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RESEARCH ARTICLE

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Flame retardancy and mechanical properties of polypropylene composites containing intumescent flame retardants, preceramic polymers, and other additives

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Abstract
This study aims to investigate the flame retardancy and mechanical properties of polypropylene (PP)-based intumescent flame retardants (IFRs) consisting of melamine phosphate (MP) and pentaerythritol (PER), and different additives; boron phosphate (BP), antimony oxide (AO), and preceramic polymers, namely poly(dimethylsilane) (PDMS) and poly(methylsilsesquioxane) (PMSQ). The composites were produced by twin-screw extrusion, and then molded by injection molding. Their characterizations were performed with limiting oxygen index (LOI), horizontal burning tests, thermogravimetric analysis (TGA), tensile and impact tests. The total amount of IFRs and the additives in polypropylene was kept constant at 20 wt%. The additive concentration was varied as 1, 3, and 5 wt% in the composites. The highest LOI value of 29% was obtained for PP/MP/PER composite with MP/PER ratio of 3/1. PP/IFR-based composites with 1 wt% additive exhibited higher LOI and horizontal burning performance than the other composites with 3 and 5 wt% additives. It is revealed that tensile modulus and impact strength of neat PP were improved with the addition of IFRs, and for each type and amount of the additives used in the study.

Highlights

- Usage of IFRs, preceramic polymers, BP and AO in PP improved flame retardancy.
- Lower amount of additives (1%) in PP/IFR composites led to higher LOI values.
- Additive incorporation enhanced tensile modulus and impact strength of neat PP.

KEYWORDS
flame retardancy, intumescent flame retardant, mechanical properties, poly(dimethylsilane), polypropylene, preceramic polymers

1 | INTRODUCTION

Polypropylene (PP) is widely preferred in today's world owing to its low density, easy processability, and versatile physical properties, which are required for many applications such as packaging, piping, textiles, containers, automotive components, and so forth. However, it can easily burn and can cause flame spread due to its wholly aliphatic hydrocarbon structure.[1] Therefore, there have been several studies conducted in order to improve the flame retardancy of PP.[2–5]

There are various types of flame retardants, which can be used for polypropylene such as halogenated additives, minerals, silicon (Si), nitrogen (N), and phosphorous (P)-based additives and nanoparticles.[2] Even though the halogen-based retardants are considered to be efficient additives even at low loadings into base polymer, they cause releasing toxic and corrosive gases during combustion, such as halogen acids and metal halides.[6] Because of environmental concerns, the amount of non-halogenated flame retardants is increasing every day.[4] Intumescent flame retardants (IFRs) can be used as alternatives for halogenated additives,[7–10] because they release low smoke and no corrosive or toxic gases during burning. In an intumescent formula, there are usually three components: an acid source, a blowing agent, and a char promoter.[8,11,12] The P-containing compound produces acid and promotes char formation, whereas N-based compound generates gaseous products so that the swelling of char occurs.[8] Char protects the material from further decomposition of polymer and also insulates the material from oxygen. Ammonium polyphosphate (APP) and melamine phosphate (MP) are the most common intumescent additives, which are generally used together with pentaerythritol (PER), which is a carbonizing agent.[13]

Intumescent flame retardants are effective in higher amounts (over 20 wt%) in the polymer, which may deteriorate the mechanical properties.[10] To reduce this higher amount in the polymer and enhance the flame-retardant property, some additives are utilized as synergistic materials with IFRs.[14] In literature, there have been different types of additives such as fly ash,[15] antimony oxide (Sb_2O_3),[14] layered double hydroxide,[9] silicon-containing additives,[3,16,17] boron containing compounds,[18] and so forth. which have been recently studied together with PP/IFR systems. Among these studies, with the addition of 2 wt% Sb_2O_3 to PP with 23 wt% IFRs consisting of ammonium polyphosphate (APP) and pentaerythritol (PER), Limiting Oxygen Index (LOI) values of PP/IFRs increased from 27.8% to 36.6%, and reached the UL-94 V-0 standard.[14] When boron compounds were used in PP together with APP and PER, they exhibited their highest synergism at 1 wt% concentration in the composite according to results of LOI and UL-94 tests. Especially, PP/IFRs containing 1 wt% boron phosphate showed the highest LOI value of 30% with the lowest maximum heat release rate and lowest total heat release values in comparison to the other boron compounds of the study.[18]

Synthesized IFRs consisting of phosphorus (P), silicon (Si), and nitrogen (N) elements (PSiN) within their structure have been found to be effective on both flame-retardant and mechanical properties of polypropylene. In the study of Li et al.,[7] the synergistic contribution of these elements on flame-retardant properties of polypropylene was investigated. LOI was obtained as 26% in the composite with 30 wt% PSiN, whereas LOI of pure PP was 17%. In addition, the char yield of the composite increased to 27% from 0% of neat PP due to the synergism among the components leading to better flame-retardant performance for polypropylene. In another study, dendritic copolymers synthesized from P-, N- and Si-containing monomer (PNSi) and melamine phosphate (MP), namely, PNSi-co-MP was compared with self-polymerized PNSi and melamine polyphosphate, PNSi-MPP system in terms of their contribution to flame retardancy and mechanical properties of PP.[10] PNSi-co-MP addition to PP led to higher flame retardancy, higher toughness and elongation at break values when compared to PP containing PNSi-MPP.

Silicon-containing flame retardants have certain advantages over other additives due to their environmental friendliness, high thermal stability, and flame-retardant efficiency.[19] Therefore, they have been widely studied together with PP in the literature because of their effective flame retandancy.[4,20] One type of these materials is silicon-based preceramic polymers which are converted to ceramic materials upon their thermal decomposition. They may contribute to the flame retardancy of PP by forming a protective layer which can act as heat and mass transfer barrier between the flame and the material, and protect the unburnt polymer.

The aim of the present work is to investigate the synergistic effects of some additives such as preceramic polymers and inorganic compounds on flammability and mechanical properties of polypropylene composites containing intumescent flame retardants of MP and PER. Poly(dimethylsilane), PDMS and poly(methylsilsesquioxane), PMSQ are the preceramic polymers decided to be used in PP-based systems. Especially, the use of PDMS together with PP/IFR systems constitutes the novelty of the work. PDMS is a linear preceramic polymer and has compatibility with PP due to its CH_3 side groups. This compatibility may provide an improvement in the flame-retardant, tensile, and impact properties of PP-based composites. Other than these additives, boron phosphate, and one commonly used commercial inorganic additive, antimony trioxide were studied for comparison purposes due to their potential performances in flame retardancy for PP/IFR composites. Within the scope of the study, first, the component ratio of the IFR system in PP was varied, and the optimum value was determined with respect to physical properties of the intumescent PP/IFR systems. Then, all the composites with varying concentrations of 1–5 wt% additives in PP/IFR systems (20 wt% in total) were assessed in terms of their flame-retardant characteristics and mechanical properties. The present work may be of interest for piping, packaging, and automotive applications of PP composites for which enhancement in both flame retardancy and mechanical performance are required.

