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Grace Chigwada
Marquette University

Charles A. Wilkie
Marquette University, charles.wilkie@marquette.edu

Marquette University

e-Publications@Marquette

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Synergy Between Conventional Phosphorus Fire Retardants and Organically-Modified Clays Can Lead to Fire Retardancy Of Styrenics

Grace Chigwada

Department of Chemistry, Marquette University, Milwaukee, WI

Charles A. Wilkie

Department of Chemistry, Marquette University, Milwaukee, WI

Abstract

Polystyrene–clay nanocomposites combined with phosphorous-containing fire retardants have been prepared and used to explore the thermal stability and mechanical properties of the polymer formed. The amounts of fire retardants and clay used were varied to study the effect of each on thermal stability and mechanical properties of the polymer. The samples were prepared by bulk polymerization and analyzed by X-ray diffraction, thermogravimetric analysis, cone calorimetry, Fourier Transform infrared

spectroscopy and the evaluation of mechanical properties. The thermal stability of the polymers is enhanced by the presence of the phosphorus-containing fire retardants.

Keywords

Polystyrene; Nanocomposites; Phosphorus fire retardants; Thermal stability

1. Introduction

Polymer nanocomposites has been a topic of great interest over the past several years. It is usually believed that there are four advantages offered by nanocomposites formation: improved fire retardancy, increased heat distortion temperature, improved flexural modulus and a decrease in permeability. The original discovery by Toyota scientists in the late 1980s showed that a polyamide-6 nanocomposite containing 5% clay offers an increase of 40% in tensile strength, 68% in tensile modulus, 60% in flexural strength, 126% in flexural modulus while the heat distortion temperature increases from 65 to 152 °C and the impact strength is lowered by only 10%.¹ There is information available to say that the majority of properties of the polymer are usually improved by the presence of a small amount of clay.²

The enhanced fire retardancy that is claimed for nanocomposites results from the significant decrease in the peak heat release rate as measured by cone calorimetry. This is a real reduction and it may amount to 60% for polystyrene but the total heat released is unchanged, which means that all of the polymer does eventually burn but it may take a little longer. One also observes that the time to ignition is almost always shorter for a nanocomposite than for the virgin polymer. One exception to this generalization is with poly(methyl methacrylate) nanocomposites³ for which the time to ignition is very slightly increased. A consequence of these observations is that nanocomposites burn and are not suitable as fire retardant systems at this time.

Aromatic phosphates have for long been known as fire retardants. Triphenyl phosphate has been used in cellulosic materials and tricresyl phosphate has been used as a primary plasticizer for flexible vinyls. The fire retardant action of aromatic phosphates occurs mainly in the condensed phase and to a less extent in the gas phase. The mechanism by which this takes place is so far not well understood.^{4,5,6,8,9,10,11}

The focus of this study has been on preparing a polystyrene–clay nanocomposites which also contain a phosphorous fire retardant. This has been achieved by the bulk polymerization of styrene in the presence of clay and the phosphorous compound. Since there are a very large number of commercial phosphorus-containing fire retardants, high throughput methods have been used to evaluate these materials. Gilman et al.⁷ have used a high throughput extrusion technique to evaluate nanocomposite fire retardant polymer compositions.

2. Experimental

2.1. Materials

An organically-modified montmorillonite, dimethylbenzyl hydrogenated tallow ammonium (hydrogenated tallow is a mixture of ~65% C18, ~30% C16, ~5% C14) substituted clay, Cloisite-10A, was supplied by Southern Clay Products. Inc. The phosphorus-containing fire retardants were provided by Great Lakes Chemical Company, Clariant Corporation, Akzo-Nobel, Monsanto, Solutia and Rhodia. Other

materials, including styrene monomer, solvents, 2,2-azobis-isobutyronitrile (AIBN) and inhibitor removal columns were purchased from the Aldrich Chemical Company.

