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Flame Retardancy Of Polystyrene Nanocomposites Based on An Oligomeric Organically-Modified Clay Containing Phosphate

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Abstract

Novel modified clays, which may enable the formation of flame retarded polystyrene nanocomposites by melt or solution blending, have been prepared using an ammonium salt which contains an oligomeric material consisting of vinylbenzyl chloride, styrene and vinyl phosphate reacting with dimethylhexadecylamine. These nanocomposites have been characterized by X-ray diffraction, transmission electron microscopy, thermogravimetric analysis, cone calorimetry and the evaluation of mechanical properties. Melt blending is an effective, economical way to produce intercalated

nanocomposites with greatly reduced peak heat release rate and a decreased total heat release; the polymer does not all undergo thermal degradation.

Keywords

Flame retardancy; Nanocomposite; Polystyrene; Phosphate

1. Introduction

Polymer clay nanocomposites have received significant research attention due to their remarkable improvement of physical and mechanical properties at very low clay loading compared to their corresponding virgin polymers.^{1,2} These improvement in the properties is the result of the nanometer scale dispersion of clay in the polymer matrix.³ The most commonly used clay for the polymer/clay nanocomposites is montmorillonite (MMT), which has sodium cations to balance the negative charges of the clay layers. The hydrophilic nature of the clay surfaces prevents homogeneous dispersion throughout the polymer phase so it is necessary to ion-exchange the sodium for a cation which is more organophilic, usually an ammonium or phosphonium cation.⁴ In recent work from this laboratory, it has been shown that oligomeric cations based upon styrene or methyl methacrylate can produce clays that are very compatible with a variety of polymers and that one can use these to prepare exfoliated and intercalated nanocomposites.⁵ This includes the preparation of polypropylene nanocomposites without the need to use maleated polypropylene, PP-g-MA.

Nanocomposites may be prepared either by bulk polymerization or by melt or solution blending methods and three types of systems can be produced, immiscible materials, also known as microcomposites in which the clay is not nano-dispersed, intercalated nanocomposites, in which the registry between the clay layers is maintained, and exfoliated nanocomposites, in which this registry is lost.

Nanocomposite formation enhances the permeability, heat distortion temperature, fire retardancy and flexural modulus of the virgin polymer. In the specific case of fire retardancy, cone calorimetry is typically used to evaluate this property and the usual observation is that the heat release curve, which is a measure of the amount of energy that is released during combustion, is changed so that the peak release rate is decreased. It is also regularly observed that the total heat release is unchanged relative to the virgin polymer, which means that everything will eventually burn. This last fact, combined with the observation that the nanocomposite will actually ignite more easily than will the virgin polymer, indicates that more work must be done in order to achieve fire retardancy through nanocomposite formation.

Two processes have been suggested to explain the reduced peak heat release rate, a barrier is formed which inhibits mass transport of polymer and prevents the flame from impacting the polymer⁶ and paramagnetic radical trapping by iron in the clay.⁷ Radical trapping is only important at very low amounts of clay, typically less than 1%, while the barrier properties seem to take over at higher amounts of clay.

The advantage of nanocomposite formation is that the clay, and its cation, is uniformly distributed throughout the polymer. This can be contrasted to an additive, which is typically not well-dispersed. If the fire retardant element(s) can be attached to the clay, nano-dispersion of these materials may be achieved, which may well enhance the fire retardancy of the material. Aromatic phosphate compounds

are highly effective fire retardants both in the condensed phase and in the vapor phase. One mechanism that has been postulated for the phosphates is that they undergo oxidation to phosphoric acid during combustion.⁸ These aromatic phosphate compounds are effective with polymers which contain oxygen, but they are not effective in styrenic resins and polyolefins, since the level that must be used will likely cause plasticization.

In this work, oligomers of styrene, vinylbenzyl chloride and diphenyl vinylphenylphosphate or diphenyl vinylbenzylphosphate have been prepared and reacted with an amine and then ion-exchanged onto clay. These organically-modified clays have then been melt blended with polystyrene and evaluated.

2. Experimental

2.1. Materials

The majority of chemicals used in this study, including vinylbenzyl chloride, styrene, vinylphosphonic acid, benzoyl peroxide (BPO), di-tert butyl peroxide, TBP, N,N-dimethylhexadecylamine, initiator removal reagents, and polystyrene (melt flow index 200°C/5kg: 7.5g/10 min, M_w 280,000) were acquired from Aldrich Chemical Co. Pristine sodium montmorillonite was provided by Southern Clay Products, Inc. The sample of 1-phenylvinylphosphonic acid and 1-vinylphosphonic acid were provided by the Monsanto Company.

2.2. Instrumentation

Fourier transform infrared spectroscopy (FT-IR), was performed on a Mattson Galaxy infrared spectrometer at 4 cm^{-1} resolution while ^1H NMR spectra were obtained on a GE-300 instrument. Thermogravimetric analysis, TGA, was performed on a Cahn TG-131 under a flowing nitrogen atmosphere at a scan rate of 10 °C per minute from 20 to 600 °C. All TGA experiments have been performed at least two times and some have been done in triplicate. Reproducibility of temperatures is $\pm 3^\circ\text{C}$ while the amount of non-volatile residue is reproducible to $\pm 3\%$. Thermogravimetric analysis coupled to Fourier transform infrared spectroscopy, TGA/FT-IR, was performed using a Cahn 131 thermogravimetric analyzer at 20 °C min under inert atmosphere interfaced to a Mattson Galaxy infrared spectrometer. Cone calorimetry was performed using an Atlas Cone 2 instrument according ASTM E 1354-92 at an incident flux of 35 or 50 KW/m^2 using a cone shaped heater. Exhaust flow was set at 24 l/s and the spark was continuous until the sample ignited. Cone samples were prepared by compression molding the sample (20–50 g) into square plaques using a heated press. Typical results from Cone calorimetry are reproducible to within about $\pm 10\%$; these uncertainties are based on many runs in which thousands of samples have been combusted.^{9,10} X-ray diffraction was performed on a Rigaku Geiger Flex, 2-circle powder diffractometer; scans were taken from 2θ 0.86 to 10, step size 0.1, and scan time per step of 10 s. 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 Riechert-Jung Ultra-Cut E microtome at room temperature to give ~ 70 nm thick sections. The sections were transferred from the knife-edge to 600 hexagonal mesh Cu grids. The contrast between the layered silicates and the polymer phase was sufficient for imaging, so no heavy metal staining of sections prior to imaging is required. Mechanical properties were obtained using a SINTECH 10 (Systems Integration Technology, Inc.) computerized system for material testing at a crosshead speed of 0.2 in/min. The samples were prepared both by injection molding, using an Atlas

