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Original Article

A new approach to improve the efficiency of intumescent flame retardant for polypropylene fibers

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Abstract

This study introduces an improved approach to enhance polypropylene (PP) flame retardancy. High intumescent flame retardant (IFR) loadings (30 wt%) often compromise PP's mechanical properties. The research investigates the impact of different mixing sequences, including novel direct and multi-step methods, on the flame retardancy and properties of PP/IFR-silane composites. Composites, prepared via a two-roll mill and melt-spun into fibers, showed significant performance improvement with a proper multi-step mixing sequence (M-1) where ammonium polyphosphate (APP) particles were pre-treated with silane. This approach allowed reducing IFR content from 30 wt% to 25 wt% while maintaining a V0 UL94-V rating. The M-1 sequence resulted in silane strongly coating APP and enhancing thermal stability because of reduced phosphorus degradation and strong C-N and C=N bond formation, indicating enhanced chemical interactions. Rheological analysis also showed greater early-stage char expansion, improving polymer protection during combustion. The PP/mod-IFR composite fibers exhibited homogeneous additive distribution and chemical compatibility.

Keywords: polypropylene, silane, intumescent fire retardant, flame retardant, composites

1. Introduction

Polypropylene (PP) is widely used for its low cost, light weight, and good mechanical properties (Mouritz & Gibson, 2007). However, its poor flame retardancy, characterized by high heat release capacity, poses safety concerns, especially in household and automotive applications (Horrocks, 1986; Lyon, 2000). Various flame-retardant additives have been explored for PP), including phosphorus-, nitrogen-, halogen-, metal-, and silicon-containing compounds, and nanocomposites (Zhang & Horrocks, 2003). Among these, phosphorus-based compounds—such as

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halogen phosphates (Listner, 1972), phosphine oxides, ammonium polyphosphates (APP) (Murray, 1972), phosphonitrilic esters (Wolf, 1975), and inorganic phosphoric acids (Miller, 1977)—are widely used. These are often combined with halogen- and/or nitrogen-containing compounds to form intumescent chars that protect the polymer substrate (Lu & Hamerton, 2002; Wilkie & Morgan 2024). The intumescent flame retardant (IFR) mechanism involves both chemical and physical reactions to create a protective char layer (Le Bras, Bourbigot, Camino, & Delobel, 1998; Wilkie & Morgan 2024). APP is one of the most commonly used IFR ingredients in PP systems (Anna, Marosi, Bourbigot, Le Bras, & Delobel, 2002), typically combined with cyclic urea-formaldehyde resins, hydroxyethylcyanurates, or piperazine-based species to enhance phosphorus–nitrogen synergy (Bertelli & Locatelli, 1983; Chiu & Wang, 1998; Landoni, Fontani & Cicchetti, 1982; Lewin, 1999; Marciandi, 1980; Scarso, 1988). APP is often used with pentaerythritol as a carbon source and melamine as a blowing agent to promote continuous char formation (Bourbigot, Duquesne, & Leroy, 1999; Nelson, 1990). Incorporating silicon-based compounds into IFR systems can further improve flame retardancy by forming a ceramic-like protective layer in the condensed phase and trapping free radicals in the gas phase (Marosi *et al.*, 2002a, 2002b). These silicon-containing systems are also considered environmentally friendly, producing low-toxicity, non-corrosive smoke (Franz & Stein1975).

While IFR systems are effective, high IFR loadings (typically 30 wt%) often compromise the mechanical properties of PP composites (Demir, Balköse, & Ülkü, 2006; Lv, Wang, Hu, & Fan, 2005; Wu & Qu, 2001; Zhou, Song, Wang, Hu, & Xing, 2008). Although silane is recognized as a synergistic agent that enhances flame retardancy and compatibility in PP composites (Li, Jiang, & Wei, 2005; Li, Zhong, Wei, & Jiang, 2005; Lin, Yan, Liu, Wei, & Xu, 2011; Wang *et al.*, 2012), and melt compounding offers better dispersion than surface coating (Ascioglu & Adanur, 2003; Rottstegge *et al.*, 2007; Schadler, 2003), a significant research gap remains. Specifically, there is limited understanding of how different mixing sequences, particularly the pre-treatment of APP particles with silane, impact the flame retardancy and mechanical integrity of PP/IFR-silane composites.

