

# Effect of a Nanoclay/Triphenyl Phosphate Hybrid System on the Fire Retardancy of Polycarbonate/Acrylonitrile–Butadiene–Styrene Blend

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**ABSTRACT:** The effect of a hybrid system of nanoclay and triphenyl phosphate (TPP) on the fire retardancy of a polycarbonate (PC)/acrylonitrile–butadiene–styrene (ABS) blend was examined in this study. The nanoclay in the polymers decreased the peak heat release rates (PHRRs) with no significant effect on the ease of ignition and times to extinguishment. Improvements in the flame retardancy were observed only when nanoparticles were used with conventional flame-retardant (FR) additives. Thermogravimetric analysis (TGA), cone calorimetry, and limited oxygen index (LOI)/UL 94 (Underwriters Laboratory) testing were used to investigate the thermal degradation, fire

behavior, and flammability of the materials. The results show that when we used a combination of TPP and nanoclay as an FR system, degradation of the polymer blends was reduced as the TGA curves shifted to higher temperatures. PHRR in cone calorimetry testing decreased from 1032 kW/m<sup>2</sup> for the PC/ABS blend to 300 kW/m<sup>2</sup> for the PC/ABS/(12% TPP–2% nanoclay) sample, and the LOI increased from 23 to 35%, respectively. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3435–3442, 2011

**Key words:** clay; flame retardance; nanocomposites; thermogravimetric analysis (TGA)

## INTRODUCTION

Polycarbonate (PC)/acrylonitrile–butadiene–styrene (ABS) blends are a target for flame retardancy because of their use as engineering polymer blends for electronic engineering and other applications in which flame resistance is a key property.<sup>1</sup> PC/ABS blends require modifications to decrease their flammability through the addition of flame-retardant (FR) compounds.

Bromine and chlorine compounds are the only halogen compounds with commercial significance as FR chemicals because of their higher efficiency over other FRs. Environmental regulations have restricted the use of halogenated FR additives because of the generation of toxic gases and high levels of smoke; this has initiated a search for alternative FR additives.<sup>2</sup> Nanoparticle fillers are highly attractive for this purpose because they can simultaneously improve the flammability and physical properties of polymer nanocomposites.<sup>2</sup> It is believed that<sup>3</sup> a

carbonaceous silicate char forms on the surface during burning and creates a protective barrier to heat and mass transfer. The accumulation of layered silicates on the burning surface is considered to be due to two possible modes. One is the layered silicates left on the sample surface as the result of the decomposition of the polymer matrix by pyrolysis. The other is the transportation of the layered silicates pushed by numerous rising bubbles of degradation products and the associated convection flow in the melt from the interior of the sample toward the surface.<sup>3</sup>

However, the char formed at the surface of the burning sample in UL 94 and limited oxygen index (LOI) tests is not effective enough to stop the flame, and the sample continues to burn slowly, ultimately displaying poor FR performances.<sup>4</sup>

When nanoclay was combined with a traditional FR additive, the nanocomposite FR formulation showed improved mechanical properties and enhanced FR performance at a lower FR additive concentration.<sup>5</sup> There have been a lot of studies involved in the investigation of the fire retardancy and thermal degradation of polymeric materials. Hussain et al.<sup>6</sup> investigated the thermal and fire performance of epoxy resins with organophosphorous and nanoclay. They found no evidence of synergy for the combination of phosphorous and clay in epoxy resins. Levchik and Weil<sup>1</sup> recently gave several overviews of

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**TABLE I**  
**Compositions of the Formulations**

Compound	PC (wt %)	ABS (wt %)	TPP (wt %)	Nanoclay (wt %)
PC/ABS	65	35	–	–
PC/ABS/2% nano	63.7	34.3	–	2
PC/ABS/4% nano	62.4	33.6	–	4
PC/ABS/6% nano	61.1	32.9	–	6
PC/ABS/10% TPP	58.5	31.5	10	–
PC/ABS/13% TPP	56.55	30.45	13	–
PC/ABS/15% TPP	55.25	29.75	15	–
PC/ABS/ (2% nano–8% TPP)	58.5	31.5	8	2
PC/ABS/ (2% nano–10% TPP)	57.2	30.8	10	2
PC/ABS/ (2% nano–12% TPP)	55.9	30.1	12	2
PC/ABS/ (4% nano–10% TPP)	55.9	30.1	10	4
PC/ABS/ (6% nano–10% TPP)	54.6	29.4	12	6

FRs for PC and PC/ABS. Hu et al.<sup>7</sup> studied the thermal stability of PC/ABS/montmorillonite nanocomposites and showed that PC/ABS/montmorillonite nanocomposites had a higher thermal stability and lower flammability. There is no available reports on the influence of triphenyl phosphate (TPP)–nanoclay hybrids on the fire retardancy and thermal degradation of PC/ABS blends.

