

## Flame retardancy and mechanical properties of pet-based composites containing phosphorus and boron-based additives

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**ABSTRACT:** Flame retardancy of poly(ethylene terephthalate), PET, was improved using different flame retardant additives such as triphenylphosphate, triphenylphosphine oxide, zinc borate, and boron phosphate (BP). Composites were prepared using a twin screw extruder and subsequently injection molded for characterization purposes. The flame retardancy of the composites was determined by the limiting oxygen index (LOI) test. Smoke emission during fire was also evaluated in terms of percent light transmittance. Thermal stability and tensile properties of PET-based composites were compared with PET through TGA and tensile test, respectively. The LOI of the flame retardant composites increased from 21% of neat PET, up to 36% with the addition of 5% BP and 5% triphenyl phosphate to the matrix. Regarding the smoke density analysis, BP was determined as an effective smoke suppressant for PET. Enhanced tensile properties were obtained for the flame retardant PET-based composites with respect to PET. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42016.

**KEYWORDS:** composites; flame retardancy; mechanical properties; PET; smoke density

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### INTRODUCTION

Polymers, like the majority of other organic compounds, will burn readily in air or oxygen. The flammability of polymers is a serious issue and severely limits their applications.<sup>1,2</sup> Recent fire-safety concerns placed even more stringent requirements for the materials used in enclosed and inescapable areas, such as electronic enclosures, high-rise buildings, submarines, ships, and aircraft cabins.<sup>3</sup> Light-weight, high-performance polymeric materials offer many advantages in these applications over conventional metallic and ceramic materials, but the fire risk is considerably increased because of the flammability of the plastic materials and possible release of toxic by-products. Previous studies and research reports have shown that most of the casualties during fire are as a result of smoke formed during fire.<sup>4,5</sup> Smoke has asphyxiant effect on living beings. Thus it causes humans not to breath sufficiently. Most of the smokes contain carbon monoxide and other unburnt hydrocarbons.<sup>6</sup> In some cases, other poisonous gases are also formed, especially when halogenated compounds are used, i.e., hydrogen halides.<sup>7</sup> This study also focuses on the formation of sooty smoke during fire which is detectable by the light transmittance test. Polymers that have aromatic groups in the structure tend to release more smoke than nonaromatic polymers, due to their high carbon

content.<sup>8</sup> Poly(ethylene terephthalate), PET, is in this group of polymers having aromatic ring in the backbone.

Because of outstanding properties such as high rigidity, thermal stability, and chemical resistance, PET is widely used in textile, packaging and engineering materials industries.<sup>9,10</sup> However, its application is limited by its high flammability. Therefore, flame retardant additives can be used to improve the fire retardancy. These additives can be halogen, phosphorus, nitrogen, or silicon containing compounds in nanometer particle size.<sup>11</sup> The widely used flame retardant components for PET have been halogenated compounds and inorganic/organic additives.<sup>12</sup> Halogenated flame retardant additives have been banned gradually due to the strict governmental regulations as the toxic gases evolved during the fire caused by the halogens.<sup>4,13</sup>

In literature, there are several studies reporting on different flame retardant chemicals or additives such as phosphorus-based compounds,<sup>7</sup> nanofillers,<sup>9,10,14,15</sup> and sulfur containing compounds.<sup>16</sup> In many cases, these additives have shown a synergistic effect in enhancing the flame retardant capability of the composite materials obtained. Examples of these flame retardant enhancers are phosphorous compounds,<sup>17</sup> metal hydrates, antimony oxide, boron compounds, metallic zinc, and its compounds,<sup>18,19</sup> and other inorganic additives.<sup>20–25</sup>

**Table I.** Limiting Oxygen Index and Smoke Density Test Results of Neat PET and the Flame Retardant Composites

Sample	Formulation	LOI value (%)	Light transmittance (%)
PT	Neat PET	21.0	78
PT1	TPP (2) + PET (98)	24.0	75
PT2	TPP (10) + PET (90)	26.5	67
PT3	TPP (15) + PET (85)	29.5	62
PT4	TPP (5) + TPP Ox (5) + PET (90)	30.5	83
PT5	TPP (10) + TPP Ox (10) + PET (80)	31.0	76
PT6	TPP (5) + BP (5) + PET (90)	36.0	85
PT7	TPP (10) + BP (10) + PET (80)	32.5	87
PT8	TPP (2) + BP (5) + PET (93)	33.0	90
PT9	TPP (5) + ZB (5) + PET (90)	29.0	78
PT10	TPP (5) + BP (5) + ZB (5) + PET (85)	29.5	84
PT11	ZB (8) + PET (92)	23.5	81
PT12	BP (8) + PET (92)	30.5	99
PT13	BP (5) + ZB (5) + PET (90)	25.5	92