model CS 183MMX mini max molder, and by stamping from a sheet; the reported values are the average of six determinations.

2.3. Synthesis of 4-vinylbenzyl alcohol¹¹

A portion of 4-vinylbenzyl chloride (61 g, 0.4 mol), potassium acetate (50 g, 0.5 mol), 0.1 g of *t*-butylcatechol as a polymerization inhibitor and 200 ml DMSO were placed in a 500 ml round-bottom flask equipped with condenser. The mixture was heated to 40 °C and kept for 20 h under nitrogen. Once reaction was completed 400 ml ether was added, and then the ether solution was separated, washed with distilled water and dried over anhydrous Na₂SO₄. Approximately 70 g (100%) of 4-vinylbenzyl acetate was obtained. Then 4-vinylbenzyl acetate was hydrolyzed with a mixture of alcohol and KOH for 10 h at 50 °C under nitrogen. The product was purified with ether and water, and dried over anhydrous Na₂SO₄. The recovered product consisted of 44 g (82% yield). ¹H NMR (CDCl₃) δ 7.36 (d, *J*=8.1 Hz, 2H), 7.25 (d, *J*=7.8 Hz, 2H), 6.69 (dd, *J*₁=17.7 Hz, *J*₂=10.8 Hz, 1H) 5.73 (d, *J*=17.4 Hz, 1H), 5.23 (d, *J*=10.8 Hz, 1H), 4.58 (s, 2H), 2.54 (broad, 1H).

2.4. Synthesis of 4-vinyl phenyl alcohol

A mixture of 53 g (0.33 mol, 50 ml) 4-vinylphenyl acetate and 0.1 g *t*-butylcatechol as a polymerization inhibitor were hydrolyzed with a mixture of alcohol and KOH for 10 h at 50 °C under nitrogen. The product was treated with dichloromethane and water; the organic layer was set aside and the water layer was washed with 10% hydrochloric acid, and then saturated ammonium chloride until it was neutral. This water solution was then extracted with dichloromethane and combined with previous dichloromethane solution and dried over anhydrous Na₂SO₄. After evaporation of the solvent, 39 g (99%) of the liquid product was obtained. ¹H NMR (CDCl₃) δ 7.28 (d, *J*=8.1 Hz, 2H), 7.16 (d, *J*=8.7 Hz, 2H), 6.64 (dd, *J*₁=17.7 Hz, *J*₂=10.8 Hz, 1H) 5.59 (dd, *J*₁=17.7 Hz, *J*₂=0.9 Hz, 1H), 5.12 (dd, *J*₁=10.8 Hz, *J*₂=0.9 Hz, 1H), 2.70 (broad, 1H).

2.5. Synthesis of diphenyl 4-vinylphenyl phosphate DPVPP

In a 500-ml flask, 39.27 g (0.33 mol) of 4-vinylbenzyl alcohol was dissolved in 300 ml anhydrous dichloromethane, then 33 g of anhydrous triethyl amine was added. This solution was then cooled to 0 °C. A 80.59 g (0.30 mol) portion of diphenyl chlorophosphate was added dropwise and a large quantity of white solid precipitated during the addition. The flask was stirred at 0 °C for 8 h then placed in refrigerator for 2 days. After the solid was filtered, the dichloromethane solution was washed with distilled water three times and dried with anhydrous Na₂SO₄. About 86.60 g (82%) product was obtained after the dichloromethane was removed. ¹H NMR (CDCl₃) δ 7.19–7.42 (m, 14H), 6.84 (dd, *J*₁=17.4 Hz, *J*₂=10.8 Hz, 1H) 5.70 (d, *J*=17.7 Hz, 1H), 5.26 (d, *J*=10.8 Hz, 1H).

2.6. Synthesis of diphenyl 4-vinylbenzyl phosphate DPVBP

A similar procedure as for DPVPP was followed using 4-vinylbenzyl alcohol. The yield is 78%. ¹H NMR (CDCl₃) δ 7.09–7.36 (m, 14H), 6.65 (dd, *J*₁=17.4 Hz, *J*₂=10.8 Hz, 1H) 5.72 (dd, *J*₁=17.7 Hz, *J*₂=0.9 Hz, 1H), 5.24 (dd, *J*₁=11.1 Hz, *J*₂=0.9 Hz, 1H), 5.14 (d, *J*=8.7 Hz, 2H).

2.7. Preparation of 75% DPVPP terpolymer modified clay

In a 250 ml three neck round-bottom flask were placed 50 g (0.14 mol) DPVPP, 13.33 g (0.13 mol) of inhibitor-free styrene, 3.33 g (0.02 mol) of 4-vinylbenzyl chloride and 3.33 g of benzoyl peroxide (BPO) and 3.33g di-*tert* butyl peroxide (TBP) as initiators. The contents of the flask were stirred until all had

dissolved at room temperature under a nitrogen flow, then it was heated with stirring to 90 °C using an oil bath until gel formation occurred. The mixture was then cooled to room temperature and then brought to 100 °C for 5 h. The resulting solid was dissolved in THF and precipitated with methanol; 64 g of a yellow solid with melting temperature range 100–110 °C was recovered and the molecular weight was in the range of 10,000, based on the Mark-Houwink constants for polystyrene.