In this study, the effects of TPP, nanoclay, and their hybrid on the thermal degradation and fire performance of PC/ABS blends were investigated.

## EXPERIMENTAL

### Materials and methods

PC (Makrolon 2858 of Bayer Co., Germany), with a density of 1.2 g/cm<sup>3</sup> and an MFI of 10 g/10 min (at 300°C, 1.2 kg), and ABS (SD0150, 27% acrylonitrile, Tabriz Petrochemical Co., TPC, Iran) with a density of 1.04 g/cm<sup>3</sup> and an MFI of 1.8 g/10 min (at 230°C, 3.8 kg), were supplied as pellets. The halogen-free FR used in this research was additive-type TPP (Merck Co.), with a 9.5% phosphorus content. Nanolin DK2, a modified organoclay [with methyl tallow bis-(2-hydroxyethyl) alkyl quaternary ammonium salt as a modifier] with a cation exchange capacity of 110–120 mequiv/100 g, was obtained from Zhejing Fenghong Clay Chemicals Co. of China.

### Compounding procedure

All ingredients (PC, ABS, TPP, and nanoclay) in a predetermined weight percentages were dry-mixed in a tumbler mixer before compounding. The formulations were prepared via melt mixing in a modular Brabender twin-screw extruder (Germany; length/

diameter = 40) with temperature profile of 200–250°C from the hopper to die at 130 rpm. The PC/ABS ratio was kept constant (65/35 wt %) in all of the formulations. The composition of the formulations is given in Table I.

### Thermal stability and flammability testing

#### Thermogravimetric analysis (TGA)

The weight loss in TGA testing indicates the rate of polymer decomposition and often gives important information related to the degradation mechanisms and other physical and chemical changes in various atmospheres. TGA tests were conducted with a PL TLI02 according to ASTM E 1131. The samples were tested under an N<sub>2</sub> atmosphere from 20 to 700°C at a heating rate of 10°C/min. The standard deviation of the TGA test results was about 1 wt %.

#### Cone calorimetry

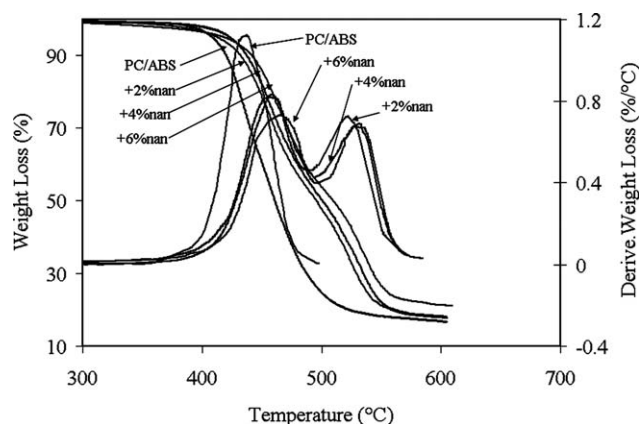
The flammability properties were measured with a cone calorimeter (Bayer Testing Technology) at an incident heat flux of 50kw/m<sup>2</sup> according to ISO 5660-1. The samples (100 × 100 × 3 mm<sup>3</sup>) were measured horizontally in a frame. The principle of the cone calorimeter is based on the relation between the oxygen depletion rate and the heat release rate (HRR). HRR was calculated with the assumption that 13,000 kJ of heat was released per 1 kg of oxygen consumed on burning. The peak heat release rate (PHRR), mass loss rate (MLR), and ignition time (*t*<sub>ign</sub>) data were collected during the test. In cone calorimetry analysis, the instantaneous amount of heat released from the unit surface of the burning material is usually defined as HRR, and it is considered as one of the most important characteristic quantities in evaluating the fire resistance. *t*<sub>ign</sub> measures the time that the entire surface of the sample burns with a sustained luminous flame. The reported cone calorimetry data are the average of three replicated experiments.