When burning, if the material is exposed to a sufficiently large heat flux radiated from a fire, the polymer matrix and organic fibers will thermally decompose to yield volatiles, solid carbonaceous char, and airborne soot particles. The volatiles consist of a variety of vapors and gases, both flammable (e.g., carbon monoxide, methane, and low molecular organics) and nonflammable (carbon dioxide, water). These volatiles diffuse from the decomposing composite into the flame zone, where the flammable volatiles react with oxygen in the fire atmosphere leading to the formation of the final combustion products (usually carbon dioxide, water, smoke particles, and a small amount of carbon monoxide) accompanied by the liberation of heat.

Flame retardant additives have different acting mechanisms in polymeric materials.<sup>26,27</sup> For example, phosphorus acts as a flame retardant in the gas and/or condensed phase, depending on the chemical nature and thermal stability of the host polymer. The gas phase mechanism dominates in most thermoplastics and nonoxygenated thermoset polymers. This mechanism involves the release of radicals containing phosphorus from the polymer at elevated temperature, although to be effective the volatilization process must occur below 350–400°C; otherwise the polymer itself will decompose. A variety of radical species can be released into the flame, depending on the temperature and composition of the phosphorus-containing flame retardant. The phosphorous-based compounds work mostly in the condensed phase to form a char layer. An effective char layer is difficult to ignite, it insulates the polymer beneath from the thermal degradation, blocks oxygen access, and prevents the release of degradation products.<sup>23,24</sup>

Boron-based flame retardant additives have been claimed to act at the condensed phase during burning.<sup>28</sup> In general, boron-based additives form a glassy protective layer at the condensed phases interrupting the contact of unburnt polymer and flame zone as well as the diffusion of the flammable gases formed during fire.<sup>29</sup> Boron-based flame retardant additives also have smoke suppressant effects. During burning, the oxygen released

from the structure could combine with the carbon monoxide to form carbon dioxide.

Herein, we report the preparation and characterization of flame retardant PET composites using different flame retardant additives such as triphenyl phosphate, triphenyl phosphine oxide, zinc borate, and/or boron phosphate (BP) at their varying amounts up to 20 wt %. To the best of our knowledge, studies on combined effects of these additives on PET matrix are limited in literature.<sup>30</sup> The composites were characterized in terms of their flame retardancy, thermal stability, smoke suppressant, and mechanical properties.

## EXPERIMENTAL

### Materials

Crystalline poly(ethylene terephthalate) (PET) was purchased from AdvanSA, Adana, Turkey. Triphenyl phosphate (TPP) and triphenyl phosphine oxide (TPP Ox) were purchased from Aldrich Chemicals. BP was synthesized by microwave method<sup>30,31</sup> and zinc borate ( $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3.5\text{H}_2\text{O}$ ) was synthesized from boric acid and zinc oxide as previously reported.<sup>32</sup>

### Experimental Procedure

Poly(ethylene terephthalate) was dried under vacuum at 130°C prior to melt blending for 4 h. The flame retardant additives were used as received or synthesized. PET-based composites were prepared by mixing the additives up to 20% in total by weight to PET matrix using a corotating twin screw extruder (Thermo Prism TSE-16-TC, L/D = 24). The temperature profile of 230–240–240–250–255°C and a screw speed of 200 rpm were applied during the extrusion in the experiments. Extruded composites were molded in an injection molding machine (DSM Xplore, 12 mL Micro Injection Molding Machine) at 14 bars, 255°C barrel temperature and 25°C mold temperature. Prior to molding, composites were dried at 120°C for 4 h under vacuum. The compositions of the additives in the polymer matrix are given in Table I. The numbers in parenthesis represent the

weight percentages of the additives and the PET polymer matrix.

