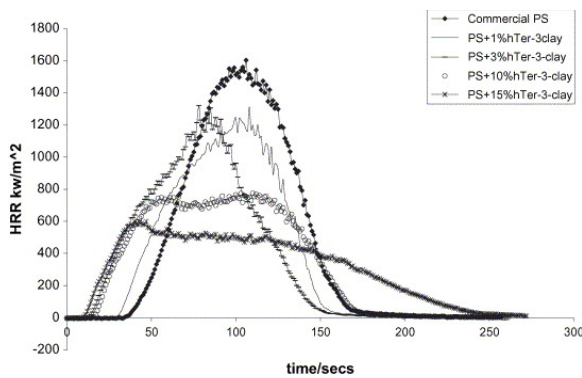


Fig. 11. Heat release curves of polystyrene nanocomposites prepared from the higher molecular weight oligomeric trimethyl ammonium hter-3-clay.

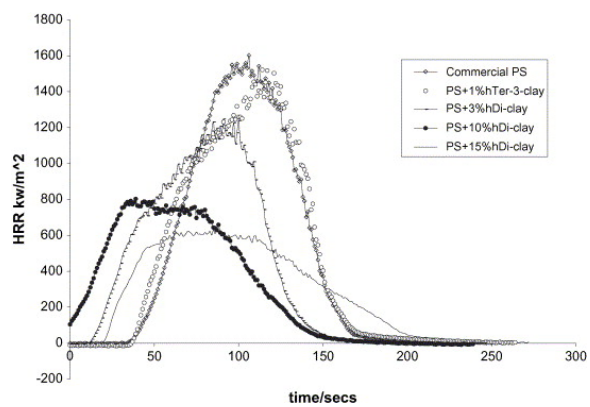


Fig. 12. Heat release curves of polystyrene nanocomposites prepared from the higher molecular weight oligomeric trimethyl ammonium di-clay.

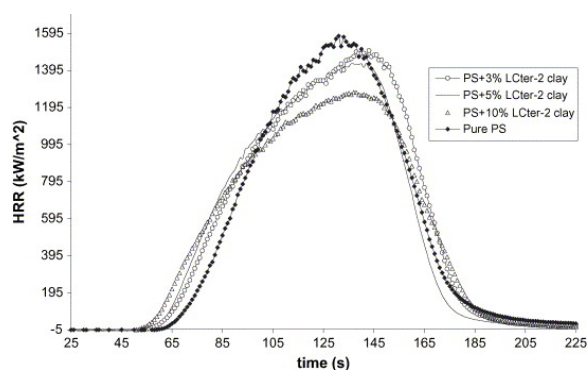


Fig. 13. Heat release rate curves for polystyrene nanocomposites prepared by melt blending of the oligomeric-long chain ammonium clay.

From previous work with polystyrene nanocomposites, it appears that the optimum content of inorganic clay is in the range of 2%–4% to achieve a significant reduction in the PHRR [21], [22]. At lower amounts of clay, there is a reduction in PHRR but it is lower than what is observed at these amounts. In this study, since the clay has a low inorganic content, about 30%, 10% organically-modified clay is required to be in the region where a significant reduction is expected. From Table 5, one can see that except for ter-2-clay, there is not a significant reduction until 10% clay is present, which corresponds to 3% inorganic clay; the heat release curves, shown in Fig. 7, show this graphically. It is interesting to note that the addition of decabromodiphenyl oxide does not bring about a reduction in PHRR but does give a 28% reduction in the total heat released. It appears that the presence of clay causes the reduction in PHRR while the presence of bromine brings about the reduction in the total heat released, i.e., the presence of bromine, even at less than 4%, prevents the burning of the polystyrene. It is notable that the mass loss rate does not show much of a change, this is unusual for nanocomposites and is likely due to the low amounts of inorganic clay that are present.