#### LOI testing

The LOIs of the formulations were determined with an LOI instrument (Analytical Instrument Factory, HC-2 model) on 100 × 6.5 × 3 mm<sup>3</sup> sample sheets according to ASTM D 2863. The test is based on the lowest oxygen gas concentration that still sustains combustion of the sample. This test is not directly relevant to a natural fire situation but provides numerical values for research and quality control.

#### UL 94 classification testing

The UL 94 classification test was carried out on 3 mm thick sheets according to ASTM D 3801. This



**Figure 1** TGA curves of the pure PC/ABS and PC/ABS/nano blends in an  $N_2$  atmosphere.

test provides qualitative classification of the samples through measurement of the ease of burning or extinguishment of a polymer sample.

## RESULTS AND DISCUSSION

### Thermal degradation and combustion

The burning behavior of polymeric materials is understood in terms of their ability to generate flammable volatile products on heating and their subsequent ignition. Accordingly, the combustion of organic polymers is a complicated process consisting of two stages: thermal oxidative degradation and burning. The burning process involves various steps, such as heat transfer, thermal oxidative decomposition to general flammable volatile products, the diffusion of gaseous products in solid state, and a gas-state combustion reaction of the mixture involving volatiles and oxygen.<sup>3</sup>

### TGA

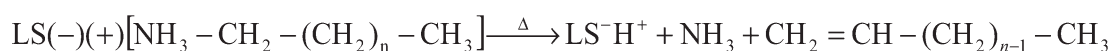
To understand the role of thermal degradation in combustion, TGA measurements on the blends were performed. Figure 1 shows the TGA curves of the pure PC/ABS and PC/ABS/nano composites. All of the PC/ABS/nano composites had a higher decomposition temperature than the neat PC/ABS resin (in relation to the peak temperature). As shown, the neat PC/ABS resin decomposed in a single-step process, whereas the PC/ABS/nano composites decomposed in a two-step process. A single-step decomposition in a TGA test of PC/ABS resin was also reported by Zong et al.,<sup>7</sup> but we did not find any report on the two-stage decomposition of PC/ABS–clay nano-

composites. In a study on polypropylene/clay nanocomposites,<sup>3</sup> a two-step degradation process was not observed. The two-step decomposition in TGA testing in our study may have been due to the interaction between nanoclay and matrix resins. This interaction led to a change in the thermal stability of the ABS resin and a two-step weight loss emerged in the TGA curve during the degradation process. We suggest that the thermal stability of the polymer–clay nanocomposite was unlikely to arise entirely from the barrier effect of the silicate layers themselves, as Hu et al.<sup>3</sup> also reported in their article. At the same time, with increasing nanoclay content, the decomposition temperature of the composites increased. As shown in Figure 1, the initial decomposition of the PC/ABS/nano composites occurred earlier than that of the neat PC/ABS resin. This suggests that the addition of nanoclay catalyzed the initial decomposition of the neat resin and decreased  $t_{ign}$ .<sup>8,9</sup> The addition of pristine clay or decomposed alkyl ammonium salts (nanoclay treated by alkylammonium salts) improved the thermal stability of the polymer in the next stages. It is known that the thermal decomposition of alkylammonium salts in clay galleries can take place through the Hoffman mechanism; this leads to the volatilization of ammonia and the corresponding olefin structure, as shown in Scheme 1. The acidic sites  $LS^-H^+$  are thus created on the silicate layers during heating and can improve the thermal stability.<sup>3</sup>

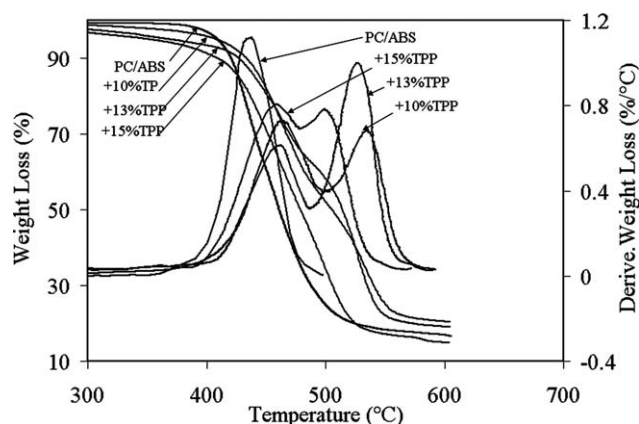
This suggests that there existed a physical crosslinking network structure composed of clay particles and polymer chains in these composites. This physical crosslinking effect could have delayed the thermal decomposition of the polymer matrix. The acidic sites generated by the thermal degradation of alkyl ammonium salts could have catalyzed the dehydrogenation process and crosslinked the polymer chains. The physical and chemical crosslinking network could have increased the thermal stability of the nanocomposites and delayed the thermal decomposition process.<sup>3</sup>

Figure 2 shows the TGA curves of the PC/ABS/TPP composites. All of the PC/ABS/TPP formulations had a higher decomposition temperature in comparison with neat PC/ABS resin and showed a preliminary weight loss.