### Characterization Experiments

**Limiting Oxygen Index (LOI) and Smoke Density Tests.** The PET-based composites were characterized in terms of flame retardancy and smoke density. LOI measurements were performed according to the ASTM D2863 standard using a Dynisco Limiting Oxygen Index Test Machine. The smoke densities of the composites were determined in terms of percent light transmittance by a Dynisco optical smoke detector, attached to the top of the LOI chamber.

**Thermogravimetric Analysis.** TG/DTA analyses of the final products were performed using a Shimadzu DTG-60/DTG-60A thermal analyzer. The measurements up to 900°C were performed under N<sub>2</sub> flow. A uniform heating rate of 10°C/min was applied during the measurements.

**Py-MS Analysis.** Py-MS analyses were performed by a direct pyrolysis mass spectrometry (DPMS) system having 5973 HP quadrupole mass spectrometer. The temperature was increased up to 500°C at a heating rate of 10°C/min. Each experiment was repeated at least twice to ensure reproducibility.

**Mechanical Properties.** Mechanical properties of the composites were determined in terms of tensile properties (ASTM D638), which were measured with a Shimadzu Autograph AG-100 KNIS MS universal testing machine at room temperature. Five specimens of each sample were tested and their average and standard deviations were reported.

## RESULTS AND DISCUSSION

### Flame Retardancy and Thermal Characterization of PET-Based Composites (LOI, TGA)

The codes of composites prepared, their formulae, results of LOI tests and the light transmittance percentages are listed in Table I. The LOI is a worldwide accepted and accurate test method to characterize flammability of plastics. The LOI value of crystalline PET is 21.0% and the light transmittance is 78%. All of the composites prepared have a higher LOI value than neat PET. For the triphenyl phosphate (TPP) content values of 2, 10, 15 (PT1, PT2, and PT3) the LOI values are 24.0, 26.5, 29.5%, respectively but the smoke density increases as TPP content in the polymer matrix increases, which is indicated by the decrease in light transmittance values as 75, 67, and 62%, respectively. All of the other composites have a lower smoke density than neat PET, except for the aforementioned composites and PT5, which contains TPP 10 wt % and TPP Ox 10 wt % in the polymer matrix.

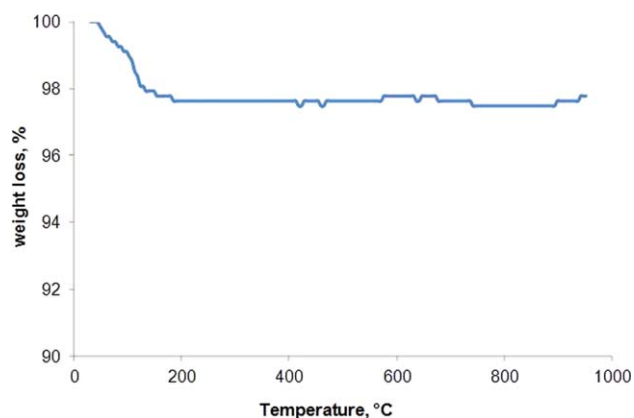
The addition of 8 wt % BP to the polymer matrix (PT12) results in a LOI value of 30.5% while the same amount of zinc borate (ZB) in the polymer matrix (PT11) causes a slight increase in the LOI of neat PET, which is 23.5%. The highest LOI values are obtained with TPP and BP combination in the polymer matrix. When 2% TPP is combined with 5% BP (PT8), a LOI value of 33.0% is obtained; further increase of TPP content to 5% (PT6), increases LOI value to 36.0%. The use of either BP or ZB with TPP is compared in samples PT6