2.2. Instrumentation

X-ray diffraction (XRD) measurements were performed using Rigaku powder diffractometer with a Cu tube source ($\lambda=1.54 \text{ \AA}$) operated at 1 kW. Scans were taken from $2\theta=0.1-10^\circ$, step size= 0.11° and scan time per step of 20 s using the high-resolution mode. Thermogravimetric analysis, TGA was performed on a Cahn TG 131 unit under flowing N_2 (flow rate=60 ml/min) at a scan rate of $10^\circ \text{ C per minute}$ from 20 to 600° C . All TGA experiments have been done in triplicate. Reproducibility of temperature is $\pm 3^\circ \text{ C}$ while amount of nonvolatile residue is reproducible to $\pm 2^\circ \text{ C}$. TGA/FTIR was performed on a Cahn TG131 interfaced to a Mattson Research Series at $20^\circ \text{ C per min}$ under flowing nitrogen. Cone calorimeter measurements at 35 kW m^{-2} were performed using Atlas Cone 2. The spark was continuous until the sample ignited. Cone samples were prepared by compression molding the samples (20–50 g) into square plaques using a heated press. All samples were run in triplicate and the average value is reported. 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^{4,8} 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 by stamping from a sheet; the reported values are the average of five determinations.

2.3. Identification of potential fire retardants(FRs)

In order to do high throughput evaluation of the various phosphorus-containing fire retardants, samples with a mass of 1.5 g were prepared by bulk polymerization in 9 mm test tubes. These samples were prepared so that they contained 3% of the organically-modified clay and 15% of the phosphorus fire retardant; 0.5% of AIBN was used as the initiator. The polymerization temperature was gradually increased from 0 to 70° C over a period of 2 weeks. The long polymerization temperature helped prevent formation of bubbles in the sample. Obviously, a 2-week polymerization time cannot be considered high throughput. Nonetheless, the technique has the potential for high throughput. The small sample size requires long polymerization times in order to achieve homogeneous systems.

The flammability was tested by placing a flame in contact with the top of the sample for 1 min, then the flame was moved on to the next sample. The time for which each sample burned was measured; any sample that did not burn at all was considered promising and was evaluated in larger scale testing. In the case of the samples that either did not burn after the flame was removed or in which the flame was extinguished before the entire sample was consumed, char formation was observed at the surface of the cylinder. There was no evidence of intumescence in any case and the flame was always homogeneous. It is recognized that some useful fire retardants systems may not be considered by this technique, but three putative materials were identified that did not burn at all under the specified conditions. These materials which were further evaluated were: tricresylphosphate (TCP), trixylylphosphate (TXP) and resorcinoldiphosphate (RDP); no mention is made herein of the supplier of the material that was tested since the chemical name is available.

2.4. Further evaluation of phosphorous containing nanocomposites

Large samples, 130 g, of polymer/clay/FR nanocomposites containing any of the above three materials were prepared by bulk polymerization using 0.5% AIBN as the initiator. The composition of the

nanocomposites were varied over the range of 1–10% clay and 5 to 25% phosphate. The typical preparation involved placing the monomer, clay and FR agent in a beaker and then treating this in an ultrasonic bath at room temperature for 4 h, or until the clay was completely dispersed. The beaker was gradually, over a period of 7 days, raised to 65 °C and was maintained at this temperature for 1 day. The samples were then placed in a vacuum oven at 80 °C to remove excess monomer.

3. Results and discussion

3.1. Initial flammability test

Approximately 30 different phosphorus-containing compounds were tested using high-throughput techniques and Table 1 shows the identity of the materials and the burning time in our apparatus. It must be emphasized that this test does not follow any existing protocol and has been developed in this laboratory. As such it may, or may not, correlate with other tests for fire retardancy. One of the purposes of this work is to evaluate this test as a screening tool for fire retardant synergistic activity with clays. A total of four phosphorus-containing compounds were found that did not burn under the test conditions and three of these, tricresylphosphate (TCP), trixylylphosphate (TXP) and resorcinoldiphosphate (RDP) were selected for further study.