This oligomer (64 g) was dissolved in 1000 ml of THF/DMSO 60/40 in a 3000 ml round bottom flask and 5.88 g (0.06 mol) of *N,N*-dimethylhexadecylamine was added to the flask and the flask was heated and maintained at 60 °C for 6 h. The quantity of amine added is a three-fold excess, assuming that the polymer contains 5% vinylbenzyl chloride.

A suspension of 21.82 g of prewashed sodium montmorillonite, Na–MMT, in 1000 ml of distilled water and 500 ml DMSO was heated to 60 °C for 24 h with vigorous stirring. The oligomeric amine prepared above was added dropwise to the dispersed clay; a precipitate appeared immediately and the slurry was stirred at 60 °C for 12 h. After cooling, the supernatant liquid was poured off and a fresh mixture of H₂O/THF(60/40) was added and the slurry was heated again for additional 12 h at 60 °C with stirring. The slurry was filtered and the precipitate was air-dried for one day and then in a vacuum oven at 40 °C for 48 h and 78 g clay was obtained.

2.8. Preparation of 55% vinyl phosphate terpolymer modified clay

A similar procedure was used to prepare 55% diphenyl-4-vinylphenylphosphate (DPVPP), diphenyl-4-vinylbenzylphosphate (DPVBP), 1-vinylphosphonic acid (VPA) and 1-phenylvinylphosphonic acid (PVPA) modified clays, each of which contain 40% styrene and 5% vinylbenzyl chloride.

2.9. Preparation of polymer-clay nanocomposites by melt blending

All the nanocomposites in this study were prepared by melt blending in a Brabender Plasticorder at high speed (60 rpm) at 190 °C for 15 min. The composition of each nanocomposite is calculated from the amount of clay and polymer charged to the Brabender.

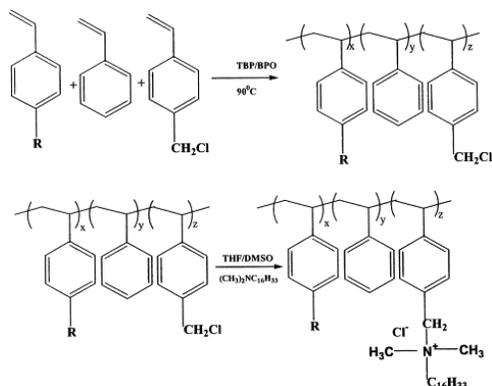
2.10. Preparation of polymer-clay nanocomposites by solution blending

A sample of the phosphate modified clay and polystyrene were dispersed in CHCl₃ in a 250 ml round-bottom flask. The contents of the flask were stirred until homogeneous at room temperature under nitrogen flow, then the temperature was increased to 50 °C with stirring for 24 h under N₂ atmosphere. After evaporation of the solvent, the resulting material was dried under vacuum for 6 h at 80 °C to obtain the nanocomposite.

3. Results and discussion

Previous work from this laboratory has shown that one can easily prepare exfoliated styrene nanocomposites by melt blending when ammonium salt that is used to modify the clay contains an oligomeric functionality.⁵ Typically the oligomeric unit contains a relatively small amount of vinylbenzyl chloride to permit facile formation of the ammonium salt that is then used to modify the clay. In this study a third component, a substituted triphenylphosphate, has been added to the oligomer; this incorporates a significant amount of phosphorus to the clay and this phosphorus will be nano-dispersed if the clay is nano-dispersed within the polymer. This means that a fire retardant element will be well-dispersed throughout the polymer and this should enhance the fire retardancy of the polystyrene. The

reactivity ratios for vinyl diphenylphosphate and styrene are $r_1=0.38$ and $r_2=1.76$ while those for vinylbenzyl chloride and styrene are $r_1=1.12$ and $r_2=0.62$. Also the homopolymerization of diphenyl-4-vinylphenylphosphate is difficult under the reactions conditions used for the formation of the terpolymer. The recovery of polymer was greater than 95% of the mass of monomers charged to the reaction flask. The composition of the terpolymer may contain a little less styrene, since it is the most volatile, and hence a little more phosphate and vinylbenzyl chloride. Infrared analysis of the resulting polymers shows the presence of the phosphate ester and the ability to quaternize an amine shows the presence of the benzylic chloride. Scheme 1 shows the details of the formation of the terpolymer.



Scheme 1. Synthetic route for the formation of the terpolymer and its ammonium salt, R=phosphate moiety.

3.1. XRD measurement of polymer/clay nanocomposites

X-ray diffraction, XRD, offers the opportunity to determine the spacing between the clay layers. In sodium montmorillonite the d-spacing is 1.4 nm and this increases when the sodium is ion-exchanged with an ammonium or other 'onium' ion. In the case of the oligomer that contains 55% of DPVPP, the d-spacing increases to 4.4 nm and it is 7.2 nm in the clay that contains 75% DPVPP. The XRD traces for these clays and the corresponding polystyrene nanocomposites prepared by melt blending are shown in Fig. 1, Fig. 2. These figures show various levels of clay and different methods of preparing the nanocomposites. The fact that peaks are seen suggests that intercalated nanocomposites have been formed. The peaks for the 75% DPVPP clay nanocomposites are more diffuse than those for the 55% material, which may indicate that there is more disorder in this system. The d-spacing in the clay is already quite large and there is little change when the polystyrene is incorporated into the system. This observation has previously been made in this laboratory for similar systems.