The results for the other amines are shown in Table 6 and Fig. 8, Fig. 9. The same observation may be made, i.e., there is no reduction in PHRR until 10% organically-modified clay is present and the total heat released is also not significantly effected until this level of clay and bromine are reached. A comparison of the various ammonium salts that have been made is shown in Fig. 10 and this shows that the oligomeric trimethyl ammonium salt gives the largest reduction in PHRR. Perhaps this is due to the absence of β -hydrogens in this amine, which means that the ammonium salt will not undergo the Hofmann elimination reaction and thus the nanocomposite may have enhanced fire stability.

The samples that were prepared using the higher molecular weight oligomeric ammonium salt also give good reductions in the heat release rate curves; the data are shown in Table 7 and the heat release curves are in Fig. 11 for the ter-3-clay and Fig. 12 for the di-clay. Once again there is no significant reduction in PHRR with less than 10% clay, which corresponds to 3% inorganic content, and the reduction is better at 15%, which corresponds to 4% inorganic content. At both 10% and 15% clay (the bromine contents 2% and 3%, respectively), the reduction in the total heat released is about the same. Thus one can say that the molecular weight of the bromine-containing clay does not appear to have an effect on the fire properties of the nanocomposite.

Table 7. Cone calorimeter data for polystyrene nanocomposites prepared using the higher molecular weight organically-modified clay

| Sample | t_{ign} (s) | PHRR (kW/m ²) (% reduction) | t_{PHRR} (s) | THR (MJ/m ²) | AMLR (g/stm ²) | ASEA (m ² /kg) |
|------------------------|----------------------|--|-----------------------|-----------------------------|-------------------------------|------------------------------|
| PS + 1% hdi-clay (0.2) | 57 ± 3 | 1533 ± 27 | 108 ± 6 | 111 ± 3 | 23 ± 1 | 1382 ± 124 |
| PS + 3% hdi-clay (0.6) | 35 ± 4 | 1274 ± 68 (9) | 96 ± 4 | 95 ± 2 | 21 ± 1 | 1525 ± 196 |

| | | | | | | |
|---------------------------|--------|----------------|---------|--------|--------|-----------|
| PS + 10% hdi-clay (2) | 21 ± 2 | 789 ± 37 (44) | 44 ± 3 | 77 ± 5 | 17 ± 0 | 1834 ± 53 |
| PS + 15% hdi-clay (3) | 42 ± 4 | 583 ± 40 (58) | 92 ± 8 | 72 ± 2 | 15 ± 1 | 1928 ± 54 |
| PS + 1% hter-3-clay (0.2) | 54 ± 2 | 1302 ± 21 (7) | 97 ± 15 | 93 ± 5 | 23 ± 1 | 1349 ± 73 |
| PS + 3% hter-3-clay (0.6) | 41 ± 3 | 1323 ± 115 (6) | 93 ± 33 | 94 ± 4 | 21 ± 2 | 1434 ± 48 |
| PS + 10% hter-3-clay (2) | 37 ± 3 | 797 ± 39 (43) | 73 ± 33 | 78 ± 7 | 17 ± 1 | 1462 ± 72 |
| PS + 15% hter-3-clay (3) | 34 ± 2 | 624 ± 42 (55) | 43 ± 8 | 81 ± 6 | 13 ± 1 | 1594 ± 31 |

tign, time to ignition; PHRR, peak heat release rate; tPHRR, time to PHRR; THR, total heat released; AMLR, average mass loss rate; ASEA, average specific extinction area.

Nanocomposites have also been prepared by melt blending and the results are not as good as those seen when the samples were prepared by bulk polymerization; a representative heat release curve is shown in [Fig. 13](#).

4. Conclusions

PS-clay nanocomposites were prepared using a novel organically-modified clay that contains bromine on the ammonium cation of the clay by bulk polymerization and melt blending. The reduction in peak heat release rate is that which one expects from the clay and the presence of the bromine brings about a significant reduction in the total heat released for bulk polymerization but not for melt blending. The amount of bromine was less than 4%, far less than that is usually used to obtain a fire retardant composition. It appears that one can obtain a useful system by the use of a bromine-containing nano-dispersed clay.

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