Table 1. Initial analysis of phosphorous+PS-clay nanocomposites

| Compound | Time/s to burn out after ignition |
|---|-----------------------------------|
| Phosphoric acid, methyl, dimethyl ester, dimethyl phosphate | 60 |
| Tributyl phosphate | 177 |
| Tricresylphosphate | 145 |
| Triphenyl phosphate | 125 |
| Isopropylated triphenylphosphate+triphenylphosphate | 137 |
| Tri(<i>n</i>) butylphosphate | 70 |
| Isopropylated triphenylphosphate and triphenylphosphate | 125 |
| Isopropylated triphenylphosphate, & triphenylphosphate | 75 |
| Tris(2-ethylhexyl)phosphate) | 110 |
| Tricresylphosphate | 0 |
| Phosphoric trichloride with bisphenol A diphosphate | 270 |
| Triphenylphosphates, isopropylated phosphates | 65 |
| Triphenyl phosphate | 70 |
| Trixylyl phosphate | 0 |
| Propylated triphenylphosphate | 185 |
| 2-ethylhexyldiphenylphosphate | 159 |
| Resorcinol diphosphate | 0 |
| 5,5,5',5'',5'',5''-hexamethyltris(1,2,3-dioxaphosphanone methane) 2,2',2'' trioxide | 130 |
| Phosphoryl chloride polymer/triphenyl phosphate | 75 |
| Isodecyldiphenylphosphate | 275 |
| 2-Ethyldiphenyl phosphate containing di-2-ethylhexylphosphate | 180 |
| Phosphoric acid, C _{12,14,16} alkylidiphenyl ester | 0 |
| Phosphoric acid, tris (2 ethylhexyl) ester | 67 |
| Trisooctylphosphite, phosphorous acid, trisooctyl ester | 470 |
| phosphoric acid, triphenyl ester) | 210 |
| Phosphoric acid,(2 chloroethyl)-bis-(2-chloroethyl) ester | 175 |
| (Trismonochloropropyl)phosphate | 175 |

| | |
|--|-----|
| Propanol 1,3 dichloro phosphate | 75 |
| Proprietary | 75 |
| Phosphoric acid, methyl dimethyl ester | 102 |
| 1,2 Ethane diammine phosphate | 105 |

3.2. X-ray diffraction characterization of the nanocomposites

It has already been shown that bulk polymerization of styrene in the presence of the Cloisite 10A gives intercalated nanocomposites.⁹ The important question is thus will the presence of the phosphates effect the nanodispersion of the clay throughout the polymer. This has been investigated using both X-ray diffraction (XRD) and cone calorimetry. The latter technique is used because it is known from previous work that nanocomposite formation causes a significant reduction in peak heat release rate while essentially no change is seen in the case of microcomposites. The XRD traces for the polystyrene nanocomposite containing various amounts of tricresylphosphate are shown in Fig. 1. It is significant that the d-spacing calculated from these traces is 3.5 nm and the d-spacing that has been observed for the PS nanocomposite without a phosphate is also 3.5 nm.⁹ Similar results are obtained for the other phosphates and one may conclude that intercalated nanocomposites are obtained for these systems.

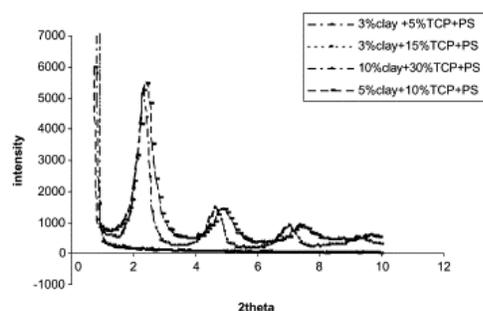


Fig. 1. XRD traces for styrene nanocomposites which also contain phosphates.