To address this gap, this research introduces a novel approach by systematically investigating the influence of both direct and multi-step mixing methods on the flame retardancy of PP/IFR-silane (PP/IFR-Si) composites. The key novelty lies in the comprehensive analysis of how these different mixing sequences, especially the multi-step approach involving the pre-treatment of APP particles with silane, influence the chemical interactions, flame retardant properties, and overall material characteristics of the composites. This innovative methodology aims to enhance flame retardancy while potentially reducing the required IFR content, a crucial aspect not thoroughly explored in previous literature. The resulting composites were rigorously evaluated for flame retardancy, chemical interactions, and various material properties, including mechanical, morphological, and thermal characteristics.

2. Materials and Methods

2.1 Materials

Polypropylene (PP) used in this study was EL-Pro P 401, with a melt flow index of 2.4 g/10 min, manufactured by SCG Plastics Co. Ltd., Thailand. The antioxidant used was Hostanox M102 (Clariant), added at 0.2 wt% of PP. N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane (molecular weight = 222.3) was obtained from Dow Corning, grade Z-6020. Ammonium polyphosphate (APP) was GD-APP 101 from Zhejiang LongYou GD Chemical Co. Ltd., China. APP particles, with an average particle size of 15 µm, are crystalline II form with a high degree of polymerization (n > 1000). Pentaerythritol (PER) or 2,2-Bis(hydroxymethhyl)-1,3-propanediol (with 98%PER) was P4755 and purchased from Sigma-Aldrich, Thailand. Melamine (MEL) or 2,4,6-Triamino-1,3,5-triazine sym-triaminotriazine (with 99%Melamine), was M2659 and also purchased from Sigma-Aldrich, Thailand.

2.2 Composite preparation

2.2.1 Mixing

Flame retardant polypropylene composites were prepared with a laboratory two-roll mill within the temperature range 165 - 170 °C and with a mixing time of 6 min. Various compositions and mixing sequences were studied, as shown in Table 1. For PP/mod-25IFR_M-1 formulation, APP particles were pre-treated with silane before being mixed with other components.

2.2.2 Sheet fabrication

Composite sheets were prepared by compression molding using 10 cm x 10 cm x 1.3 mm aluminum plates. The composites were pre-heated at a temperature of 190°C for 5 min, followed by the application of 0.5 MPa pressure for 5 min. Cooling was performed under the same pressure for an additional 5 min.

2.2.3 Fiber fabrication

For fiber fabrication, the composites were cut into small pieces and dried in a vacuum oven at 60°C under pressure of -100 kPa for 15 hrs before fiber fabrication. PP and PP/IFR composite fibers were fabricated by using a Randcastle monofilament line with single-screw extruder (L/D = 25/1) from Intro Enterprise Co., LTD., Thailand. For as-spun fiber fabrication, the four temperature zones were set at 20ºC, 160 °C, 170 °C, and 185 °C, respectively, with a screw speed of 10 - 15 rpm and a leader speed of 3.5 - 5 rpm. The extruded monofilament (as-spun fiber) was first drawn into water tank at ambient temperature by a leader, then further drawn through a hot glycerol bath at approximately 105°C by a follower to form drawn fiber at the draw ratio 7x; this is the ratio of the follower speed to the leader speed.

Table 1. Formulations of PP/IFR composite sheets with their flame-retardance properties