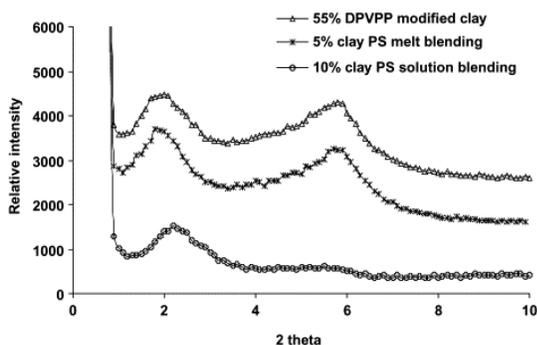


Fig. 1. XRD traces for polystyrene melt blended with 55% DPVPP clay.

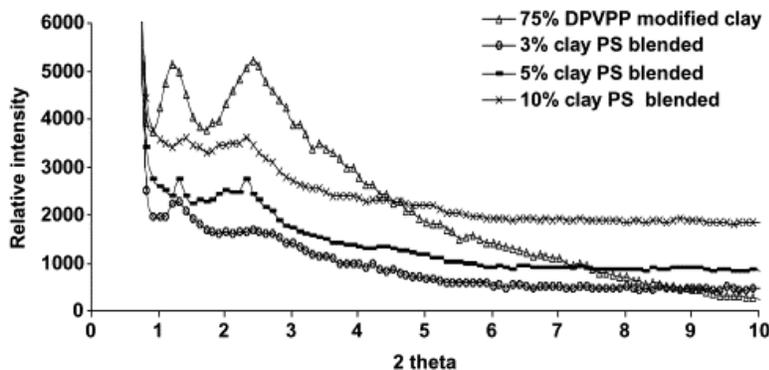


Fig. 2. XRD traces for polystyrene melt blended with 75% DPVPP clay.

3.2. TEM measurement

X-ray diffraction alone can never provide the details of the type of nanocomposite that has been produced, an additional technique, usually transmission electron microscopy, TEM, is required to identify the exact state of the nanocomposite. Recently it has been reported that NMR relaxation measurements can also be used to identify the type of nanocomposite and there is an advantage to this technique, since it measures the bulk sample rather than a very small portion of the sample. In work from this laboratory, it has been shown that cone calorimetry can also be used to identify nanocomposites versus microcomposites.

The TEM images of the nanocomposites are shown in Fig. 3, Fig. 4 for the two phosphate containing systems. In the low magnification images, on the left in each figure, one can see that nano-dispersion has been achieved. In the higher magnification images, on the right, one can see the presence of individual clay layers and the registry between the layers appears to be maintained; these are intercalated nanocomposites. The d-spacings calculated from the TEM images are 4–5 nm for the 55% DPVPP clay nanocomposite and 6–8 nm for the 75% DPVPP clay nanocomposite, in excellent agreement with XRD measurements.

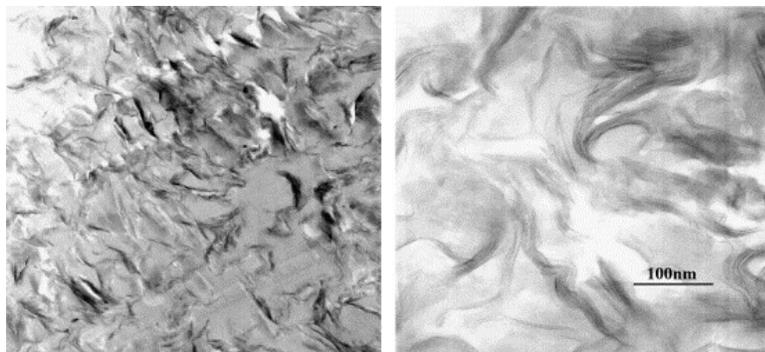


Fig. 3. TEM images for polystyrene nanocomposites containing 5% clay (using 55% DPVPP modified clay) at low (left) and high (right) magnification.

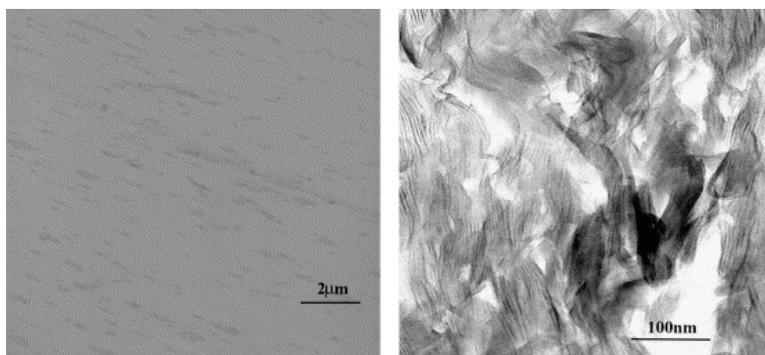


Fig. 4. TEM images for polystyrene nanocomposites containing 5% clay (using 75% DPVPP modified clay) at low (left) and (right) magnification.

3.3. TGA characterization of nanocomposites

The thermal stability of the clays and nanocomposites has been examined using thermogravimetric analysis and the results are shown in Table 1 and Fig. 5, Fig. 6, Fig. 7. The reported data include the onset temperature of the degradation, as measured by the temperature at which 10% of the mass has been lost, the mid-point of the degradation, another measure of thermal stability, and the fraction that does not volatilize at 600 °C, denoted as char. The clays show very good thermal stability with the onset temperature of the degradation in the range of 330–340 °C. This is comparable stability to that achieved with a clay that contains only styrene and vinylbenzyl chloride.¹² The amount of residue is quite surprising since the 75% DPVPP clay contains only 28% aluminosilicate. This means that a significant portion of the organic material is retained at 600 °C. The temperature at the mid-point of the degradation is invariably increased upon nanocomposite formation and the fraction of non-volatile material is significantly larger than would be expected from the clay alone. This must indicate that a char layer is formed and the polymer is retained. The results for the onset temperature are somewhat dependent upon the mode of blending and the amount of clay. It is not surprising that solution blended material has a lower onset temperature because of the opportunity to retain solvent. The variations in onset temperature for the 75% DPVPP clays is surprising, one would imagine that the onset temperature would either not vary with the amount of clay or it would increase. No explanation is currently available for the observed decrease.