3.3. Thermogravimetric analysis

One can understand the course of the thermal degradation from thermogravimetric analysis (TGA). The important parameters are the onset temperature of the degradation, which is measured as the temperature at which 10% of the sample is lost, the mid-point of the degradation, another measure of thermal stability and the fraction of material which is non-volatile at 600 °C, known as char.¹⁰ The TGA data for all of the nanocomposites are shown in Table 2 while the TGA curves are shown in Fig. 2, Fig. 3, Fig. 4. The addition of clay to PS caused an increase in the degradation temperatures, however the addition of phosphate to the sample causes a decrease in the onset temperature and a smaller decrease in the mid-point temperature of the degradation. This is almost certainly due to the lower thermal stability of the phosphate, compared to the polymer; as is seen in Fig. 2, the most volatile species is the phosphate. The mid-point temperature is less depressed because the phosphate is entirely removed by the time the mid-point of the degradation is reached. In the particular case of RDP, the onset temperature is actually increased and this may be attributable to the greater thermal stability of RDP versus the other phosphates that were studied.

Table 2. TGA data for polystyrene nanocomposites that also contain various phosphates

| Sample | T _{10%} | T _{50%} | Char (%) |
|------------|------------------|------------------|----------|
| PS | 351 | 404 | 0 |
| PS+3% clay | 401 | 454 | 4 |

| | | | |
|--|-----|-----|----|
| "1" | | | |
| <i>Tricresylphosphate-containing nanocomposites</i> | | | |
| 15%TCP, 0%clay | 353 | 419 | 2 |
| 5%TCP, 3%clay | 356 | 436 | 6 |
| 10%TCP, 3%clay | 365 | 440 | 6 |
| 15%TCP, 3%clay | 374 | 439 | 6 |
| 30%TCP, 3%clay | 332 | 432 | 3 |
| 30%TCP, 5%clay | 329 | 420 | 7 |
| 15%TCP, 10%clay | 332 | 428 | 11 |
| "1" | | | |
| <i>Trixylylphosphate-containing nanocomposites</i> | | | |
| 15%TXP+PS | 370 | 437 | 3 |
| 15%TXP+3%clay+PS | 376 | 443 | 6 |
| 15%TXP+5%clay+PS | 371 | 439 | 6 |
| 30%TXP+PS | 346 | 428 | 2 |
| 30%TXP+5%clay+PS | 345 | 438 | 8 |
| 30%TXP+10%clay+PS | 340 | 426 | 10 |
| "1" | | | |
| <i>Resorcinoldiphosphate-containing nanocomposites</i> | | | |
| RDP15%+PS | 417 | 447 | 2 |
| RDP15%+3%clay+PS | 387 | 438 | 8 |
| RDP15%+5%clay+PS | 404 | 446 | 8 |
| RDP15%+10%clay+PS | 406 | 447 | 12 |
| RDP30%+PS | 415 | 450 | 8 |
| RDP30%+3%clay+PS | 407 | 450 | 8 |
| RDP30%+10%clay+PS | 386 | 441 | 13 |

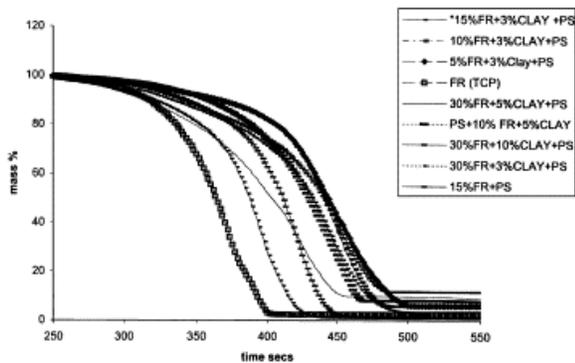


Fig. 2. TGA curves for polystyrene nanocomposites that also contain TCP.