Sample	Composition (wt%)				Mixing time (min)			Mixing	UL94-V	Burning time (s)	TGA under air atmosphere			
	PP	IFR	APP: PER: MEL	Si	2 min	2 min	2 min				$T_{0.05}$	$T_{0.10}$	$T_{0.50}$	T_p
PP	100	-	-	-		PP		D	Fail	>30	262	271	304	469
PP/30IFR_1-1-0_D	70	30	1:1:0	-	PP	APP + PER+MEL		D	V2	10	-	-	-	-
PP/30IFR_2-1-0_D	70	30	2:1:0	-	PP	APP + PER+MEL		D	V2	12	-	-	-	-
PP/30IFR_3-1-0_D	70	30	3:1:0	-	PP	APP + PER+MEL		D	Fail	>30	-	-	-	-
PP/30IFR_1-1-1_D	70	30	1:1:1	-	PP	APP + PER+MEL		D	V2	2	-	-	-	-
PP/30IFR_2-1-1_D	70	30	2:1:1	-	PP	APP + PER+MEL		D	V0	2	-	-	-	-
PP/30IFR_3-1-1_D	70	30	3:1:1	-	PP	APP + PER+MEL		D	V0	3	-	-	-	-
PP/25IFR_D	75	25	2:1:1	-	PP	APP + PER+MEL		D	Fail	-	255	274	338	348
PP/mod-25IFR_D	75	25	2:1:1	1	PP	APP + PER+MEL+Si		D	Fail	-	258	270	328	311
PP/mod-25IFR_M-1	75	25	2:1:1	1	PP	APP+Si	PER+MEL	M	V0	-	263	279	371	391
PP/mod-25IFR_M-2	75	25	2:1:1	1	PP	MEL+Si	APP+PER	M	Fail	-	-	-	-	-
PP/mod-25IFR_M-3	75	25	2:1:1	1	PP	APP+PER+Si	MEL	M	Fail	-	-	-	-	-
PP/mod-25IFR_M-4	75	25	2:1:1	1	PP	PER+Si	APP+MEL	M	-	-	-	-	-	-

Note : V-0: if the flame extinguishes within 10 seconds with no dripping, V1: if the flame extinguishes within 30 seconds with no dripping, and V2: if the flame extinguishes within 10 seconds with dripping.

2.3 Characterizations

2.3.1 Flame retardant property test

Sheet sample: UL94-V testing was performed as a vertical burning test with sample size of 125 x 12.5 x 1.3 mm^3 under standard of IEC 60695-11-4.

Pyrolysis-Combustion Flow Calorimeter (PCFC): Fire Testing Technology-FAA Micro Calorimeter, was used to perform heat release testing of PP/IFR-silane composites under ASTM D-7309. Samples of about 2-4 mg were heated from 150°C to 750°C (pyrolysis temperature) with heating rate of 1 °C/min, combustion temperature of 900°C, and rate of flow of O_2/N_2 gases set at 20/80 cm^3/min.

Fiber sample: According to NFPA 705, the recommended practice for a field flame test for textiles and film, the samples should be dry with a minimum size of 12.7 mm × 101.6 mm. The fire exposure should be from a common wood kitchen match or an equivalent flame, applied to the sample for 12 seconds. NFPA 705 defined two alternative ratings: "PASS" means the flame must be extinguished within 2 seconds without flaming dripping particles; and "FAIL" means the sample flame did not stop within 2 seconds and the flame can spread over the complete length of sample.

2.3.2 Mechanical properties

Fiber sample: PP and composite fibers were investigated by using a XLW (PC) Auto Tensile Tester. The gauge length was 100 mm, the cross-head speed 50 mm/min, and the load cell capacity 0.5 kN. The average for each sample type is reported based on ten specimens.

2.3.3 Chemical composition

Samples were cut by using a microtome (Leica Jung RM2065) to a thickness of 50 μm at ambient temperature in the cross-sectional direction, before performing XPS. X-ray photoelectron spectroscopy (XPS) was used to determine the chemical compositions. The analysis was carried out using a VG Scienta FG300 with Al Kα of 1,486.6 eV under ultrahigh vacuum (10^{-9} mbar).

2.3.4 Electron probe micro-analyzer (EPMA)

EPMA was used to determine the elemental composition of composites. Samples were embedded within some epoxy resin and were polished by using Al_2O_3. The elemental composition analysis was performed at 15 kV and 40 nA for phosphorus (P), nitrogen (N), and silicon (Si) mappings.

2.3.5 Condensed phase analysis

Rheometre (ARES 20A) is used to measure char expansion of PP/mod-IFR composites in a plate-plate configuration with the force of 2g from room temperature to 500 °C under an oxidative atmosphere.

2.3.6 Gaseous phase analysis

Thermogravimetric analysis (TGA) was performed on TA Instruments SDT Q600. Samples of about 10 mg were placed in an aluminum crucible and were heated from 40°C to 800°C under N_2 atmosphere at a heating rate of 10 °C/min to allow for equilibration and to get a better resolution of the pyrolytic decomposition steps; and under air atmosphere at a heating rate of 20 °C/min to simulate more rapid combustion conditions and to ensure that the oxidative degradation process is completed within a reasonable experimental time frame. This allowed observing the complete combustion profile, which might occur quickly.