2 | EXPERIMENTAL

2.1 | Materials

Polypropylene (PP, PETOPLEN MH418) with a density of 0.85 g/cm^3 and a melt flow index of 4–6 g/10 min (2.16 kg, 230°C) was obtained from Petkim Petrokimya Holding A. Ş. in İzmir, Türkiye. Silicon-based additives of the study were synthesized in our laboratories. Poly(dimethylsilane) (PDMS), a linear preceramic polymer was produced by electrochemical polymerization from dichlorodimethylsilane monomer.[21] The synthesized product was a transparent gel-like polymer. Poly(methylsilsesquioxane) (PMSQ), another preceramic polymer but with a network structure, was synthesized by condensation polymerization.[22] PMSQ particles were spherical in shape with an average size ranging between 0.7 and 1.1 μm. Boron phosphate (BP) with 97.5% purity was prepared by microwave method.[23,24] BP particles had nearly spherical shape and their size varied between ~200 and 400 nm. Antimony trioxide (AO, purity: ≥99.9%) with an average particle size of ≤250 nm was purchased from Sigma Aldrich. Melamine phosphate (MP, purity: 98%, density: 1.74 g/cm^3) with the trade name of Melapur MP and pentaerythritol (PER, purity: 99%, density: 1.37 g/cm^3) were the products of Ciba Chemicals and Sigma Aldrich, respectively. They were in the form of white powder. The MP and PER particles were irregular and close to spherical shape with approximate size of 20 and 200 μm, respectively.[21]

2.2 | Composite preparation

Polypropylene pellets were ground to powder form using a Wiley mill intermediate grinder to achieve better mixing with the additives. The materials were dried at 100°C for 2 h in a vacuum oven before the extrusion process. The total concentrations of the additives were kept constant at 20 wt%. They were mixed with PP in a co-rotating twin-screw extruder (Thermo Prism TSE 16 TC, L/D = 24) to prepare PP-based composites. The processing temperature profile in the five zones of the extruder was 180–185–195–205–215°C from hopper to die, and the screw speed was 100 rpm. After the extrusion process, the composites were oven dried at 100°C for 4 h, and then they were injection molded using a DSM Xplore Micro Injection Molding Device. The injection pressure of 13 bar, barrel temperature of 210°C, and mold temperature of 30°C were applied during the injection molding process. The compositions of polypropylene-based composites are given in Table 1.

2.3 | Characterization

The limiting oxygen index (LOI) test was performed for neat PP and PP with intumescent FR systems using a Dynisco Limiting Oxygen Index Test machine according to the ASTM D2863:2009 standard. The horizontal burning test was carried out according to the standard of ASTM D635:2003 to determine the rate of burning and time for burning of the samples when they are in horizontal position. Thermogravimetric Analysis (TGA) was performed with a Shimadzu, DTG-60/60H machine to obtain average decomposition temperatures and residue values of neat PP and PP-based composites. The term "residue" refers to both carbonaceous and inorganic residues at the end of the thermal analysis.[25,26] The samples were heated under nitrogen atmosphere from room temperature to 700°C with a heating rate of 10°C/min. Tensile properties were determined with a Shimadzu Autograph AG-IS 100 kN universal test instrument according to the ASTM D638:2010 test standard. The dimensions of the tensile specimens were 80 mm overall length, 20 mm gauge length, 4 mm width of narrow portion, 12.5 mm width at ends and 2 mm thickness. Charpy impact tests of the samples were performed using a Ceast Resil Impactor 6967 impact device equipped with a 7.5 J pendulum, consistent with ISO179-1:2010 standard. LOI, horizontal burning, and impact testing were implemented using injection molded samples with dimensions of 80 mm length, 10 mm width and 4 mm thickness. All the mechanical tests were carried out at room temperature.

3 | RESULTS AND DISCUSSION

3.1 | Flame retardancy (LOI and horizontal burning tests) and TGA characterization of PP/IFR-based composites

Flame-retardant characteristics in terms of LOI, horizontal burning rates, decomposition temperature and residue

TABLE 1 Compositions of PP-based composites.

Sample code/wt%	PP	MP	PER	BP	AO	PMSQ	PDMS
PP	100	-	-	-	-	-	-
PP/10MP/10PER	80	10.00	10.00	-	-	-	-
PP/15MP/5PER	80	15.00	5.00	-	-	-	-
PP/5MP/15PER	80	5.00	15.00	-	-	-	-
BP1	80	14.25	4.75	1	-	-	-
BP3	80	12.75	4.25	3	-	-	-
BP5	80	11.25	3.75	5	-	-	-
AO1	80	14.25	4.75	-	1	-	-
AO3	80	12.75	4.25	-	3	-	-
AO5	80	11.25	3.75	-	5	-	-
PMSQ1	80	14.25	4.75	-	-	1	-
PMSQ3	80	12.75	4.25	-	-	3	-
PMSQ5	80	11.25	3.75	-	-	5	-
PDMS1	80	14.25	4.75	-	-	-	1
PDMS3	80	12.75	4.25	-	-	-	3
PDMS5	80	11.25	3.75	-	-	-	5

Abbreviations: AO, antimony oxide; BP, boron phosphate; MP, melamine phosphate; PER, pentaerythritol; PDMS, poly(dimethylsilane); PMSQ, poly(methylsilsesquioxane); PP, polypropylene.

TABLE 2 LOI, horizontal burning, and TGA test results of neat PP and PP-based composites.