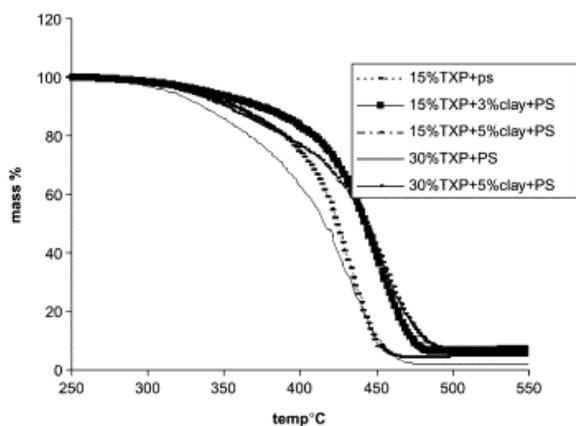


Fig. 3. TGA curves for polystyrene nanocomposites that also contain TXP.

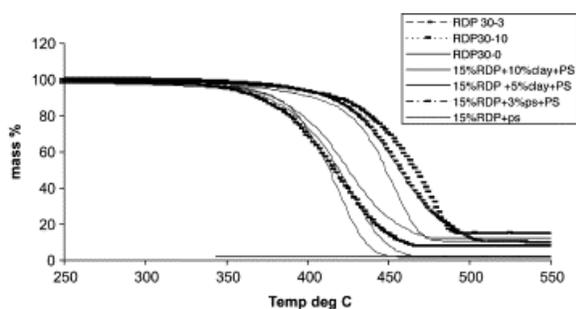


Fig. 4. TGA curves for polystyrene nanocomposites that also contain RDP.

When the degradation of a single component is investigated, one can be sure that one is observing only the degradation of that component. In cases where more than one component is present, reactions may occur between the components and this can mean that one is now examining the thermal stability of some new material which was not originally present. If the phosphates act as fire retardants in the condensed phase, then one can expect reaction while, if these are vapor phase active, it is not certain if reaction will or will not occur. TGA cannot tell in which phase the material may be active, but identification of the volatile species that evolve during the degradation may help to address this question.

3.4. TGA/FTIR evaluation of the phosphate-containing nanocomposites

Tricresylphosphate is a volatile compound and is thus expected to have vapor phase activity as a fire retardant. The evolution of TCP from blends of polystyrene with TCP and clay was followed by TGA/FTIR using the evolution of a peak at 960 cm^{-1} , which may be assigned to P–O–C vibration.¹¹ The first appearance of this band for TCP alone is at $230\text{ }^{\circ}\text{C}$. When clay is also present, this temperature increases by 10 to $30\text{ }^{\circ}\text{C}$, depending upon the composition of the material. Since the evolution of the TCP occurs at a higher temperature in the presence of clay, one may invoke some reaction between these components.

3.5. Cone calorimetric evaluation of the phosphate-containing nanocomposites

The technique of choice to evaluate the fire properties of polymeric materials is cone calorimetry. The parameters that may be obtained include the time to ignition, peak heat release rate data and the time to the peak heat release rate, the total heat released, the mass loss rate, and the specific extinction area, SEA, a measure of smoke. The usual observations for nanocomposites are that the time to ignition

is shorter, the PHRR is decreased, while the total heat released is unchanged, the mass loss rate is decreased while a somewhat larger amount of smoke is emitted. The former means that it is actually easier to ignite a nanocomposite than the virgin polymer, which implies higher, rather than lower, flammability. The decrease in PHRR means that the maximum size of the fire is smaller but, since the total heat released is unchanged, everything does eventually burn. The decrease in the mass loss rate goes along with the change in shape of the heat release rate curve. It is impossible to say with certitude what will be required to achieve fire retardancy for nanocomposites but one may make suggestions. It seems that the time to ignition must be increased and the total heat released must be decreased while maintaining the large reduction in PHRR. The reduction in total heat released means that not all of the sample burns, which implies that either the clay is forming a better barrier or that the additive prevents burning.