Generally, the mechanism whereby phosphorus FR functions varies and depends on both the type of phosphorus compound and the specific polymer. These additives work in both the condensed and gas phases (with the condensed phase being predominant). In the condensed phase, phosphates and other phosphoric acid derivatives decompose thermally to



**Scheme 1**<sup>3</sup>



**Figure 2** TGA curves of the pure PC/ABS and PC/ABS/TPP blends in an  $N_2$  atmosphere.

form phosphoric acid, which is a good FR because of its own low volatility. The phosphoric acid acts as a dehydration catalyst in the presence of hydroxyl-rich polymers. It forms polyphosphoric acid when it is strongly heated. In some polymers, the phosphorous-rich FR causes an initial crosslinking reaction through the polymer. This implies that the polymer is prevented from volatilizing, and thus, less combustible species are formed.

In the gas phase, the hydrogen radicals react with oxygen to form hydroxyl and oxygen radicals. The hydroxyl and oxygen radicals react with the fuel and combustion is sustained. The volatile phosphorous compounds, such as  $P_2$ , PO,  $PO_2$ , and  $HPO_2$  produced during the thermal decomposition of the phosphorous-based FR, are effective FRs. They extinguish the flame by reducing the hydrogen-atom concentration in the gas phase. Many phosphorous-based FRs form water during a fire situation. This water is volatilized to form inert water vapor. Water vapor helps to extinguish the flame.<sup>10</sup>

The initial weight loss of the PC/ABS/TPP blends was due to the volatility of TPP. The lower the TPP content in the blends, the higher the solid residues in the PC/ABS/TPP blends. This is discussed later; in cone calorimetry testing, the volatilized TPP played a major role in the gas-phase flame-retardation effect. According to Kollman and Cote,<sup>11</sup> all FRs increase charring at a relatively low temperature and improve the thermal insulation characteristics.

The TGA curves of PC/ABS composites containing a hybrid of TPP and nanoclay are shown in Figure 3. As shown, when a hybrid of TPP and nanoclay was used, the initial decomposition of the blends occurred earlier than the initial decomposition of the PC/ABS/nano (where nano represents nanoclay) and PC/ABS/TPP blends. This observation resulted from the hybridization of TPP and the nanoclay.

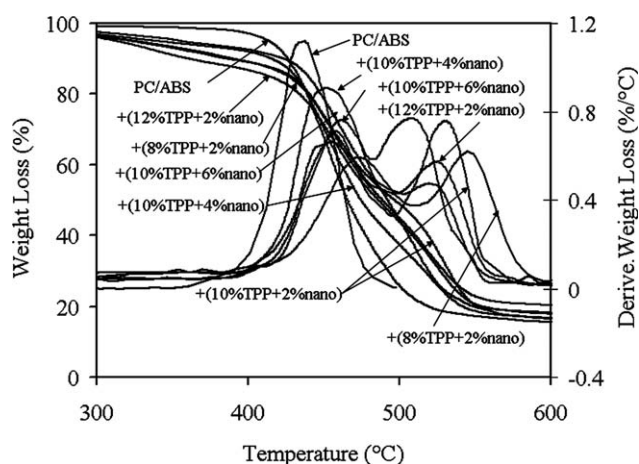
The TGA curves of the PC/ABS/TPP and PC/ABS/(TPP-nano) composites showed a three-step weight loss. The first weight loss occurred at temperatures between 300 and 400°C. This was due to the presence of weak P—O—C linkages in the TPP structure, which were very susceptible to chain scission, and its reaction with the PC decomposition products. Upon Fries rearrangement, shown in Scheme 2, PC generated phenolic groups, which reacted with TPP by a transesterification mechanism. As TPP has several reactive P—O—C bonds, one might expect it to react with another PC chain to crosslink. This effect was observed by Levchik et al.<sup>12</sup> in a study of a PC/ABS blend flame retarded by Resorcinol Bis (diphenyl phosphate).