Sample	LOI (%)	Burning rate (mm/min)	Decomposition temperature (°C)	Residue (%)
PP	17.5	21.49 ± 1.39	442	0.1
PP/10MP/10PER	27.0	N/A	444	10.8
PP/15MP/5PER	29.0	N/A	448	13.5
PP/5MP/15PER	21.5	21.27 ± 3.32	461	0.1
BP1	26.0	N/A	425	9.6
BP3	22.5	31.13 ± 2.58	449	6.8
BP5	22.0	28.89 ± 3.89	467	4.4
AO1	28.0	N/A	444	12.8
AO3	25.0	30.36 ± 4.37	446	12.7
AO5	21.0	38.13 ± 2.51	462	9.2
PMSQ1	25.0	20.72 ± 0.69	469	12.9
PMSQ3	22.0	38.31 ± 0.82	467	5.3
PMSQ5	21.5	36.47 ± 2.83	468	0.9
PDMS1	24.0	16.83 ± 2.41	469	9.0
PDMS3	23.5	20.22 ± 2.09	483	7.9
PDMS5	22.5	20.43 ± 5.71	491	3.9

Abbreviations: AO, antimony oxide; BP, boron phosphate; LOI, limiting oxygen index; MP, melamine phosphate; PER, pentaerythritol; PDMS, poly(dimethylsilane); PMSQ, poly(methylsilsesquioxane); PP, polypropylene; TGA, thermogravimetric analysis.

values of the neat PP and PP-based composites are given in Table 2, and some representative TGA curves are illustrated in Figures 1–3. Pure PP exhibits a single-stage decomposition with a maximum weight loss at 442°C. On the other hand, there are at least two stages in thermal degradation behaviors of PP/IFR systems. The early stage degradations are expected to contribute to the char layer formation.[15]

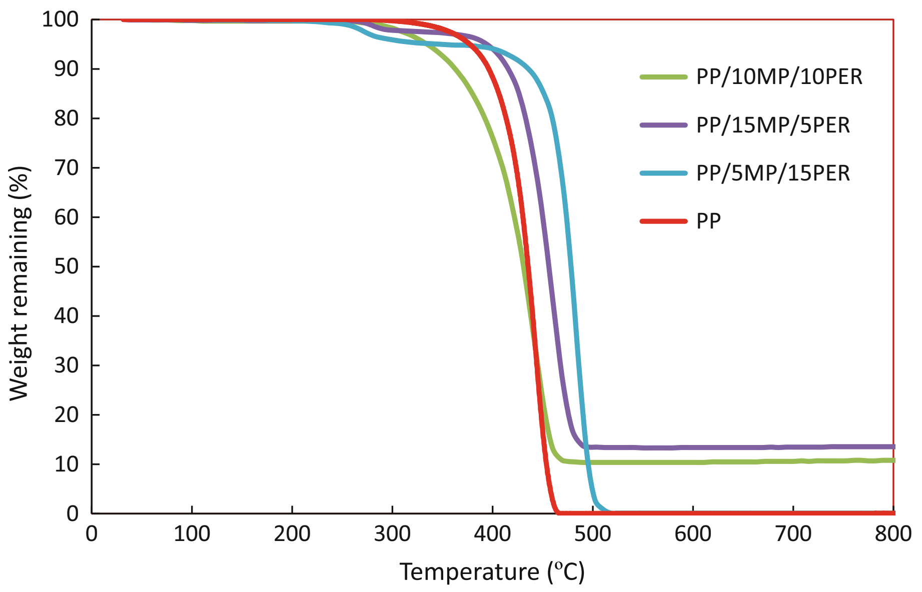

FIGURE 1 Thermogravimetric analysis (TGA) curves of neat polypropylene (PP) and PP/melamine phosphate (MP)/pentaerythritol (PER) composites.

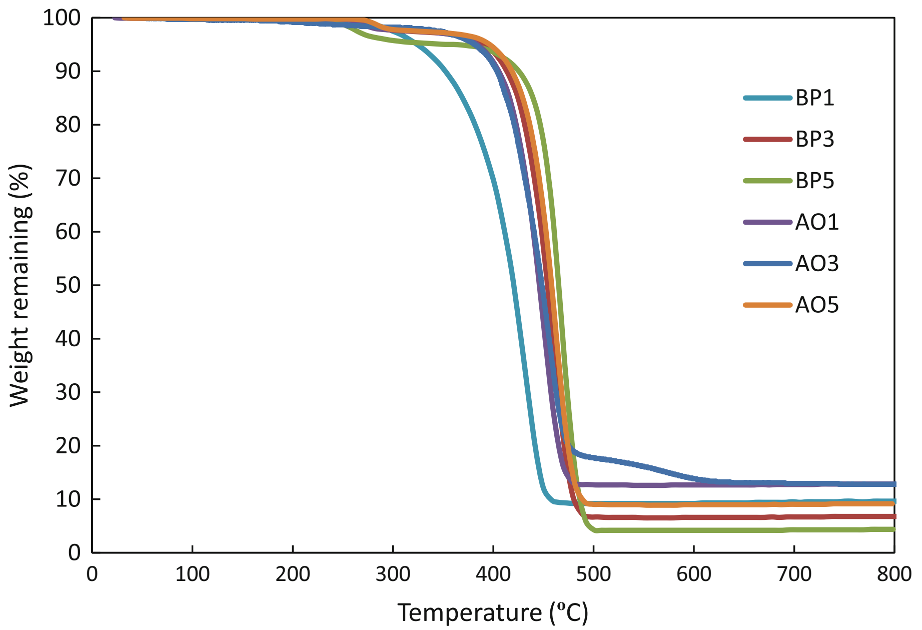

FIGURE 2 Thermogravimetric analysis (TGA) curves of neat polypropylene (PP)/intumescent flame retardant (IFR)-based composites with boron phosphate (BP) and antimony oxide (AO).

First, MP/PER weight ratios of 10/10, 15/5, and 5/15 used in PP/IFR composites were optimized according to the related flammability and thermal stability results, as can be seen in Table 2. There exists a significant improvement in LOI value of neat PP from 17.5% to 29% with the incorporation of 15MP/5PER into PP. The use of 10/10 and 5/15 MP/PER ratios results in LOI values of 27% and 21.5%, respectively. Melamine phosphates can form char, generate foam, and act as a char-forming catalyst at the same time,[27] and pentaerythritol acts as a carbonizing agent.[12] Table 2 and Figure 1 represent that residue yield of 13.5% for PP composite with 15MP/5PER ratio is the highest among the other composites due to higher concentration of MP as a char former. On the other side, PP with 15 wt% PER and 5 wt% MP has the highest decomposition temperature (461°C) among these PP/IFR composites, which may result from the higher concentration of PER, being responsible for carbonization of the polymer; therefore, thermal stability of the materials increase.

The results of horizontal burning tests indicate that neat PP and PP with 10MP/10PER and 15MP/5PER composites are not burnt, so their results are reported as not available (N/A). However, PP/5MP/15PER composite exhibits a 21.27 mm/min burning rate. Based on these results from LOI and horizontal burning tests, 15/5 ratio of MP/PER yields the most effective composition among the IFRs and is kept constant in PP-based IFR composites for the further compositions of the additives.