The cone data for the synergistic combination of the nanocomposite with the phosphates is shown in Table 3. The total heat released is significantly changed when phosphate is added, and it is lower the more phosphate that is added, regardless of the identity of the phosphate. The time to ignition is also variable; in some cases, it is lower for the synergistic combinations while in others, it is increased. In most cases, if one applies the normal $\pm 10\%$ error bars to the values, the time to ignition is more or less constant. There is a very significant reduction in the PHRR, in one case as high as 92%. The typical reduction that is observed for polystyrene nanocomposites is in the range of 50–60% so this is much larger and indicates a very high degree of fire retardancy. The plots of heat release rates are shown in Fig. 5, Fig. 6, Fig. 7, Fig. 8. For that same system, 30% RDP+5% clay, the total heat release is decreased by more than 50%. Unfortunately, the SEA is approximately doubled for this system. The presence of both a clay and a phosphate appears to give an enhanced reduction in the peak heat release rate and a very significant reduction in total heat released, both compared to the virgin polymer and to a styrene nanocomposite.

Table 3. Cone calorimetric data for polystyrene nanocomposites containing phosphates

| Sample | $t_{ign}(s)$ | $t_{PHRR}(s)$ | PHRR Kw/m ² (% reduction) | Total heat released (MJ/m ²) | Mass loss rate (g/stm ²) | Avg SEA (m ² /kg) |
|----------------|--------------|---------------|--------------------------------------|--|--------------------------------------|------------------------------|
| PS | 62 | 124 | 1419 | 109.7 | 17 | 1097 |
| PS+3%Clay | 57 | 85 | 610 (56) | 85.5 | 14 | 1695 |
| 15%TCP+PS | 59 | 108 | 1122 (20) | 63.4 | 14 | 1560 |
| 15%TCP+3%Clay | 59 | 109 | 495 (65) | 59.1 | 14 | 1803 |
| 30%TCP+3%Clay | 43 | 60 | 378 (74) | 49.5 | 14 | 2401 |
| 30%TCP+5%Clay | 53 | 87 | 342 (76) | 45.8 | 14 | 2310 |
| 30%TCP+10%Clay | 55 | 119 | 324 (79) | 47.3 | 14 | 2285 |
| 5%TCP+3%Clay | 60 | 108 | 704 (50) | 75.3 | 15 | 1560 |
| 10%TCP+3%Clay | 49 | 101 | 485 (65) | 62.4 | 15 | 2159 |
| 10%TCP+5%Clay | 48 | 115 | 508 (64) | 70.7 | 14 | 1660 |
| RDP5%+3%Clay | 67 | 101 | 502 (64) | 69.8 | 14 | 2057 |
| RDP5%+5%Clay | 59 | 97 | 458 (67) | 79.1 | 14 | 2641 |
| RDP15%+3%Clay | 68 | 118 | 474 (66) | 58.3 | 14 | 1995 |
| RDP30%+3%Clay | 75 | 129 | 358 (74) | 42.3 | 14 | 2157 |
| RDP15%+PS | 63 | 126 | 710 (49) | 56.8 | 15 | 1551 |
| RDP15%+3%Clay | 68 | 118 | 474 (66) | 58.3 | 14 | 1995 |
| RDP15%+5%Clay | 74 | 113 | 433 (69) | 57.5 | 14 | 2391 |
| RDP15%+10%Clay | 73 | 96 | 424 (70) | 60.1 | 14 | 1905 |
| RDP30%+PS | 77 | 128 | 499 (64) | 41.0 | 14 | 1852 |

| | | | | | | |
|----------------|----|-----|----------|------|----|------|
| RDP30%+3%Clay | 75 | 129 | 358 (74) | 42.3 | 14 | 2157 |
| RDP30%+5%Clay | 55 | 110 | 110 (92) | 43.1 | 14 | 2322 |
| RDP30%+10%Clay | 63 | 125 | 307 (78) | 44.7 | 14 | 1892 |
| 15%TXPI+PS | 64 | 137 | 890 (36) | 58.5 | 14 | 1443 |
| 15%TXP+3%Clay | 69 | 134 | 390 (72) | 62.4 | 12 | 1763 |
| 15%TXP+5%Clay | 58 | 101 | 449 (68) | 59.4 | 13 | 1884 |
| 15%TXP+10%Clay | 61 | 121 | 475 (66) | 63.2 | 13 | 1700 |
| 30%TXP+PS | 57 | 131 | 864 (38) | 53.9 | 15 | 2122 |
| 30%TXP+5%Clay | 38 | 98 | 313 (78) | 45.5 | 13 | 2287 |
| 30%TXP+10%Clay | 59 | 109 | 372 (73) | 49.4 | 13 | 2028 |