It is believed that during the thermal decomposition process of TPP, phosphorous-rich residues are produced and protect the polymer from heat; this makes the materials more stable at higher temperatures.<sup>13</sup> This plays a critical role in phosphorous-based flame-retarded polymeric materials through the condensed-phase and gas-phase mechanisms.<sup>10,14</sup>

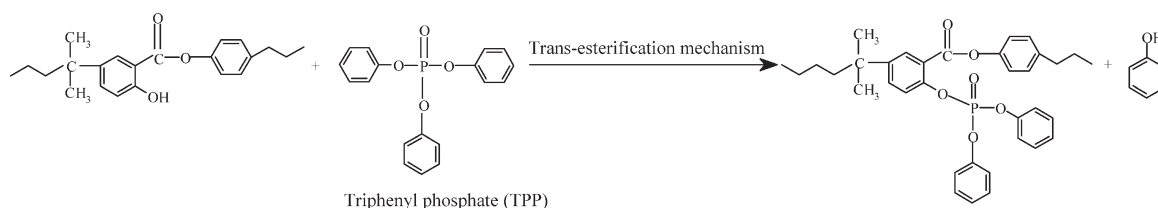
The degradation behavior of the hybrid system seemed to be more complicated than those of the composites with TPP or nanoclay because of the possible interactions between the components. The synergistic effect of TPP and nanoclay led to an improved thermal stability of the PC/ABS blend by promotion of the intercalation of nanoclay by TPP and its evaporation hindrance effect.<sup>15</sup> The evaporation hindrance effect of nanoclay was seen in TGA of the PC/ABS/(10% TPP-4% nano) and PC/ABS/(10% TPP-6% nano) blends. When the nanoclay content was increased, the initial weight loss due to TPP evaporation decreased.

### Cone calorimetry analysis

The combustion properties of the samples were characterized by means of a cone calorimetry



**Figure 3** TGA curves of the PC/ABS/TPP/nano blends in an  $N_2$  atmosphere.

Scheme 2<sup>12</sup>

technique. Some of the cone calorimetric data for the PC/ABS blends are shown in Table II. MLR and PHRR of the PC/ABS/TPP, PC/ABS/nano and PC/ABS/(TPP-nano) composites decreased with increasing TPP and nanoclay contents.

This suggests that the improved flammability of these composites was due to a difference in the condensed-phase and gas-phase decomposition processes.<sup>3</sup> The HRR plots for the PC/ABS blend and PC/ABS/nano composites are shown in Figure 4. The PC/ABS/nano system had a lower peak HRR but a little longer burn time; this suggests a dominant condensed-phase (char forming) mechanism of flame retardancy. The decrease in PHRR of PC/ABS/nano was mainly due to the delay in the thermal oxidative decomposition process. We also observed that the initial decomposition of the PC/ABS/nano composites occurred earlier than that of the neat PC/ABS resin and shortened  $t_{\text{ign}}$ . This was due to the decomposition of the polymer matrix catalyzed by clay. On the other hand, the acidic active sites  $\text{LS}^{-}\text{H}^{+}$  could have catalyzed the formation of a protective coatlike char on the nanocomposites, as mentioned previously in the TGA section. Therefore, MLR and PHRR decreased, and the thermal oxidative stability of the samples increased.

As shown in Table II, the MLR value of the PC/ABS neat resin was greater than that of the PC/ABS/nano composites. This trend in MLR changes in the cone calorimetry testing was similar to the variation

of the slope of the weight loss curve in TGA testing; these were observed visually in the TGA graph and MLR data of the PC/ABS/nano composites.