Table 1. TGA data for polystyrene nanocomposites

	T _{10%} (°C)	T _{50%} (°C)	Char (%) at 600 °C
<i>Melt blended with 55%DPVPP modified clay</i>			
55% DPVPP Clay	331		60
Commercial PS	389	434	0
5% clay PS brabender	425	465	11
10% clay PS solution blending	348	464	20
<i>Melt blended with 75% DPVPP modified clay</i>			
75% DPVPP Clay	345	455	40
Commercial PS	389	434	0
3% clay	430	470	9
5% clay	421	472	12

10% clay	404	470	16
<i>Solution blended with 75% DPVPP modified clay</i>			
75% DPVPP Clay	345	455	40
Commercial PS	389	434	0
5% clay	417	466	12
10% clay	348	470	20

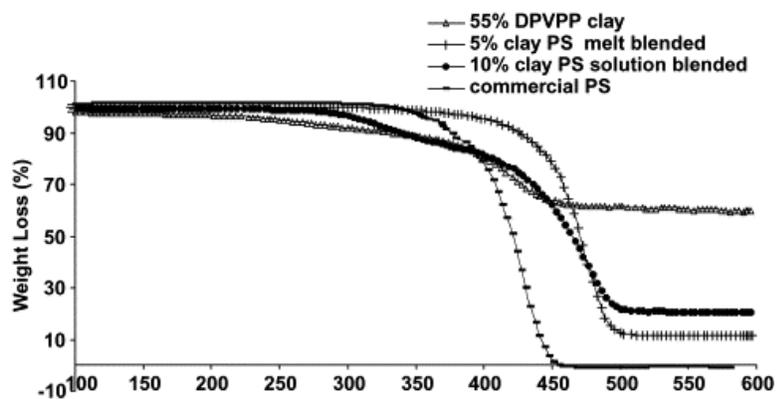


Fig. 5. TGA curve for 55% DPVPP modified clay and its PS nanocomposites.

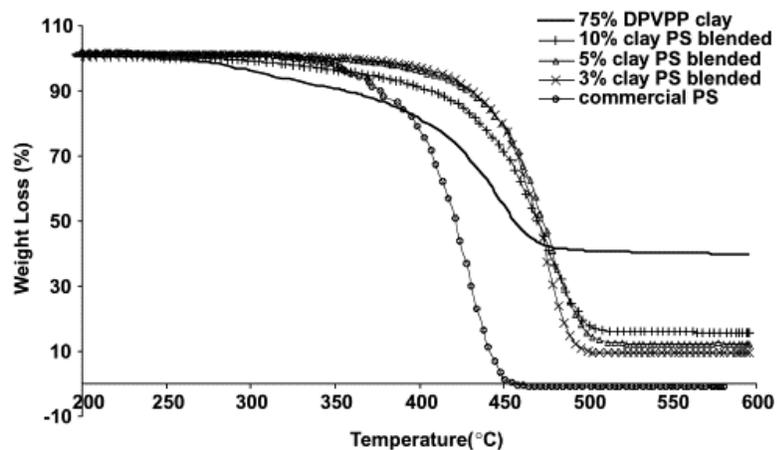


Fig. 6. TGA curves for 75% DPVPP modified clay and its PS nanocomposites via melt blending.

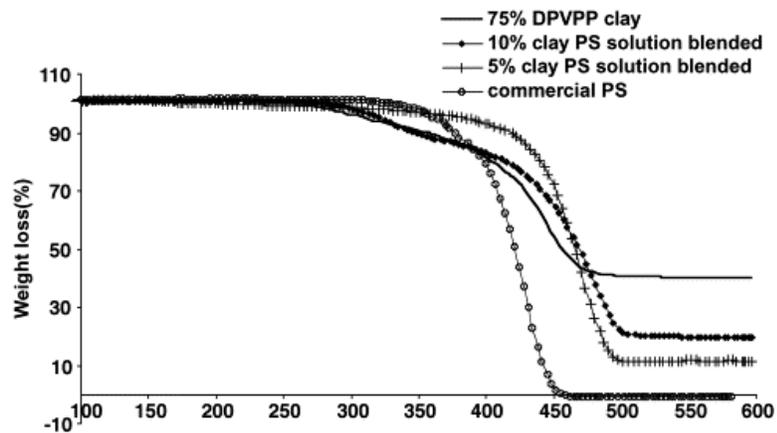


Fig. 7. TGA curve for 75% DPVPP modified clay and its PS nanocomposites via solution blending.

3.4. TGA/FTIR analysis of nanocomposites

Examination of the gaseous products which evolve during the course of thermal degradation can provide information on the reaction mechanism. In this instance, it is of interest to determine if phosphorus-containing compounds are evolved. If the phosphorus is active as a vapor phase fire retardant, it must evolve. If no phosphorus-containing species are seen, then a condensed phase process must be invoked.

The suggested mechanism for polystyrene thermal degradation (pyrolysis) is that, when $T > 300\text{ }^{\circ}\text{C}$, volatile products are formed containing monomer (40–45%) via a depolymerization process and oligomers (dimer, trimer, tetramer, and pentamer) via an intramolecular transfer or monomer radical termination process.^{13,14,15}

Peaks of interest in the degradation include the aromatic C–H stretching frequency, a little above 3000 cm^{-1} and the corresponding aliphatic frequency, near 2900 cm^{-1} ; styrene monomer, 900 and 1630 cm^{-1} ; styrene oligomers, 980 and 1600 cm^{-1} ; phosphate ester, P–O–C, 1100 – 950 cm^{-1} and $\text{P}=\text{O}$, 1315 – 1180 cm^{-1} .^{16,17}

Fig. 8 shows the TGA/FTIR data for the clay alone. The first product that is lost is the phosphorus compound at 1189 cm^{-1} . This is followed by styrene oligomers and monomers at higher temperature. In comparison to the set of spectra for virgin polystyrene (Fig. 9), the production of styrene monomer is lower than the oligomer. Fig. 10 shows a representative set of spectra for one of the melt blended compositions. The evolution of phosphate bands is diminished, possibly due to reactions of these materials with radicals formed in the degradation. The presence of phosphate bands from the clay and their decreased intensity in the nanocomposite suggests that these species are evolved and react with the degrading polymer to quench radicals and thus act as a fire retardant.