**Table II.** TGA Analysis Results of Selected Flame Retardant Additives

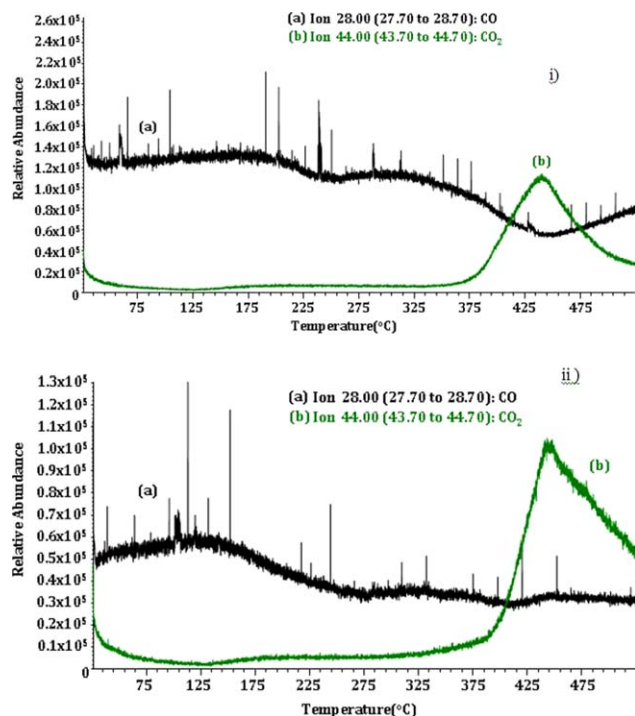
Sample	Decomposition temperatures			Weight loss (%) at 800°C
	$T_{\text{initial}}$ (°C)	$T_{\text{final}}$ (°C)	$T_{\text{maximum}}$ (°C)	
TPP	180.0	320.0	303.0	100.0
TPPO	200.0	350.0	331.0	99.7
BP	-	-	-	2.3
ZB	280.0	450.0	396.0	12.9

and PT9. It is observed that although the use of ZB with TPP gives a higher LOI (PT9) value (29%), a much higher LOI value (36%) is obtained with the combined use of BP and TPP (PT6), which points to a synergistic effect of BP and TPP. BP and TPP are the two most effective flame retardants for the PET matrix. The acting mechanisms of those additives are proposed as for BP in the condensed phase, and for TPP in both condensed and gas phase.<sup>33</sup> As mentioned before, the increase of flame retardancy related to the addition of BP and ZB are mainly because of the formation of a protective glassy layer in the polymer matrix at high temperatures, which protects the unburnt polymer from the flame. In addition, ZB loses its crystalline water during fire (Table II), which dilutes the flammable gases, and the released water also acts as a heat sink, decreasing the temperature at the burning zone. Besides, BP does not decompose till the end of test temperature, 1000°C, Figure 1. It only loses 2.3% of its weight. The high thermal stability and the high char yield, in other words the low weight loss (Table II) of BP might be the reason for the high LOI value attained for BP added polymer composites.

TPP is expected to increase the char formation of the polymer as it has three phenyl groups and a high carbon content, the acting mechanism of which is in the condensed phase. It decomposes first to pyrophosphoric acid, which promotes the formation of char. Furthermore, the decomposition products of TPP function in the gas phase in a manner similar to halogenated flame retardant additives by inhibiting the hydrogen (H•) radicals. Thus the formation of phosphate-based ions and



**Figure 1.** TGA of boron phosphate. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 2.** Single ion current program of CO and CO<sub>2</sub> during (i) PET and (ii) PET (92%)/BP (8%) (PT12) decomposition. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

radicals have been proposed in the literature to inhibit the hydrogen cycle during fire.<sup>34–36</sup> Since the phosphate based flame retardants have been found to be effective in the polymers containing oxygen in the main backbone by forming phosphorous oxides to interrupt radical formation,<sup>37</sup> TPP and TPP Ox, which are both members of triaryl phosphates, appear to be suitable additives for the PET matrix, and exhibit similar behavior. When 5 or 10% TPP Ox is used together with TPP in the polymer matrix (PT4 and PT5), the LOI value increases to 30.5 and 31%, respectively, in comparison to the composites containing TPP only (PT1, PT2, and PT3), among which a higher LOI value of 29.5% is obtained (PT3).

Results of the smoke density measurements of flame retardant composites are also given in Table I. When 8% BP is added to the PET matrix (PT12), a light transmittance value of 99% is obtained, which is a significant improvement in the smoke density. BP is concluded to be a successful smoke suppressant for the PET matrix. It is proposed that during formation of the glassy layer, BPO<sub>4</sub> turns into BPO<sub>3</sub>, PO<sub>2</sub>, PO•, and the released oxygen atom, O•, combines with the carbon monoxide to form carbon dioxide. This is also proved using Py-MS as seen in Figure 2. There is a significant increase in the amount of CO<sub>2</sub> formed at the 8% BP-PET decomposition range when compared to the case of neat PET decomposition. The CO<sub>2</sub>/CO ratio for the 8% BP-PET decomposition is almost twice that of neat PET. In general, one way of acquiring smoke suppression is to convert CO to CO<sub>2</sub> as much as possible so that incomplete combustion is reduced.<sup>33</sup>