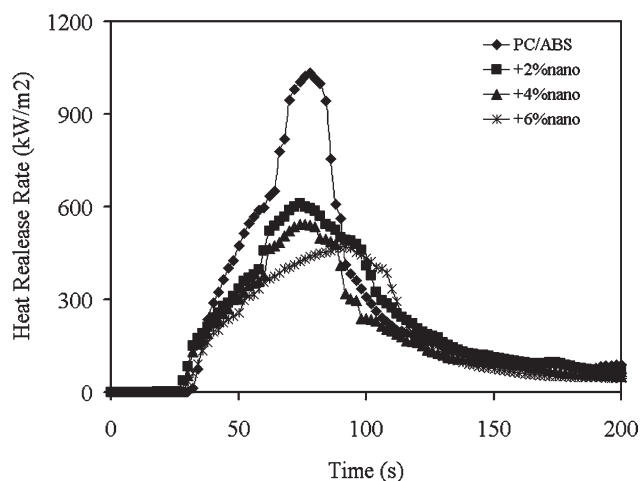
The HRR plots for the PC/ABS blend and PC/ABS/TPP composites are shown in Figure 5. The PC/ABS/TPP blends had more delayed  $t_{\text{ign}}$  values than the PC/ABS neat resin. TPP and, generally, all phosphate FRs, could have protect the polymer, simultaneously by the gas-phase and condensed-phase (char-forming) mechanisms. The combination of these two mechanisms may have been responsible for the delayed  $t_{\text{ign}}$ .<sup>10</sup> Moreover, TPP promoted the char formation of the PC phase and delayed the release of flammable products.<sup>14</sup> Because of the higher amount of volatilized TPP in the PC/ABS/15% TPP formulation,  $t_{\text{ign}}$  of this composite was higher than those of the PC/ABS/10% TPP and PC/ABS/13% TPP blends.

The variations of MLR in the PC/ABS/TPP formulations were the same as those of the PC/ABS/nano composites and were in agreement with the TGA results.

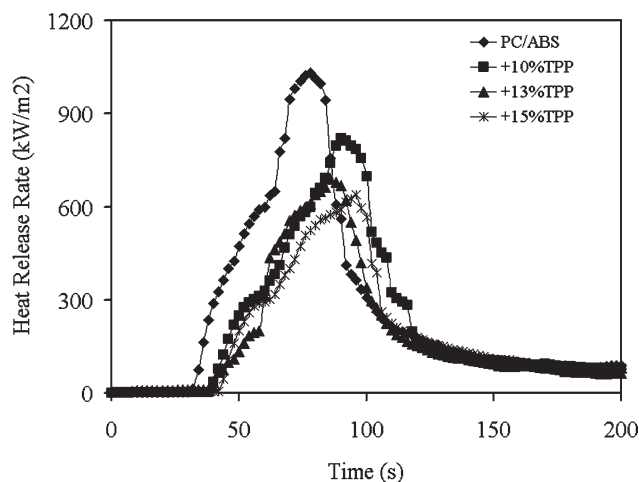
The HRR plots of the pure PC/ABS and PC/ABS/(TPP-nano) composites are shown in Figure 6. The amount of TPP in the blends showed a distinct effect on the prime retardation ( $t_{\text{ign}}$ ). The hindrance effect of the nanoclay at 4 and 6% in the PC/ABS/(TPP-nano) composites decreased the release rate of the volatilization of TPP and improved the flame

**TABLE II**  
Cone Calorimetric Data of the PC/ABS Blends  
at 50 kW/m<sup>2</sup>

Compound	$t_{\text{ign}}$ (s)	Peak HRR (kW/m <sup>2</sup> )	MLR (g m <sup>-2</sup> s <sup>-1</sup> )
PC/ABS	35	1032	4.87
PC/ABS/2% nano	30	600	4.45
PC/ABS/4% nano	29	543	3.94
PC/ABS/6% nano	28	470	3.23
PC/ABS/10% TPP	40	820	4.14
PC/ABS/13% TPP	44	689	4.03
PC/ABS/15% TPP	46	638	3.12
PC/ABS/(2% nano-8% TPP)	38	435	3.07
PC/ABS/(2% nano-10% TPP)	44	320	3.62
PC/ABS/(2% nano-12% TPP)	45	300	3.16
PC/ABS/(4% nano-10% TPP)	40	380	3.12
PC/ABS/(6% nano-10% TPP)	37	331	3.81



**Figure 4** HRR plots for the PC/ABS and PC/ABS/nano blends.



**Figure 5** HRR plots for the PC/ABS and PC/ABS/TPP blends.

retardancy. The minimum PHRR data was observed for the composite containing hybrid packages of 10% TPP–2% nano and 12% TPP–2% nano; however, PC/ABS/(12% TPP–2% nano) was the preferred formulation due to its longer burning time.