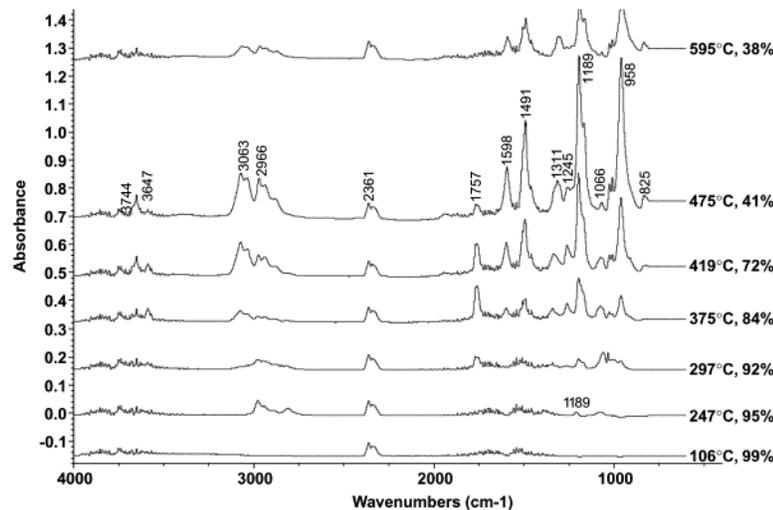


Fig. 8. TGA/FTIR data for the degradation of the 75% DPVPP modified clay. The legend to the right shows the temperature and the amount of material that has not volatilized.

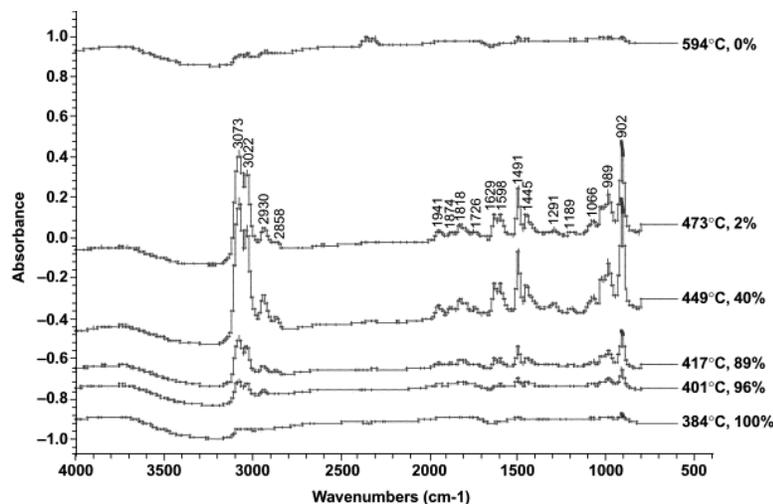


Fig. 9. TGA/FTIR data for polystyrene. the legend to the right shows the temperature and the fraction that has not volatilized.

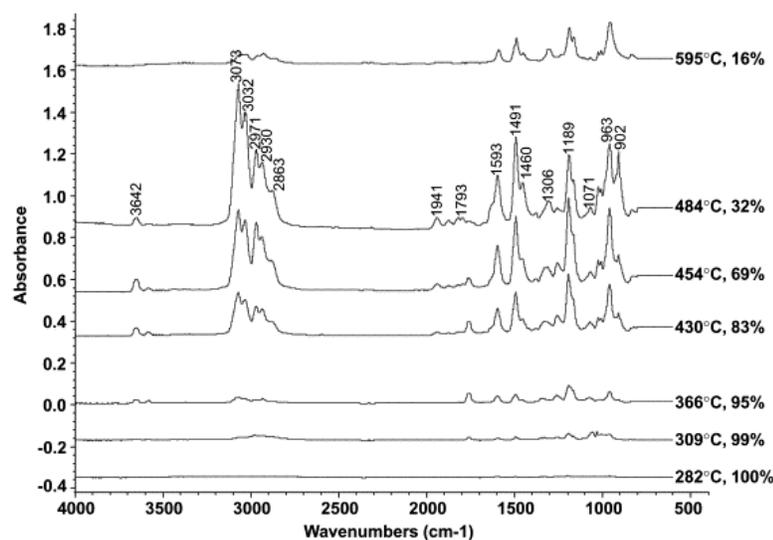


Fig. 10. TGA/FTIR data for a 10% clay polystyrene nanocomposite (using 75% DPVPP modified clay). The legend to the right shows the temperature and the fraction that has not volatilized.