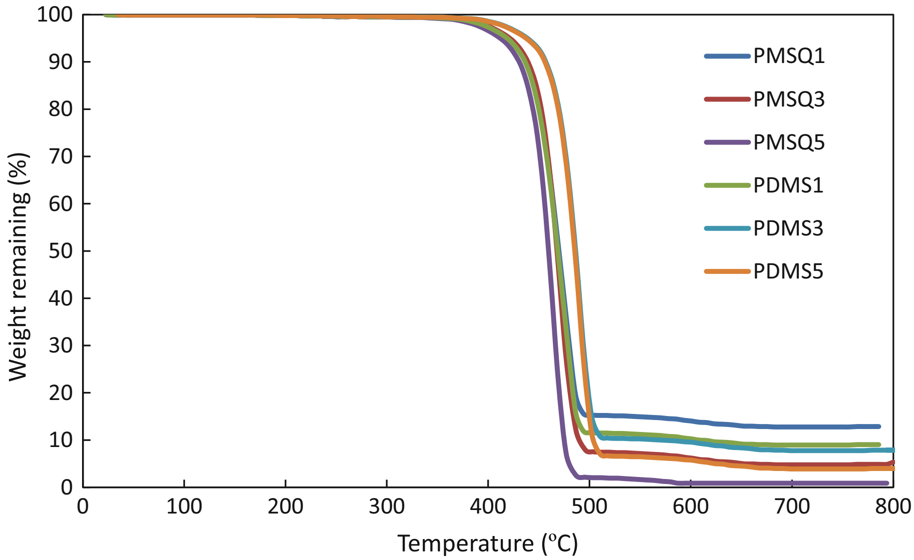

FIGURE 3 Thermogravimetric analysis (TGA) curves of polypropylene (PP)/intumescent flame retardant (IFR)-based composites with poly(methylsilsesquioxane) (PMSQ) and poly(dimethylsilane) (PDMS).

As can be seen in Table 2, increases in the amount of additives such as BP, AO, PMSQ, and PDMS from 1 to 5 wt% in 15MP/5PER system lead to decreases in LOI results of PP/IFR/additive composites, because total amount of IFR (MP and PER) reduces in the composites. Moreover, flame-retardant mechanisms of IFR systems and the additives other than IFRs are expected to be different from each other. N-based material in IFR compound forms char swell by generating gaseous products. However, for BP, PDMS, and PMSQ-containing composites, it is expected to see a rigid char formation, and this may cause to prevent the blowing of char. It can be said that there is an antagonism between these additives and IFRs. On the other hand, antimony trioxide is known to be effective in vapor phase, depending on the radical capture mechanism.[12] Also, it can catalyze chemical reactions together with IFRs to form stable char layer.[14]

Table 2 shows that LOI results of all PP/IFR-based composites are higher than that of pure polypropylene. PP/MP/PER composite with 1 wt% AO has the maximum LOI value among the other composites with the same amount of additives, resulting in the LOI sequence of AO1 > BP1 > PMSQ1 > PDMS1. For PP-based composites containing 3 wt% additive and 17 wt% IFR, the LOI sequence is AO3 > PDMS3 > BP3 > PMSQ3. This reveals that antimony trioxide is effective at both 1 and 3 wt% in PP/IFR composites. When AO concentration is increased from 3 to 5 wt% in PP/MP/PER composite, LOI value changes from 25% to 21%, respectively, indicating that further increase in AO concentration causes antagonism rather than synergism. Therefore, 1 or 3 wt% antimony oxide addition to PP/IFRs systems can be considered as more effective concentration than higher AO loadings according to their LOI results. This is due to their higher residue yields when compared to PP/MP/PER/AO5 composite (Table 2).

When the composites with 3 wt% other additives (BP, PDMS, PMSQ) are taken into account, it is seen that LOI result of PP/IFR/PDMS3 composite is higher than its counterparts with BP and PMSQ. When silicon-based compounds (PDMS and PMSQ) of the study are compared, PDMS seems to be more efficient at this concentration. The highest LOI value among all PP/IFR composites with 5 wt% additives is obtained for PDMS case. Moreover, the highest decomposition temperature belongs to PP/IFR/PDMS5 among all composites of the present study (Table 2). This may be possibly responsible for the decrease in flammability. In terms of their LOI values, boron phosphate incorporation to the PP/IFR composites at low (1 wt%) and high loadings (3 and 5 wt %) result in similar flame retardancy to the PP/IFR composite with 1 wt% AO and to PDMS with 3 and 5 wt% loadings, respectively.

Horizontal burning test results for PP/MP/PER composites containing four different compounds with three different loadings (1, 3, and 5 wt%) are also given in Table 2. The addition of 1 wt% AO and 1 wt% BP to PP/IFR composite does not result in burning under flame. On the other hand, PDMS1 composite is burnt with a rate lower than the burning rates of neat PP, PP/IFR/PMSQ1 and most of the composites with 3 and 5 wt% additives. Besides, LOI results and burning rates are not related to each other at higher concentrations of the additives. For example, horizontal burning rate of PP/IFR/AO3 composite is higher than PP/IFR/PDMS3, which means that 3 wt% PDMS in the composite imparts slower burning than AO3 under atmospheric condition. When compared to LOI results given in Table 2, the LOI of PP/IFR composite with 3 wt% AO is higher than PP/IFR/PDMS3 composite, which may be attributed to the different flame-retardant mechanisms for each type and concentration of the components and their combined effects on the flammability. Nevertheless, it can be mentioned that the composites have LOI values higher than 25% also achieve better performance in horizontal burning results. A material with LOI value of 21% is considered to be as "slow-burning" material.[28] Moreover, if LOI value is higher than 25%, then the material is classified as "self-extinguishable" in air.[29] Thus, PP/IFR composites with BP1 and AO1 exhibit better flame-retardant behavior than the other additives and their concentrations in PP/IFR composites. This may be due to the vapor phase flame-retardant mechanisms regarding potential chemical reactions among the radicals of the additives and polypropylene, which are expected to occur during burning of the samples.[30]

TGA curves and the decomposition temperature and residue yield results of PP/IFR/BP and PP/IFR/AO composites are represented in Figure 2 and Table 2, respectively. It is obvious from the table that residue yields of the composites reduce with decreasing concentration of the intumescent flame retardants. For example, when BP and IFR concentrations are 1 and 19 wt% in PP-based composite, the residue yield results in 9.6%. However, for PP/IFR/BP5 composite, the residue yield of 4.4% is obtained, which can be attributed to decreasing amount of char promoter (MP) in PP/IFR composites. The higher LOI value and better horizontal burning rate of PP/IFR/BP1 than its other composites with higher BP amounts, can be related to its higher residue yield. Other than this, BP thermally decomposes at higher temperatures than 800°C.[21,24] As seen in Table 2, when BP concentration increases in PP/IFR composite, the decomposition temperatures of these composites increase as well. The addition of 1 and 3 wt% AO in PP/IFR composites results in approximately similar residue yields and decomposition temperatures. Among the four additives, the highest residue yields mostly belong to AO containing PP/IFR composites. Also, the highest decomposition temperature (462°C) for PP/IFR/AO composites is obtained for PP/IFR/AO5 system. Since the average decomposition temperature of pure AO is around 655°C which is higher than those of neat PP and PP/IFR composites,[21] the increasing concentration of antimony trioxide provides an increase in thermal decomposition temperature of the composites.