#### LOI and UL94 testing

The LOI and UL 94 test results are summarized in Table III. The PC/ABS/nano composites showed a slight decrease in LOI data, for example, from 23% for the PC/ABS neat resin to 22% for the PC/ABS/2% nano. With increasing nanoclay content to 4 and 6 wt %, the LOI decreased to a lower value; this was because of the promoted burning of alkylammonium with nanoclay treatment. Meanwhile, an opposite trend in the LOI test results was observed for the PC/ABS/TPP composites at various TPP contents. LOI of the PC/ABS/10% TPP composite (26%) was higher than that of the PC/ABS neat resin (23%). The PC/ABS/(8% TPP–2% nano) composite showed an obvious synergy with an LOI of 31%. The improved flammability behavior of the TPP–nano system was attributed to the enhanced barrier properties of their hybrid and also to improved char formation due to increased viscosity.<sup>1</sup>

The comprehensive effect of TPP on the LOI test results and, from the other side, the significant effect of nanoclay on the cone calorimetry test results of the nanocomposites were the reasons for the use of their hybrid as an FR package for the PC/ABS resin.

PC/ABS, PC/ABS/nano, and PC/ABS/TPP failed in vertical UL 94 test and were burned completely. In the horizontal test, they self-extinguished before the mark at 25 mm. The failure of the samples in the vertical UL 94 burning test may have been due to

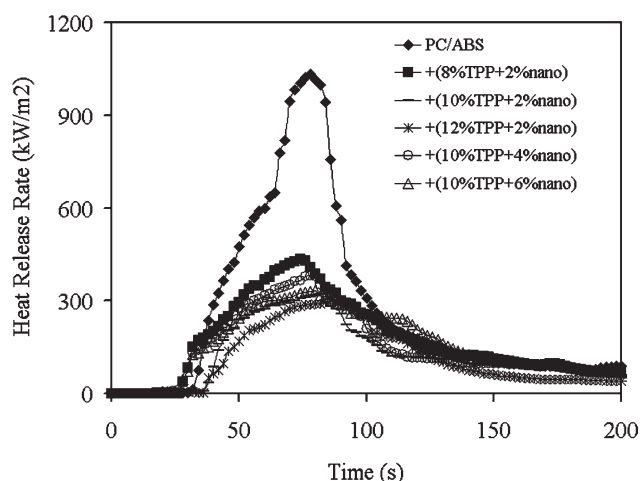
the porosity of char, formed during the burning of TPP/nanoclay. The durability of porous char was not strong enough to prevent the release of combustible gases and inhibited flame propagation; this led to an HB rating in this test. The PC/ABS/(TPP–nano) hybrid composites showed immediate self-extinguishment after the burner was removed, and the V-0 classification was achieved.

#### Synergetic effect of the nanoclay/TPP hybrid system on the fire retardancy of the PC/ABS blend in LOI testing

As shown in Table III, LOI of PC/ABS/2% nano was 22%, that is, even 1% lower than the PC/ABS neat resin. The LOI of PC/ABS/10% TPP was 26%, which was 3% higher than the value of PC/ABS neat resin. With the hybrid package of FRs, an LOI of 33% for the PC/ABS/(10% TPP–2% nano) composite was obtained; this was much more than the value expected according to the mixing rule (25%). The considerable improvement in LOI of PC/ABS/(10% TPP–2% nano) was attributed to the synergistic effect of the nanoclay/TPP hybrid package on the flammability behavior of the PC/ABS resin. According to our calculation, this finding was also supported by the LOI data of the other formulations.

#### Synergetic effect of the nanoclay/TPP hybrid system on the fire retardancy of the PC/ABS blend in the cone calorimetry analysis

The PHRR value of PC/ABS/2% nano was 600 kW/m<sup>2</sup> (Table II). This indicated a 432 kW/m<sup>2</sup> improvement in PHRR of the PC/ABS neat resin (1032 kW/m<sup>2</sup>). The use of TPP in the PC/ABS/10% TPP sample led to an improvement of 212 kW/m<sup>2</sup> with a PHRR of 820 kW/m<sup>2</sup>. The PC/ABS/(10% TPP–2%