3.5. Cone calorimetric characterization of nanocomposites

In previous work from this, and other, laboratories, it has been shown that the rate of heat release is significantly changed for nanocomposites relative to the virgin polymers. The parameters that may be obtained from the cone calorimeter include: the time to ignition, the peak heat release rate, PHRR, and the time to PHRR, the specific extinction area, SEA, a measure of smoke, and the mass loss rate, MLR. Two processes have been suggested to explain the reduction in heat release, barrier properties and paramagnetic radical trapping by iron in the clay. Radical trapping is probably only important at very low amounts of clay. At any reasonable amount of clay, i.e. above 1 or 2%, the barrier mechanism is the dominant process. A simple way to view this barrier process is to consider that the clay platelets overlap and form an impermanent barrier. This barrier will prevent sometimes raise the temperature at which degradation occurs but all of the polymer will eventually burn and all of the energy will ultimately be lost. The results for this study are presented in Table 2, Table 3, Table 4, Table 5 and the heat release

rate curves are shown in Fig. 11, Fig. 12, Fig. 13, Fig. 14. The results for all systems are approximately the same; the *total* heat release does fall by almost 50% upon incorporation of the clay into polystyrene. This is not typical behavior for a nanocomposite and this suggests that the presence of the phosphorus must play a major role in this system. It is routinely observed for nanocomposites that the time to ignition is shorter than that for the virgin polymer. The hope was that the presence of phosphorus would lengthen the time to ignition and that this would thereby increase the potential for nanocomposite compositions as fire retardants. As seen in the table, this increase was realized.

Table 2. Cone calorimetric data for polystyrene nanocomposites prepared using the 55% DPVPP modified clay

Commercial PS	5% Clay melt blended	10% Clay solution blended	
Time to ignition (s)	36±5	40±5	39±0
PHRR (Kw/m ²) (% reduction)	1411±18	837±32(41)	374±(73)
Time to PHRR (s)	87±4	93±7	100±8
Average HRR (kw/m ²)	755±11	571±20	237±7
Total heat released (MJ/m ²)	102±1	58±11	47±20
Specific extinction area SEA (m ² /kg)	1134±24	1323±28	1488±50
Average mass loss rate (g/m ²)	29±0	25±1	12±0

Table 3. Cone calorimetric data for melt blended polystyrene nanocomposites prepared using the 75% DPVPP modified clay

Composition	Commercial PS	3% Clay	5% Clay	10%Clay
Time to ignition (s)	36±5	54±2	43±3	44±3
PHRR (kw/m ²), (% reduction)	1411±8	638±10 (55)	416±12 (71)	268±1 (81)
Time to PHRR (s)	87±4	71±3	69±6	100±4
Average HRR (kw/m ²)	755±11	380±4	234±2	158±2
Total heat released (MJ/m ²)	102±1	76±3	58±5	54±0
Specific extinction area, SEA (m ² /kg)	1134±24	1481±11	1492±46	1475±27
Average mass loss rate (g/m ²)	29±0	20±1	13±1	10±1

Table 4. Cone calorimetric data for solution blended polystyrene nanocomposites prepared using the 75% DPVPP modified clay

Composition	Commercial PS	5% Clay	10% Clay
Time to ignition (s)	36±5	42±3	35±4
PHRR (kw/m ²) (% reduction)	1411±18	389±23 (72)	331±39 (77)
Time to PHRR (s)	81±4	98±10	100±4
Average HRR (kw/m ²)	755±1	239±1	204±18
Total heat released (MJ/m ²)	102±1	57±3	55±2
Specific extinction area, SEA (m ² /kg)	1134±24	1903±13	1903±11
Average mass loss rate (g/m ²)	29±0	13±0	11±1

Table 5. Cone calorimetric data for melt blended polystyrene nanocomposites (5% clay) with various phosphate-containing modified clay

Composition	Commercial PS	DPVBP modified clay, melt blending	DPVPP modified clay melt blending	VPA modified clay melt blending	PVPA modified clay melt blending	PVPA modified clay solution blend
Time to ignition (s)	36±5	42±3	40±5	31±2	42±2	39±5
PHRR (kw/m ²) (% reduction)	1411±18	893±12(37)	837±32(41)	638±2(55)	503±24(64)	360±1(74)
Time to PHRR (s)	81±4	112±3	93±7	73±4	57±1	120±10

Average HRR (kw/m ²)	755±11	625±12	571±20	400±12	292±14	222±21
Total heat released (MJ/m ²)	102±1	79±3	58±11	57±3	48±1	48±3
Specific extinction area, SEA (m ² /kg)	1134±24	1311±11	1323±18	1364±13	1818±43	1592±20
Average mass loss rate (g/m ²)	29±0	27±1	25±1	19±2	17±1	10±2

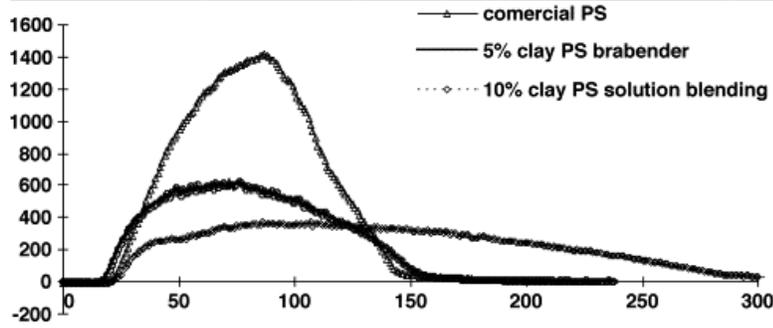


Fig. 11. Heat release curves for polystyrene nanocomposites prepared using the 55% DPVPP modified clay.

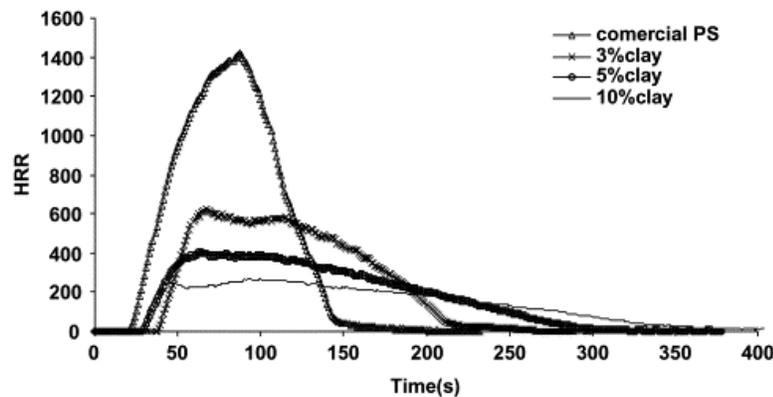


Fig. 12. Heat release curves for melt blended polystyrene nanocomposites, prepared using the 75% DPVPP modified clay.