The effects of preceramic polymers on TGA results of PP-based IFR composites can be seen in Table 2 and Figure 3. It is expected that the thermal decomposition temperature is improved by preceramic polymers for polypropylene.[31] As seen in Table 2, addition of PMSQ and PDMS into PP composites improves the average decomposition temperature of neat polypropylene and PP/IFR composites due to their preceramic structures. All concentrations of preceramic additives in the composites lead to improvement in the decomposition temperature of PP. Among preceramic polymer composites, the best residue yield of 12.9% belongs to PP/IFR/PMSQ1 composite. Similar to PP/IFR-based composites with AO and BP; preceramic additive containing composites also exhibit decrease in residue yield with decreasing total IFR amount. While LOI value of PP/IFR/PMSQ1 is 25%, the composite with 1 wt% PDMS has the value of 24%, possibly due to the higher residue yield of PMSQ1. For the composites with PMSQ and PDMS at 3 and 5 wt% loadings, the trend in their residual mass values is found to be the same. The higher LOI value at 3 wt% PDMS amount can be associated to its higher residue yield and higher decomposition temperature than PMSQ at the same loading. In addition, the horizontal burning test results of PP/IFR/preceramic additives support the TGA results with lower burning rate of the composites resulting in higher decomposition temperatures. Among all sets of the samples, PP/IFR composite containing 5 wt% PDMS had the highest decomposition temperature, but with a lower residue yield. Even though both PDMS and IFRs in PP lead to stable char formation, their char formation mechanisms are not similar to each other. PDMS converts the sample to a dense and rigid char,[32–34] whereas MP/PER system to a voluminous char.[35] This may cause an antagonistic effect in the composites.

3.2 | Mechanical properties of PP/IFR-based composites

While improving the flame-retardant performance of PP, it is also important to preserve its inherent mechanical properties. For this purpose, tensile and impact tests are applied to neat PP, PP/IFR composites and PP/IFR/additive systems to assess their mechanical properties.

Tensile test results of PP/IFR composites with varying MP/PER ratios are illustrated in Figures 4–6. Figure 4 shows that PP/IFR composites have ~16−19% lower tensile strengths than pure PP. This can be attributed to agglomerations occurring at high loadings of additives, resulting in weak points and irregular stress distribution within the polymer. In literature, it has been claimed that maximum loading amounts of additives should be in the range of 15–20 wt% into base polymers, which might otherwise cause losses in mechanical strength.[1]

Figure 5 represents the elastic moduli of neat PP and PP/IFR composites containing different ratios of MP/PER. It is seen that the IFR additives significantly improve the elastic modulus of neat polypropylene. This can be attributed to higher modulus of the additives compared to PP. PP/IF composite with 5MP/15PER ratio

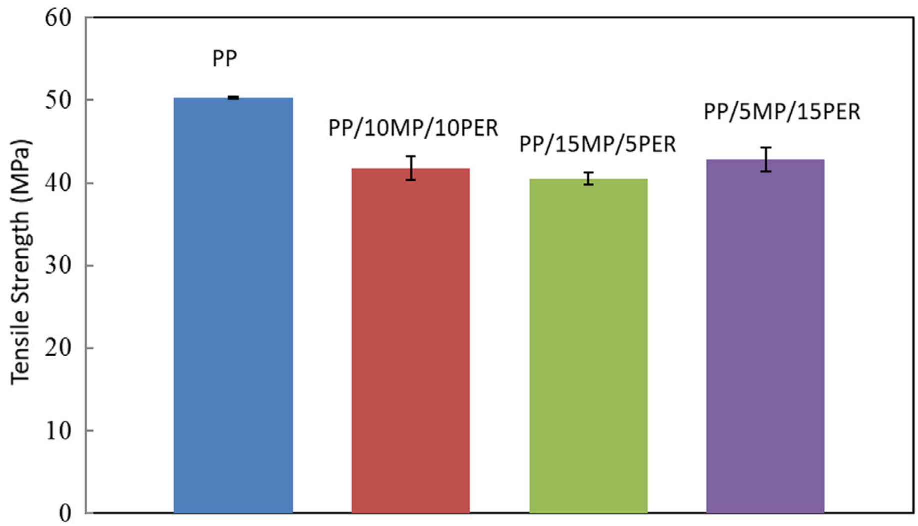

FIGURE 4 Tensile strengths of neat polypropylene (PP) and PP/intumescent flame retardant (IFR) composites.

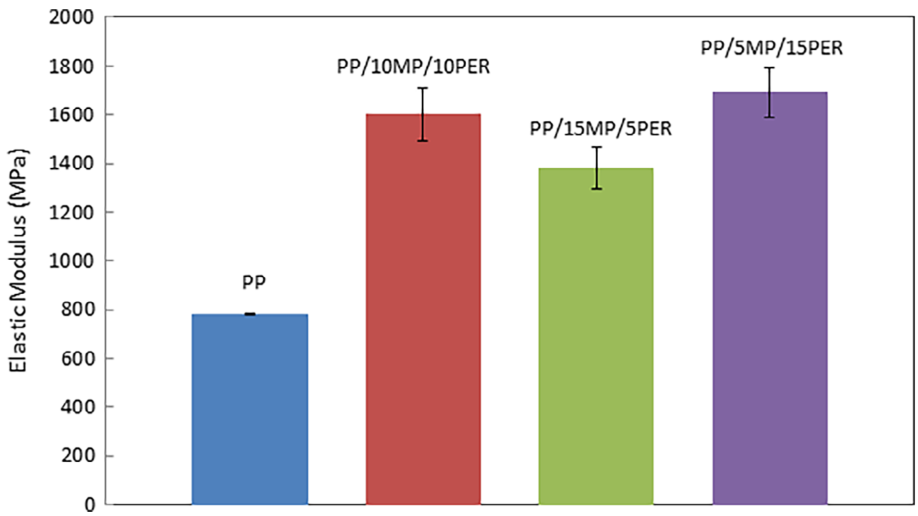

FIGURE 5 Elastic moduli of neat polypropylene (PP) and PP/intumescent flame retardant (IFR) composites.