**Figure 6** HRR plots for the PC/ABS and PC/ABS/TPP/nano blends.

TABLE III  
Fire Behavior of the PC/ABS Blends

Compound	LOI (%)	$t_1$ (s) <sup>a</sup>	$t_2$ (s) <sup>b</sup>	$t_3$ (s) <sup>c</sup>	$V$ (mm/min) <sup>d</sup>	UL 94 (3 mm)
PC/ABS	23	–	–	–	39	HB
PC/ABS/2% nano	22	–	–	–	37	HB
PC/ABS/4% nano	21	–	–	–	36	HB
PC/ABS/6% nano	20	–	–	–	35	HB
PC/ABS/10% TPP	26	–	–	–	38	HB
PC/ABS/13% TPP	27	–	–	–	36	HB
PC/ABS/15% TPP	29	–	–	–	35	HB
PC/ABS/(2% nano–8% TPP)	31	10	9	26	–	V-0
PC/ABS/(2% nano–10% TPP)	33	8	7	25	–	V-0
PC/ABS/(2% nano–12% TPP)	35	9	8	27	–	V-0
PC/ABS/(4% nano–10% TPP)	34	7	6	23	–	V-0
PC/ABS/(6% nano–10% TPP)	33	6	5	21	–	V-0

<sup>a</sup> Flaming time per flame application.

<sup>b</sup> Flaming time per flame after the second application.

<sup>c</sup> Afterglow time.

<sup>d</sup> Burning rate for specimen at 3–13 mm.

nano) sample showed improved flammability properties with the use of the hybrid package system with a PHRR of 320 kW/m<sup>2</sup>. This was clearly more than the expected value of 338 kW/m<sup>2</sup> estimated according to the mixing rule; this was attributed to the synergetic effect of TPP–nano in the flame retardation of the PC/ABS composites.

In some formulations, for example, PC/ABS/(6% nano–10% TPP), each member of the package (TPP and nanoclay) additively played their role in decreasing the PHRR value; this was still an advantage for the hybrid system, but no synergistic effect could be addressed.

The same effect was observed for the MLR value of samples. The combustion rate of PC/ABS/2% nano with an MLR of 4.45 g m<sup>-2</sup> s<sup>-1</sup> was 0.42 g m<sup>-2</sup> s<sup>-1</sup> lower than that of the PC/ABS neat resin. The MLR of PC/ABS/10% TPP (4.14 g m<sup>-2</sup> s<sup>-1</sup>) was 0.73 g m<sup>-2</sup> s<sup>-1</sup> lower than the value of the PC/ABS neat resin (4.87 g m<sup>-2</sup> s<sup>-1</sup>). The PC/ABS/(10% TPP–2% nano) sample showed a decreased combustion rate when the hybrid package system with an MLR of 3.62 g m<sup>-2</sup> s<sup>-1</sup> was used. This was clearly lower than the expected rate of 3.72 g m<sup>-2</sup> s<sup>-1</sup> estimated by the mixing rule and was attributed to the synergetic effect of the hybrid system.

As discussed for some previous formulations, PC/ABS/(6% nano–10% TPP), TPP, and nanoclay additively played their role in decreasing the MLR value; this was still an advantage, but no synergistic effect could be addressed for the hybrid package system.

As discussed so far, the use of the hybrid of nanoclay and TPP enhanced the thermal stability of the composites at elevated temperature, as shown by the TGA test results. The cone calorimetry analysis revealed that the simultaneous use of TPP and nano-

clay in the formulations promoted the formation of a more thermally stable char and, as a physical protective barrier, led to the decrease of HRR and MLR, as evaluated by cone calorimetry.

## CONCLUSIONS

The combustion behavior and thermal stability of the PC/ABS blend and its composites with TPP, nanoclay, and their hybrid were examined in this study. On the basis of the experimental works and test results, the following conclusions were drawn:

- The use of a combination of nanoclay and traditional FR improved the flame retardancy with enhanced mechanical properties at a lower concentration of traditional FR additives.
- The protective char layer and physicochemical crosslinking were counted as the reasons for the improved thermal stability of the PC/ABS composites with a hybrid of TPP and nanoclay.
- The MLR and PHRR results in the cone calorimeter analysis for the composites containing a hybrid of nanoclay and TPP were lower than those of the other formulations. The enhanced thermal stability in TGA and the improved PHRR of the PC/ABS/(TPP–nano) composite were evidence of the synergistic effect of nanoclay and TPP in some formulations.
- With increasing nanoclay content, the LOI value decreased. For PC/ABS/TPP composites, an increase in LOI was observed with increasing TPP content. The PC/ABS/

(TPP–nano) composite showed an obvious synergetic effect in the LOI test results.

- The PC/ABS/(TPP–nano) hybrid composites showed immediate self-extinguishment with V-0 classification.

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