PET composites with only TPP added (PT2, PT3) have the lowest light transmittance values as TPP releases high amount of

smoke during fire due to the aromatic groups in its structure. When the flame retardant additives have a high aromatic content, more carbon monoxide and more smoke are formed due to the high amounts of the carbon in the structure during a fire. When BP and TPP additives are used together (PT6, PT7, and PT8), the light transmittance value of the composites increases to 85%, 87%, and 90%, respectively, from 78% of neat PET (PT).

The TGA analysis of the polymer composites, given in Table III, shows that the usage of triaryl phosphates (PT1–PT5) does not result in a significant decrease in char formation, as shown by the decrease in the weight loss of the composites. On the other hand, the use of BP and/or ZB in the composites (PT10–PT13) increases the char yield as compared to the neat PET. Table III also shows the initial and final decomposition temperatures, and the temperature at the maximum weight loss for all the composites studied. In general, the initial decomposition temperature decreases from 340°C of neat PET to 200°C of the flame retardant composites. This may be due to the phosphate groups in TPP and TPP Ox (Table II). However, use of BP and/or ZB (PT12, PT13) increases the initial decomposition temperature. The temperature values at the maximum weight loss do not differ considerably from one another.

### Mechanical Properties

Tensile strength data of the flame retardant composites are given in Figure 3. The tensile strength of neat crystalline PET is determined as 55 MPa. In general, the tensile strength values of BP containing composites are higher than neat PET at less than 10% total additive content. This can be due to the homogeneous dispersion of BP in the polymer matrix especially in the presence of TPP (PT6, PT8). Other than this, addition of ZB either used with other additives or alone, decreases the tensile

**Table III.** TGA Analysis Results of Neat PET and the Flame Retardant Composites

Sample	Decomposition temperatures			Weight loss (%) at 800°C
	T <sub>initial</sub> (°C)	T <sub>final</sub> (°C)	T <sub>maximum</sub> (°C)	
PT	340.0	480.0	445.0	92.3
PT1	320.0	470.0	441.0	90.7
PT2	230.0	500.0	444.0	88.7
PT3	230.0	500.0	445.0	88.3
PT4	250.0	500.0	444.0	89.5
PT5	200.0	480.0	440.0	92.0
PT6	250.0	500.0	447.0	84.7
PT7	230.0	500.0	444.0	89.5
PT8	280.0	500.0	446.0	85.3
PT9	250.0	480.0	437.0	84.5
PT10	250.0	500.0	434.0	78.5
PT11	240.0	500.0	435.0	75.8
PT12	370.0	520.0	441.0	85.7
PT13	370.0	520.0	435.0	80.1



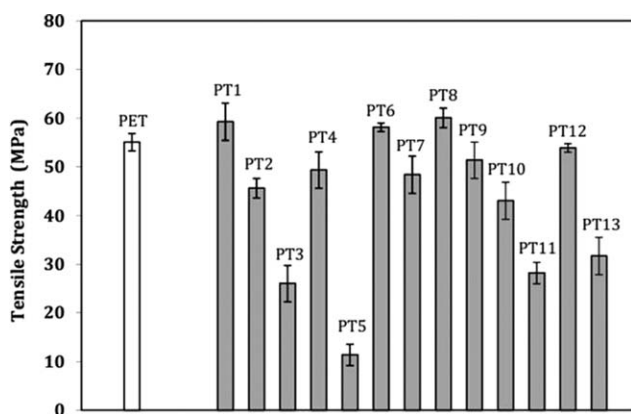


Figure 3. Tensile strength data of the flame retardant composites.