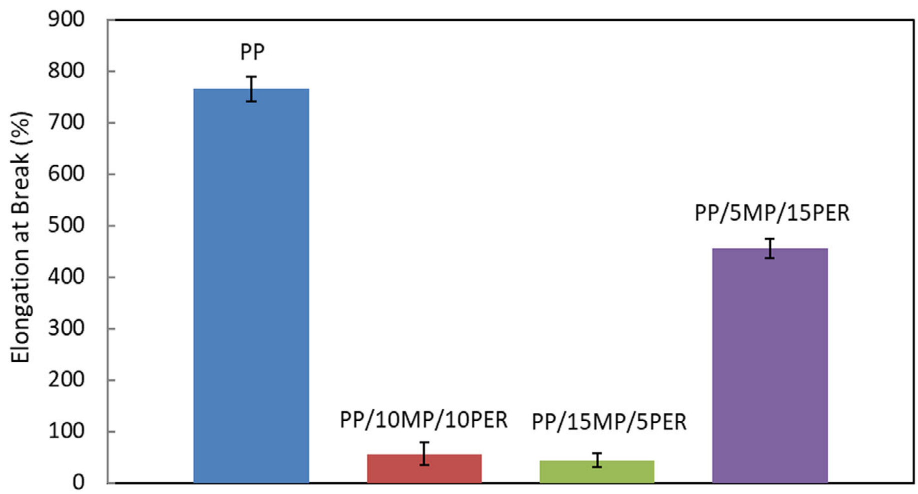

FIGURE 6 Elongation at break of neat polypropylene (PP) and PP/intumescent flame retardant (IFR) composites.

possess the highest elastic modulus value (1692 MPa) which means more than 100% increase in tensile modulus of neat PP (783 MPa). When MP concentration in PP matrix increases, tensile modulus of PP/IFR composites decreases slightly, but still higher than that of PP. The decrease in elastic modulus of the PP/IFR composite with

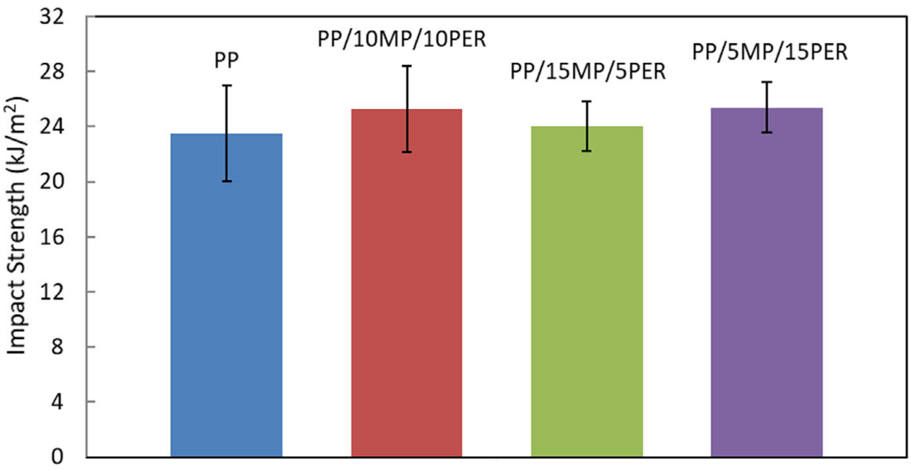

FIGURE 7 Impact strengths of neat polypropylene (PP) and PP/intumescent flame retardant (IFR) composites.

MP amount can be related to lower interfacial adhesion between the matrix and the IFR components.

Elongation at break results of neat PP and PP/MP/PER composites are shown in Figure 6. While pure PP has the highest elongation at break value among the samples, PP/IF composites with 10/10 and 15/5 MP/PER ratios have the lowest values of elongations. When PER concentration is increased to 15% in the binary composites, elongation at break value also increases, but still lower than that of neat PP. Lv et al.[35] reported that the IFR systems have some drawbacks such as being sensitive to moisture due to the presence of PER, and not being able to compatible with the base polymer matrix; thus lowering the mechanical performance of the composite.

Figure 7 illustrates the impact strength results of neat PP and PP/IR composites with different MP/PER ratios. It is observed that there is not a significant change in impact strengths of PP/MP/PER composites, and the changes in the values are in the limit of the standard deviation. PP/IR composite with MP/PER ratio of 15/5, which is the one chosen among IFR systems for studying the different additive effects on the flame retardancy, exhibits an impact resistance of 24 kJ/m^2. The similar impact strength values of neat PP and PP/MP/PER composites may result from the competing effects of the distribution of the particles within the polymer and the compatibility between the components of the composites.

The representative tensile stress versus strain curves of pure PP and some PP/IFR-based composites with 1 wt% additives are illustrated in Figure 8. Typical ductile deformation of polypropylene can be seen with neck propagation and drawing.[10,20] When the additives are incorporated into PP, tensile strength and elongation at break of neat PP decrease, and its elastic modulus increases. The reduction in strain at break values is possibly due to the additives which restrict the chain mobility of polypropylene during tensile deformation.

Figure 9 shows tensile strength behavior of neat PP and PP/IFR-based composites with different type of additives. These composites exhibit ~20–32% decrease in their tensile strengths with respect to pure PP. This can be due to the formation of agglomerates in the polymer matrix resulting from the higher amounts of IFRs together with additives, which may disturb the polymer chain alignment during tensile testing. Nevertheless, the tensile strength values of PP/IFR-based composites with different additives indicate that type and concentration of the additives do not significantly affect the tensile strengths of PP/MP/PER composites.