TGA/FTIR analysis was performed on TGA Q5000IR from TA Instrument, combined with FTIR Nicolet iS10 spectrometer to study the gaseous phase. Samples of about 15 mg were put in an aluminum crucible and were heated from 40 °C to 800 °C at a heating rate of 10 °C/min under N_2 atmosphere. Samples were purged with N_2 flushing for 2 h at a flow rate of 100 ml/min.

3. Results and Discussion

3.1 Effects of direct and muti-step mixing sequences on flame retardancy of PP/IFR composites

3.1.1 Determining the optimal IFR ratio (APP:PER:MEL)

This section focuses on the compounding of PP/IFR composites using direct mixing and multi step mixing to study what would be an appropriate ratio for reducing the amount of IFR content. Flame retardancy of PP/IFR composites depends on the proportions in APP:PER:MEL. Table 1 shows the effects of IFR ratio on flame retardant properties. The ratings of UL94-V testing are categorized as follows: V0 (if the flame extinguishes within 10 seconds with no dripping), V1 (if the flame extinguishes within 30 seconds with no dripping), and V2 (if the flame extinguishes within 10 seconds with dripping).

The absence of MEL in the PP/30IFR composites resulted in poor flame retardancy under UL94-V testing, with V2 and Fail ratings for PP/30IFR_1-1-0_D, PP/30IFR_2-1-0_D, and PP/30IFR_3-1-0_D samples. However, PP/30IFR_2-1-1_D and PP/30IFR_3-1-1_D with 30 wt% IFR achieved a V0 rating, attributed to MEL particles enhancing flame retardancy by reducing burning time (Costa & Camino, 1988). Flame retardancy occurs in both the condensed phase, where a protective char forms, and in the gas phase, where phosphorus-based radicals reduce combustion (Costa & Camino, 1988). The optimal IFR ratio (APP:PER:MEL) is 2:1:1, which effectively promotes char formation. Reducing IFR content to 25 wt% resulted in a "FAIL" rating, as flame retardancy decreased.

The performance of IFR can be enhanced by microencapsulating APP particles with silane [26-29]. N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane (Si) was added to improve the compatibility between IFR and PP through surface functionalization. The PP/mod-25IFR_D composites, containing 25 wt% IFR with a 2:1:1 IFR ratio and 1 wt% Si, prepared by direct mixing, received a "FAIL" rating under UL94-V testing.

3.1.2 Investigating the effects of different mixing sequences (direct and multi-step mixing) on the flame retardancy of PP/IFR composites

A unique multi-step mixing approach was devised, involving four substances: APP, PER, MEL, and silane, loaded into the molten polymer mixture in different combinations. We hypothesize that a multi-step mixing approach, particularly the pre-treatment of APP particles with silane (M-1 sequence), will significantly enhance the synergistic effect between silane and IFR. This enhancement is expected to improve the efficiency of the flame-retardant system, thereby enabling a reduction in the total IFR content from 30 wt% to 25 wt% in PP/IFR-silane composites, while still achieving a UL94-V0 classification. Four mixing sequences were designed to prepare PP/mod-25IFR composites, consisting of 25 wt% IFR with a 2:1:1 IFR ratio and 1 wt% silane, as shown in Table 1. Each sequence is designated with an "M" for multi-step mixing. In the M-1 sequence, APP and silane were mixed first, followed by PER and MEL, which modified the APP particles with silane, resulting in improved char formation and a more compacted char layer in the condensed phase as in Figure 3. In the M-2 sequence, MEL and silane were mixed first, then APP and PER, enhancing the blowing agent with more nitrogen compounds. For M-3, APP, PER, and silane were mixed first, followed by MEL, aiming to link APP and PER for greater thermal stability. In the M-4 sequence, PER and silane were mixed first, followed by APP and MEL, but the mixture became too thin and sticky, making mixing difficult. Flammability testing under the multi-step mixing sequences showed that only the M-1 sequence, where silane and PP were mixed at 165°C for 4 minutes, achieved a V0 rating, while the other sequences failed. In the PP/mod-25IFR composites with V0 flame retardancy under M-1, silane and PP were mixed at 165°C for 4 minutes. The organofunctional silanes likely acted as a synergistic agent with IFR, triggering thermal-induced reactions between components, which may have altered the properties of the composites. Therefore, the effect of sequential addition was investigated to determine whether IFR components could undergo such thermally-induced reactions.