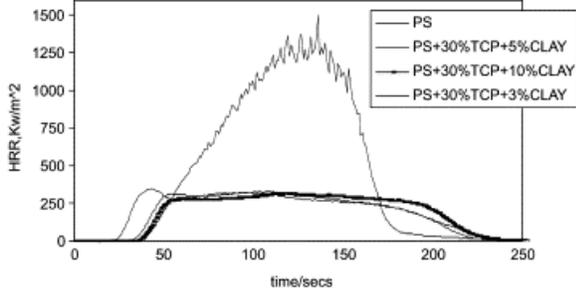


Fig. 5. Heat release rate curves for polystyrene and polystyrene nanocomposite containing TCP.

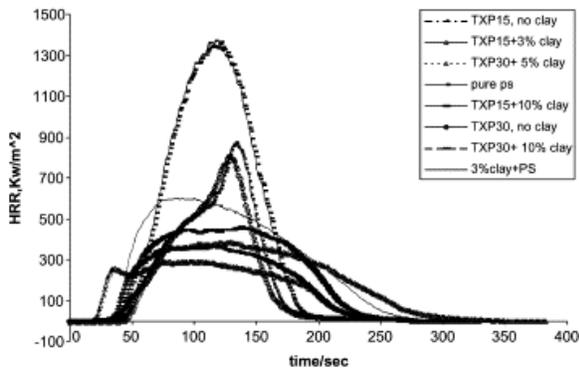


Fig. 6. Heat release rate curves for polystyrene and its nanocomposites containing TXP.

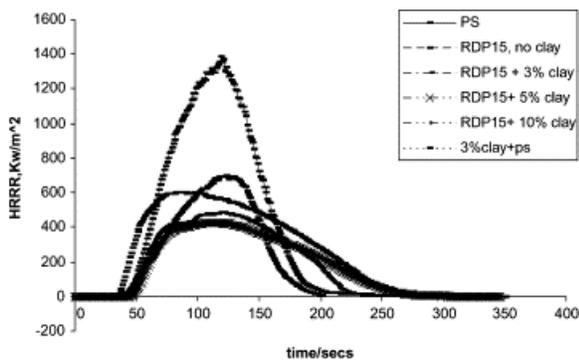


Fig. 7. Heat release rate curves for polystyrene and its RDP-containing nanocomposites.

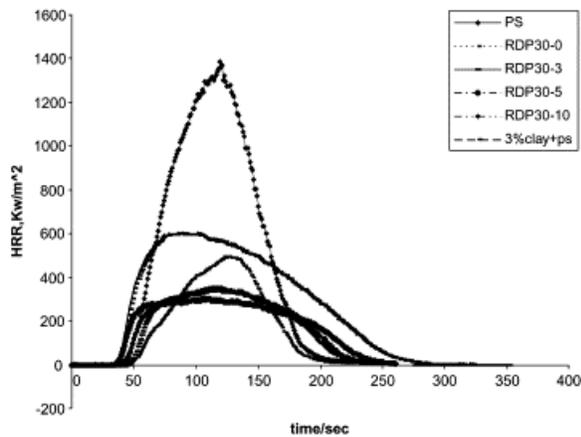


Fig. 8. Heat release rate curves for polystyrene and its nanocomposites containing 30% RDP.