Additives of BP, AO, PMSQ, and PDMS at different concentrations used together with IFRs in PP-based composites improve the elastic modulus of PP (Figure 10). The significant increase in elastic moduli of PP/IFR composites containing 1 wt% AO and BP in comparison to that of polypropylene is owing to the high elastic moduli of these additives. However, with further increase in concentrations of AO and BP in PP/IR system, at 3 and 5 wt% loadings; the elastic moduli of PP/IFR/AO and PP/IFR/BP composites decrease. Because higher loadings of AO and BP cause more agglomerations in the polymer matrix, resulting in lower tensile modulus values. When the use of PMSQ in the composites is taken into account, it is seen that the composite with 5 wt% PMSQ has lower elastic modulus than the composites containing 1 and 3 wt% PMSQ. At higher concentration of PMSQ, less uniform dispersion of these particles causes formation of agglomerates. When PDMS containing composites are compared with the composites of other additives, it is observed that the improvement in elastic modulus of PP is much less with PDMS loading, but this additive is still effective on the elastic modulus of neat polypropylene. PDMS can be considered as a compatible polymer with polypropylene due to its chain structure, because it has a linear structure in which CH_3 groups bonded to Si

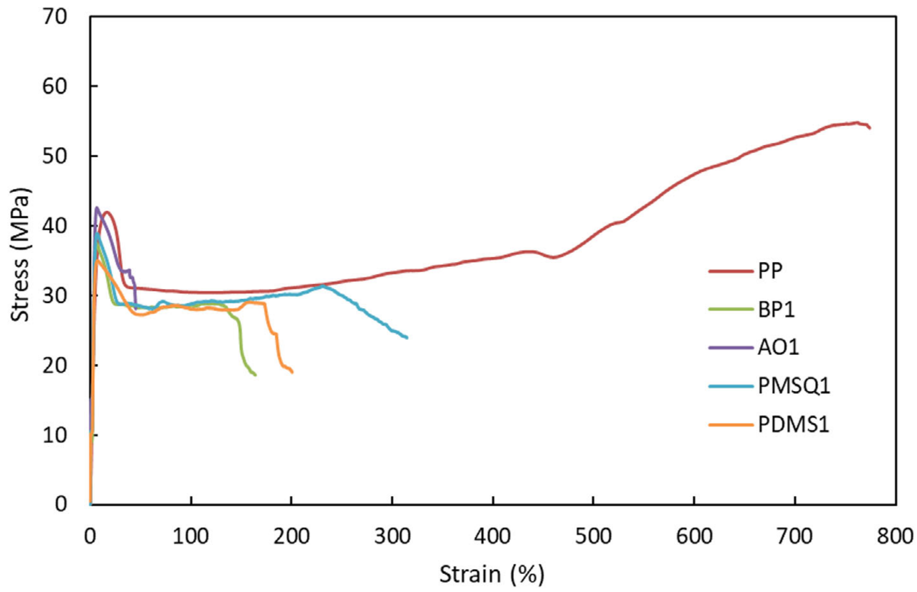

FIGURE 8 Tensile stress versus strain curves of neat polypropylene (PP) and PP/intumescent flame retardant (IFR)-based composites.

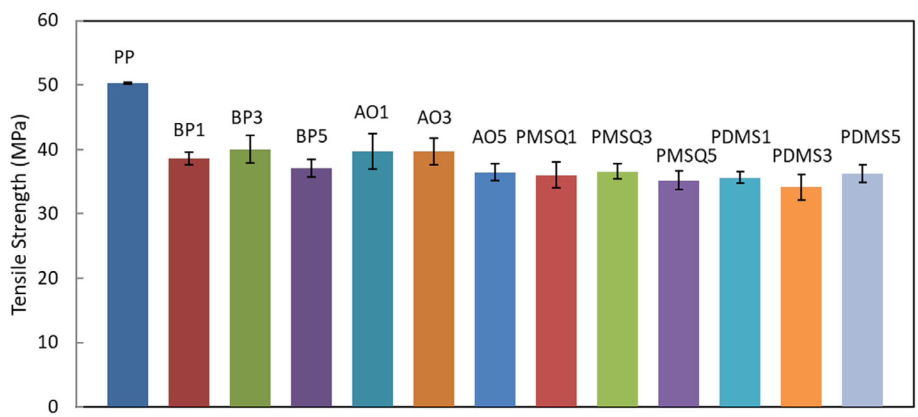

FIGURE 9 Tensile strengths of neat polypropylene (PP) and PP/intumescent flame retardant (IFR)-based composites with different additives.

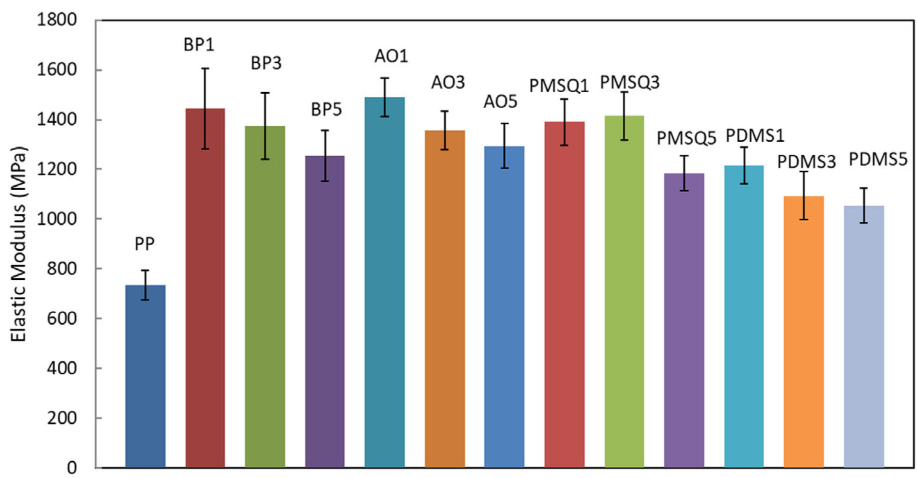

FIGURE 10 Elastic moduli of neat polypropylene (PP) and PP/intumescent flame retardant (IFR)-based composites with different additives.

backbone, which improves the mechanical properties of the composites. Nevertheless, as the amount of PDMS in PP/IFR system increases, elastic moduli of the composites decrease due to potential agglomerations occurring in the polymer matrix.

Figure 11 shows the elongation at break results of neat PP and PP/IFR/additive composites with the most distinct variety among tensile properties of the composites. The most remarkable decrease in the elongation values belongs to PP/IFR/AO composites. The corresponding values of the

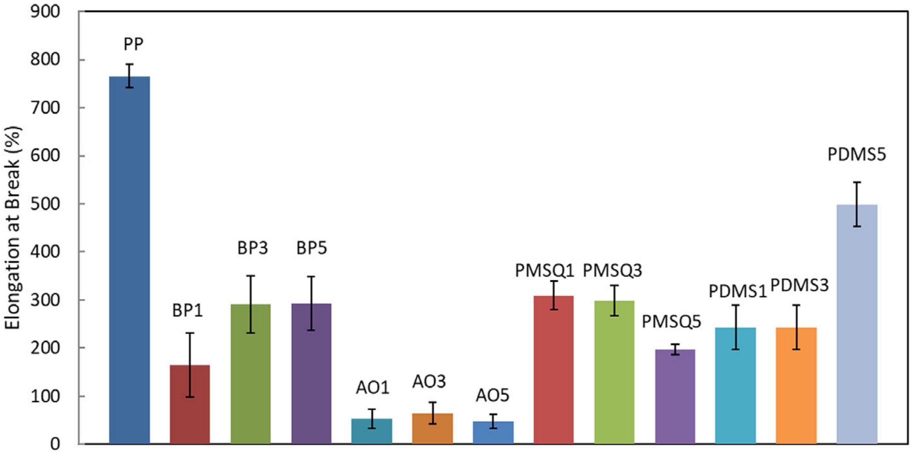

FIGURE 11 Elongation at break results of neat polypropylene (PP) and PP/intumescent flame retardant (IFR)-based composites with different additives.