The reaction between silane and APP/IFR during melting was analyzed using EPMA for chemical composition and XPS for bonding insights. Figure 1 shows BSE images of composite cross-sections after mixing, including samples with and without silanes (PP/25IFR_D, PP/mod-25IFR_D, PP/mod-25IFR_M-1, and PP/mod-12.5APP_D). Light elements (PER/MEL) appear as gray particles, while heavier elements (APP) are white. X-ray mapping of phosphorus, nitrogen, and silicon was conducted using EPMA. In the composites with 25 wt% conventional IFR under direct mixing (PP/25IFR_D), phosphorus particles (less than 50 μm) and nitrogen particles (~50 μm) were observed, but silicon mapping was not detected due to the absence of silanes. When silane was added, phosphorus and nitrogen mappings in both direct and multi-step mixing were similar to the sample without silanes. Under direct mixing, silicon was randomly distributed, strongly observed on MEL particles and in the matrix, but weakly on large APP particles, with minimal presence on small APP particles. Under multi-step mixing (M-1), phosphorus and nitrogen mappings remained similar to direct mixing, while silicon mapping was strongly observed on small APP particles but very weakly on MEL particles. Figure 1 confirms silicon mapping in the first step of composite preparation under multi-step mixing (M-1).

For the M-1 sequence with a V0 rating, XPS wide scan spectra of the composites after mixing with different blending methods are shown in Table 2. The O/C and P/C ratios indicate phosphorus compound degradation from the APP-PER reaction (Delobel, Bras, Ouassou, & Alistiqsa, 1990). Composites under direct mixing showed higher phosphorus degradation than M-1, with the latter exhibiting less degradation than those without silane. Increased N/C ratios suggest more nitrogenated compounds in silane-containing composites. M-1 composites showed strong C-N and C=N bond formation. Nitrogenated compounds, especially those involved in C-N and C=N bonds, play a vital role in promoting intumescent char formation. These bonds contribute to the cross-linking and stability of the char layer when exposed to heat. A more robust and compact char layer provides better insulation and a barrier against heat and mass