strength of the composites. This may be attributed to the zinc borate agglomerations that occur during processing. These can be observed in composites PT9, PT10, PT11, and PT13. When additive amounts higher than 15% are used, the tensile strength values decrease drastically with respect to neat PET. This may have resulted from plasticizing effects and agglomeration at high percentages of additives. TPP has a dual effect in the PET matrix. It acts as a chain extender in the polymer matrix that causes an increase in the tensile strength value of the composites and also it acts as a plasticizer, which helps to improve the elongation of the composite. The tensile modulus analysis of the composites are given in Figure 4. In general, composites containing either ZB or BP have higher tensile modulus values compared to neat PET. This is due to the higher modulus of the additives. Combination of the triaryl phosphate-based additives (PT5) drastically reduces the tensile modulus value of the matrix. Addition of TPP and TPP Ox increases the elongation behavior of the composites as seen from Figure 5. This is due to the plasticizing effect of triaryl phosphates (PT1–PT5). In composites PT6–PT9, the elongation at break values are increased slightly due to the presence of TPP in the polymer matrix when compared to the composites containing BP and/or ZB only. Existence of inorganic fillers in the absence of TPP generally restricts the chain mobility in the composites, which results in lower elongation values. Among the above mentioned composites, PT6 composite possesses the highest LOI and tensile modulus values. PT12 has the highest smoke suppression effect on the composites with satisfactory tensile strength and

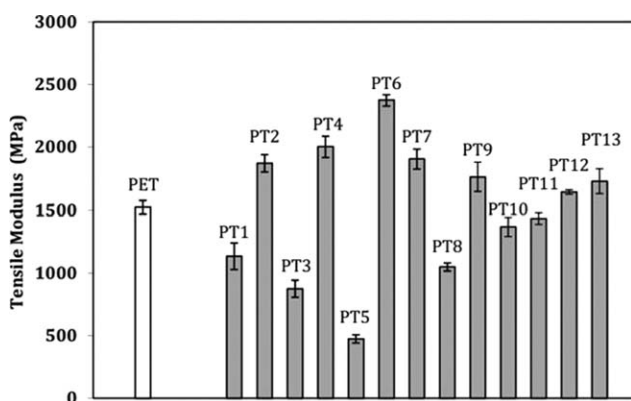


Figure 4. Tensile modulus data of the flame retardant composites.

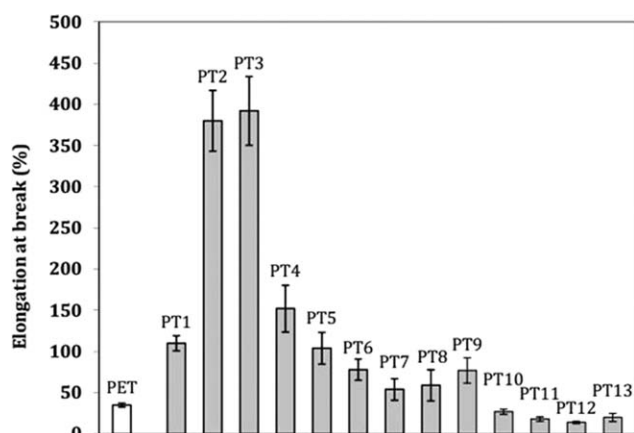


Figure 5. Elongation at break data of the flame retardant composites.

modulus properties. PT2 and PT3 composites exhibit significantly higher elongation values than the other composites owing to the plasticizing effect of TPP. Therefore, it can be said that boron and phosphate-based additives lead to improved flame retardancy, smoke suppression and mechanical properties in PET-based composites.

## CONCLUSIONS

Different amounts and combinations of flame retardant additives such as zinc borate, BP, triphenyl phosphate, and triphenyl phosphine oxide were used in the preparation of PET-based composites. According to the flammability analyses, BP and triphenyl phosphate were found to be effective flame retardants for PET composites. In addition, according to the LOI test results, BP was a very effective smoke suppressant for PET system, unlike triphenyl phosphate. Combinations of TPP-BP and TPP-TPP Ox had synergistic effect on the flame retardancy of PET composites. The synergistic effect was reflected by the high LOI value of 36% for the composite materials compared to the LOI value of 21% for the neat PET. BP acts in the gas phase as well as in the condensed phase, and is a successful smoke suppressant for the PET matrix that releases  $O\cdot$  radicals during the decomposition, which combines with carbon monoxide to transform it to carbon dioxide. According to the TGA results, PET tended to decompose around 445°C. The addition of triphenyl phosphate increased the char yield of the composites. Considering the mechanical properties of composites, TPP caused a significant increase in elongation at break values of the composites due to its plasticizing effect. With the combination of BP and TPP, especially when 5% of each was used, composites had both high flame retardancy and high mechanical properties which can be desired for many applications without the use of halogenated flame retardant additives.

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