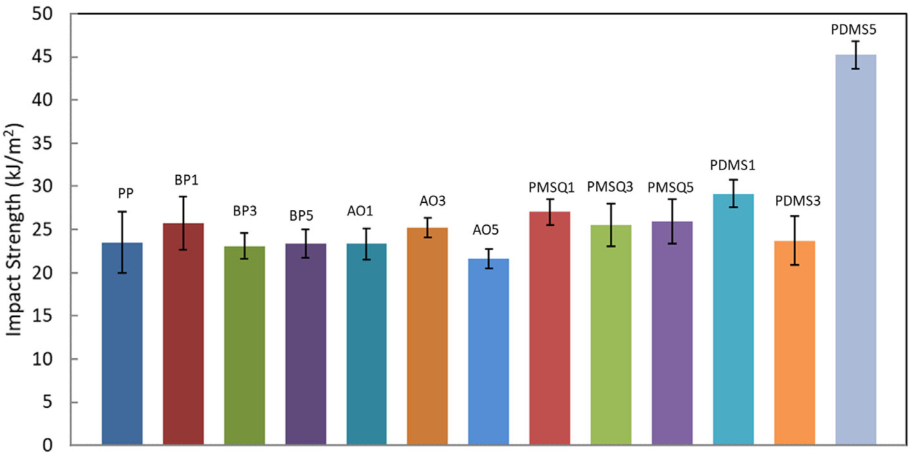

FIGURE 12 Impact strengths of neat polypropylene (PP) and PP/intumescent flame retardant (IFR)-based composites with different additives.

composites with 1, 3, and 5 wt% AO additions are determined as 53%, 65%, and 48%, respectively. This decrease in % elongation values with respect to neat PP and the other composites is probably as a result of its high rigidity which may disrupt the alignment of PP chains during the tensile test. When BP addition to PP/IFR system is considered, it is seen that increasing BP loading in PP leads to increase in elongation at break values of PP/IFR composites, which can be attributed to the decreasing IFR amount in the composite. On the other hand, for PP/IFR/PMSQ composites, increasing PMSQ loading from 1 to 5 wt% in PP results a decrease in percent elongations of the composites. This may be due to the network structure of PMSQ, which may affect the PP chain alignment by disturbing the stress loading during tensile test. On the other hand, PDMS addition at 5 wt% loading in the composites results in a positive effect on elongation at break value of PP/IFR system, compared to the other PP/IFR/additive composites. The linear structure of PDMS must be responsible for this improvement in the percent elongation, by providing compatibility in the alignment of polypropylene chains while stretching is applied during tensile test.

Figure 12 represents the impact test results of neat PP and PP/IFR-based composites with the additives of BP, AO, PMSQ, and PDMS. When 1 wt% boron phosphate is added to PP/IFR system, slight increase in impact strength of polypropylene is obtained; however, higher loadings of BP in the matrix do not cause any significant change for impact strengths of neat PP and PP/IFR/BP composites. Furthermore, AO incorporation to PP/IFR composites exhibit similar impact strength behavior to those of PP/IFR/BP composites. On the other hand, at each concentration of PMSQ in the composites, the impact strengths of PP-based composites are higher than their counterparts with AO and BP additives. There exists up to ~15% improvement in the impact strength of neat polypropylene, owing to the network structure of PMSQ. The maximum impact strength with 92% increase with respect to PP is obtained for the composite containing 5 wt% PDMS among neat PP and PP/IFR-based composites containing other additives. This can be attributed to the presence of Si atoms in the backbone of PDMS with side groups of CH_3, which leads to better compatibility with PP, and as a result improves the mechanical properties.[31]

Impact strengths of PP/IFR-based composites containing BP and AO additives are independent of the type, amount, and size of the additives used in PP/IFR systems. BP and AO are inorganic rigid fillers with average particle diameters in submicron size. Although their surfaces are not modified, these materials are expected to be well dispersed during twin screw extrusion process; thus impact resistance of neat PP is maintained. When preceramic polymers of PMSQ and PDMS are added to PP/IFR systems at 1 wt% loading, impact strength of neat PP is improved up to a certain extent. However, this is not related to size of the materials, but is mainly due to the improved adhesion between the components of the composite. PMSQ and PDMS are inorganic polymeric materials providing compatibility with PP/IFR systems. The significant improvement in the impact strength of PP/IFR composite containing 5 wt% PDMS indicates that this material possibly possesses higher load bearing capacities than its counterparts owing to higher interfacial adhesion between the polymer and the additive, and well dispersion of PDMS in the polymer matrix.

4 | CONCLUSIONS

PP-based composites containing intumescent flame retardants of MP and PER, and different additives such as AO, BP, PMSQ, and PDMS were investigated in terms of their flame retardancy and mechanical properties. First, the ratio of MP/PER and then the type and concentration of additives from 1 to 5 wt% were varied in order to understand their effects on the properties of neat PP and PP-based composites. The best flame retardancy of the work was obtained for PP/15MP/5PER composite with a LOI value of 29%, and no ignition was observed in horizontal burning test. However, this composition caused a reduction in tensile strength and elongation at break of neat PP. PP/IFR composites with 1 wt % additives had higher LOI values and better horizontal burning performance than the related composites with 3 and 5 wt% of these additives. In general, the residue yield of PP/IFR composites decreased with increasing amount of the additives. Tensile moduli and impact strengths of PP/IFR composites improved with the addition of all type and concentration of the additives, whereas their tensile strengths and elongation at break values reduced with respect to PP. The addition of 5 wt % PDMS together with IFRs into PP lowered the decrease in tensile strength and elongation at break, and significantly improved the impact strength of neat PP. In summary, enhancement in thermal stability, flame retardancy, rigidity, and impact resistances of PP/IFR-based composites can be obtained at the same time with the addition of silicon-containing preceramic polymers and thermally stable inorganic compounds into the polypropylene matrix. These types of materials can benefit property improvement studies in the packaging, piping and automotive applications.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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