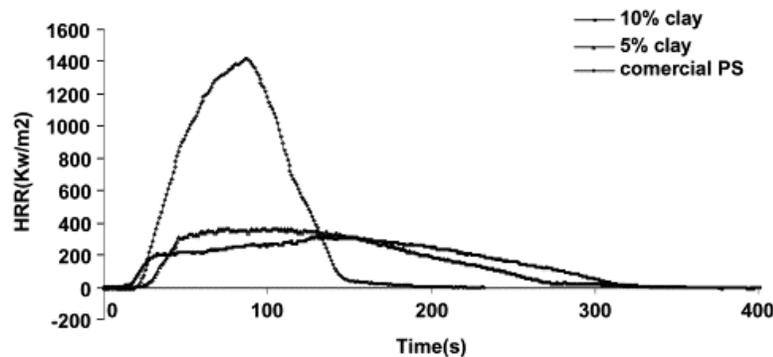


Fig. 13. Heat release curves for solution blended polystyrene nanocomposites, prepared using the 75% DPVPP modified clay.

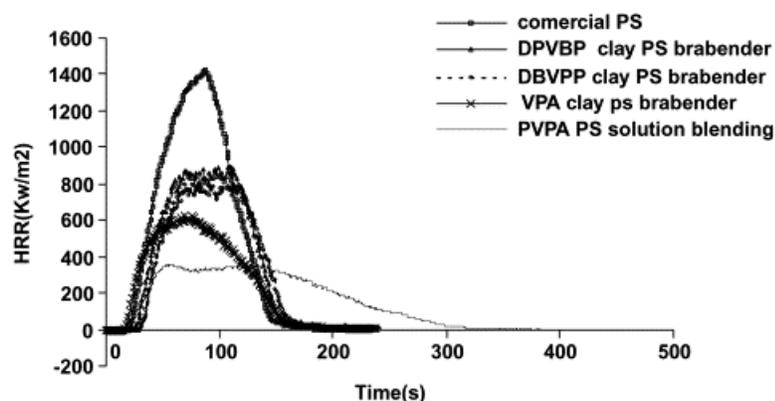


Fig. 14. Heat release curves for polystyrene melt blendd with various phosphate modified clays (5% clay).

There is a substantial reduction in the peak heat release. The previous maximum reduction that had been observed was about 60% for polystyrene nanocomposites and with these systems this number is raised to 70 and even 80% with some systems. The decrease in PHRR must be attributable to the presence of the phosphate clay. As expected the mass loss rate drops and the amount of smoke is constant or slightly increases.

Table 5 and Fig. 14 are the cone results for other vinylphosphate modified clay nanocomposites, specifically 1-phenylvinylphosphonic acid (PVPA) and vinylphosphonic acid (VPA). In both of these compounds, since there is a smaller amount of organic substituent, there is a larger phosphorus content. At a given clay content, the reduction in PHRR is greater for these materials with higher phosphorus content than for DPVPP and DPVBP. It is likely that the reduction in PHRR may be attributed to both the presence of the clay and the presence of the phosphorus.

It is of interest to note that the reduction in peak heat release rate correlates rather well with the phosphate content, as shown in Table 6. The solution blended system does not show the same regularity that is seen in the melt blended system and this suggests that melt blending is the preferred method for the preparation of these materials. It is known from previous work that the addition of a well-dispersed organically-modified clay causes a reduction in PHRR on the order of 50–60%; the observation that the reductions are larger in many cases suggests that phosphorus plays a role in the fire retardancy of these systems.

Table 6. Effect of phosphate on the reduction in PHRR

<i>Solution blending</i>	
8.60	73
11.25	72
18.75	77
<i>Melt blending</i>	
4.30	41
11.25	55
18.75	71
37.50	81

3.6. Evaluation of mechanical properties

All the mechanical properties, including Young's modulus, stress at break, strain at break of all nanocomposites and virgin polymers, are reported in Table 7. At low amounts of clay, the mechanical properties are improved. As the amount of clay increases, there is a decrease in all of the mechanical properties. It is possible that above some level, there is some plasticization, which results in a reduction of the melting point or softening point. Data for polystyrene with phosphate is unavailable, since the presence of the phosphate causes such a strong decrease in mechanical properties that it is not possible to even prepare the samples. The presence of the clay imparts some mechanical stabilization and it is only because of this that these samples can be prepared at all.

Table 7. Tensile strength at break of PS blending with DPVPP modified clay

Materials	Tensile strength at break (MPa)	Elongation at break (%)	Young's Modulus (GPa)
Commercial PS	24.6	1.5	1.60
5% Clay (55% DPVPP) PS brabender	13.1	1.1	1.86
10% Clay (55% DPVPP) PS solution blending	10.1	0.6	1.71
3% Clay (75% DPVPP) PS brabender	16.8	0.5	4.76
5% Clay (75% DPVPP) PS brabender	12.4	0.5	2.92
10% Clay (75% DPVPP) PS brabender	9.5	0.6	2.91
5% Clay (75% DPVPP) PS solution blending	11.8	0.5	2.81

4. Conclusions

The incorporation of phosphate as a component of an oligomeric ammonium salt that can be ion exchanged onto a clay permits the formation of nanocomposites in which phosphorus, one of the fire retardant elements, is nano-dispersed throughout a polymer. There is some loss in mechanical properties due to the presence of such a large amount of phosphate but the samples do still have some mechanical integrity. The reduction in peak heat release rate suggests that this system has potential for the formation of fire retardant polymeric systems.

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