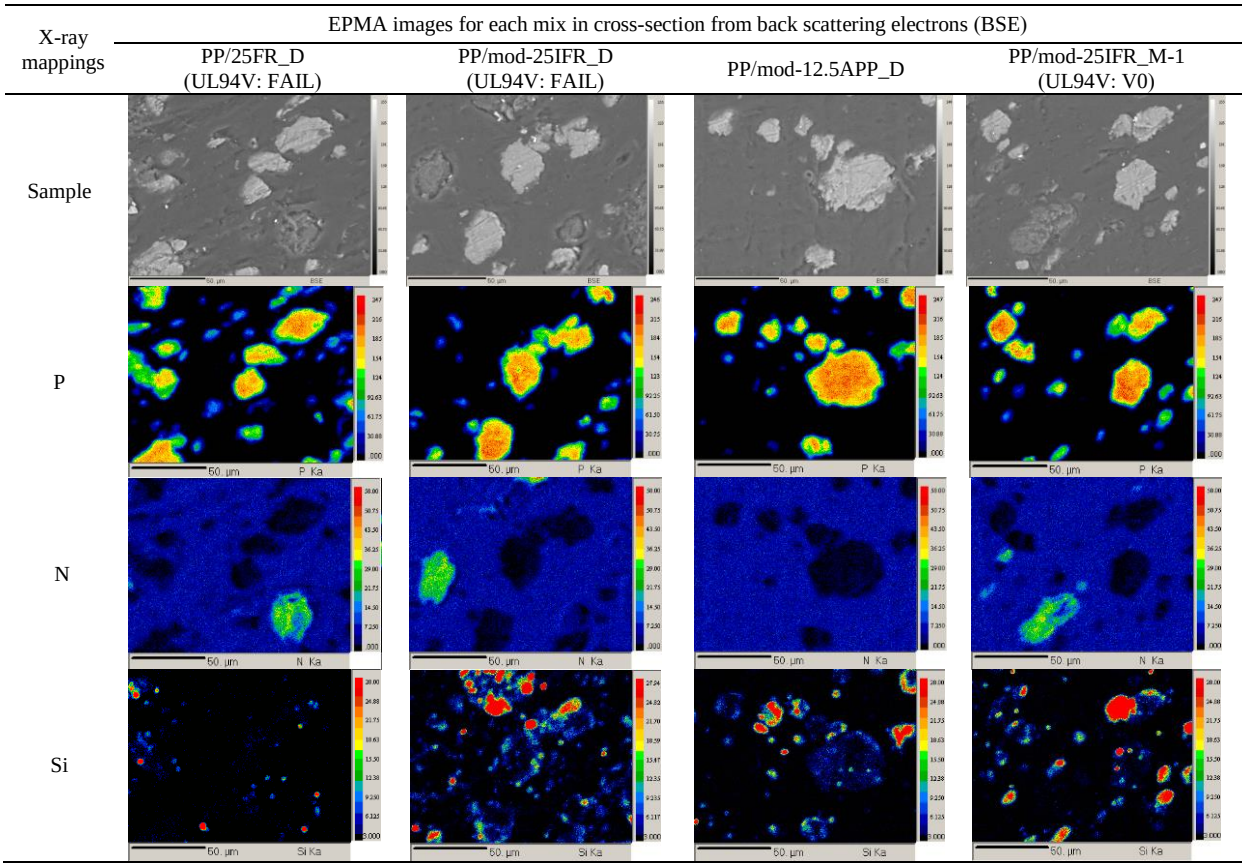

Figure 1. EPMA images of the after mixing composites prepared with different methods, in cross-section for back scattering electrons (BSE); PP/25IFR_D (direct mixing), PP/mod-25IFR_D (direct mixing with silane), PP/mod-12.5APP_D (direct mixing with only APP), and PP/mod-25IFR_M-1 (multi-step mixing with silane). X-ray mappings of phosphorous (P), nitrogen (N), and silicon (Si).

Table 2. XPS analysis for the after mixing composites with different reactive blending processes

Sample	UL94V	Atomic concentration (%)							Proportions			
		C1s	O1s	P2p	N1s	Si2p	C-N C 1s (285.9eV)	C=N C 1s (285.9eV)	O/C	P/C	N/C	Si/C
PP/25IFR_D	FAIL	81.4	8.8	0.6	9.2	-	4.3	4.3	0.108	0.007	0.113	-
PP/mod-25IFR_D	FAIL	77.4	9.2	0.3	12.6	0.5	7.1	7.1	0.119	0.004	0.163	0.006
PP/mod-25IFR_M-1	V0	75.6	9.2	0.5	13.5	0.5	12.3	12.3	0.131	0.007	0.179	0.007

transfer, thus enhancing flame retardancy (Costa & Camino, 1988). In the O 1s spectra (Figure 2a), two peaks at 531 eV and 533 eV were observed. The 531 eV peak corresponds to =O in phosphate or carbonyl groups (González-Elipe, Martínez-Alonso, & Tascón, 1988; Marletta, Oliveri, Ferla, & Pignataro, 1988; Beamson, 1992), and the 533 eV peak is assigned to –O– bonding. The N–C=O peak showed a 23.7% area for M-1 composites with silanes, compared to 20.4% for direct mixing. Composites with silanes showed Si–O bonding in the 533 eV peak fitting, while composites without silanes exhibited C–O, C=O, and P–O. The Si 2p spectrum for both direct and M-1 composites with silanes showed a peak at 102.3 eV (Si(-O)3). Regarding the P 2p spectrum, all composites showed a peak around 133.8–134.3 eV, indicating pyrophosphate bonding. Composites with silane (both direct and M-1) showed both P=O and N–C=O bonding. The presence of nitrogenated compounds was further supported by the N–C=O peak area. Quantitative XPS analysis confirmed that composites with silanes under M-1 exhibited improved thermal properties in both air and nitrogen environments, due to reduced phosphorus degradation and strong C-N and C=N bond formation.