3.6. Evaluation of mechanical properties

Mechanical properties of the TCP-containing system have been obtained and are shown graphically in Fig. 9, Fig. 10. From Fig. 9, one can see that at low amounts of TCP, the strength is enhanced by the presence of clay but above 15% TCP, there is no difference that may be attributable to the presence of the clay. The elongation of the material does not change below 15% TCP whether clay is present or absent but, above 15%, there is slightly enhanced elongation for the nanocomposite (Fig. 10). Up to about 15% TCP, the mechanical properties of the styrene nanocomposite are not significantly impacted by the presence of the fire retardant. Above this value, the mechanical properties are changed enough that it could not be used in situations where polystyrene is typically used.

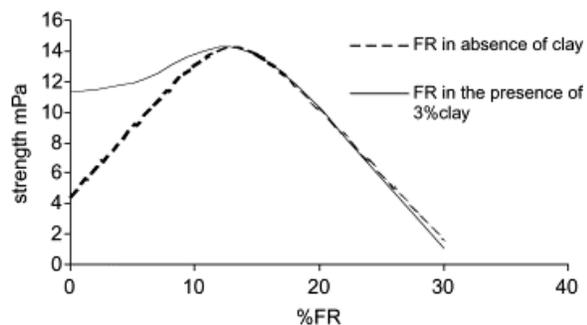


Fig. 9. Strength as a function of polystyrene and its nanocomposites.

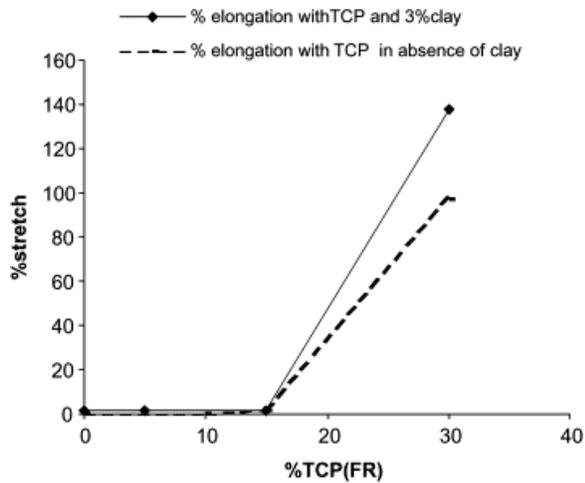


Fig. 10. Elongation of polystyrene and its nanocomposites in the presence and absence of TCP.

3.7. Evaluation of the phosphate-containing nanocomposites following the UL-94 protocol

The academic community usually evaluates fire retardancy by tests that are different than those used by our industrial brethren. The academic community is usually fond of the tests that were noted above while the industrial scientist relies on the UL-94 test. This is a test of the ease of ignition of a polymeric material. In order to communicate with the industrial community, we have evaluated these samples following the UL-94 protocol at a thickness of about 3 mm, and the results are shown in Table 4. In some cases, it is difficult to decide on which value should be given and therefore two values are recorded; the first is the most likely UL-94 result. The general observation is that at 30% of the phosphate, a rating may be obtained but the materials are NR at lower amounts of phosphate. As noted above, at 30% these materials have lost virtually all of their strength. This may prove to be a useful means to obtain fire retardancy of expanded polystyrene but it is unlikely to be useful for either rigid or high impact polystyrene.

Table 4. UL-94 results for polystyrene nanocomposites containing phosphates

| Sample | Observation |
|-------------------|-------------|
| 30% TCP+5%Clay+PS | V1 |
| 30%TCP+10%clay+PS | V1/VO ? |
| 30%TCP+3%Clay+PS | V2 |
| 30%RDP+5%Clay+PS | V2? |
| 30%RDP+10%Clay+PS | V0/V1? |
| 30%TXP+5%Clay | V2 |

4. Conclusions

Synergy between phosphate fire retardants and nanocomposite technology does occur and can lead to fire retardancy for styrenics, and there is every reason to believe that this methodology can be extended to other polymeric systems. A good result in the UL-94 test requires the presence of 30% of the phosphate; significant deterioration in the mechanical properties are observed at this level of phosphate. On the other hand, the presence of clay along with the phosphate does give a system that is workable. This synergy does hold promise to achieve fire retardancy through the combination of conventional fire retardants and clays.

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