To investigate char formation in PP/mod-25IFR_M-1 composites (25 wt% IFR at a 2:1:1 ratio with 1 wt% silane), condensed phase analysis using a rheometer was performed (Figure 3). The 200-300°C temperature range is crucial because it's where the reaction between APP and pentaerythritol (PER) occurs, forming cyclic phosphate ester

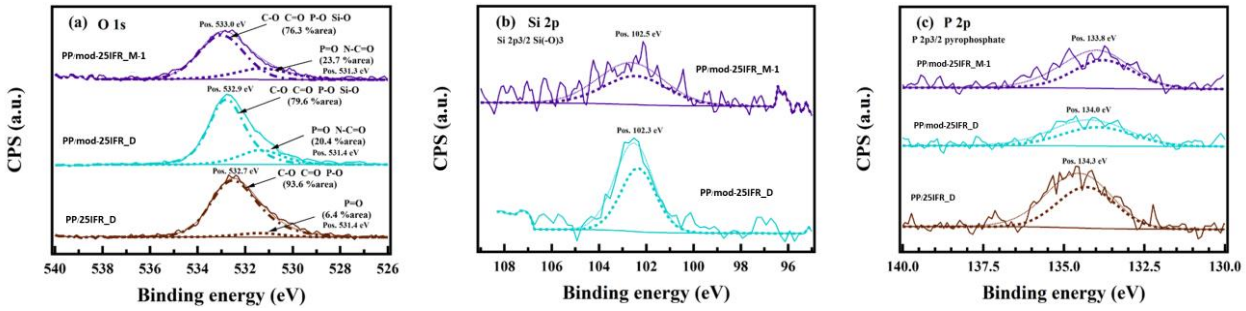

Figure 2. XPS spectra of after mixing composites prepared with different methods; (a) O 1s, (b) Si 2p, and (c) P 2p.

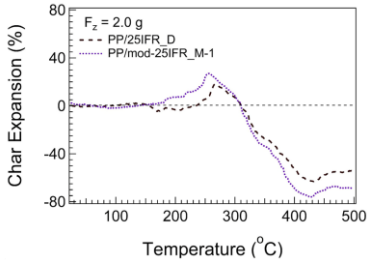

Figure 3. The char expansion of PP/mod-IFR_D (Fail for UL94-V) and PP/mod- IFR_M-1 (V0 for UL94-V) composites

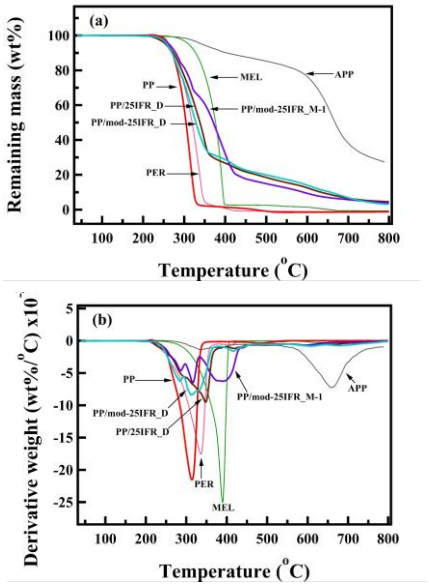

Figure 4. Thermal properties of APP, PER, MEL, PP, and the after mixing composites under air atmosphere: (a) TGA curves, and (b) DTG curves

structures and releasing ammonia and water as the early-stage char formation. The results show greater char expansion in PP/mod-25IFR_M-1 compared to PP/25IFR_D in the 200-300°C range. This increased expansion is attributed to the reaction between APP and PER around 210°C, forming cyclic phosphate ester structures and releasing ammonia and water (Camino, Costa, & Martinasso, 1989). These findings suggest that silane enhances early-stage char formation, providing better protection for the polymer during combustion.

TGA results under air atmosphere indicate that silane acts as a synergistic agent in PP/mod-25IFR_M-1 composites under M-1. Silane was strongly coated onto APP particles with strong C-N and C=N bond formation, resulting in a higher thermal stability of the APP with improvement of all thermal stability parameters. As shown in Table 1 and Figure 4, the thermal stability parameters $T_{0.05}$, $T_{0.10}$, $T_{0.50}$, and T_p were significantly improved in PP/mod-25IFR_M-1 compared to both PP/mod-25IFR_D and PP/25IFR_D. At the early-stage char formation, $T_{0.05}$ for the M-1 composites showed more improvement (by 5°C) compared with the direct mixing. The MEL particles of the after mixing composites under multi-step mixing are more resistant to degradation than under direct mixing. At T_p of 391°C, MEL particles enhance thermal stability, contributing to better flame-retarding performance. The M-1 approach, using 25 wt% IFR at a 2:1:1 ratio with 1 wt% silane, enhances flame retardancy and may reduce the required IFR content, improving drawability, mechanical, and flame-retardant properties in PP/IFR composite fibers.

3.2 PP/IFR composite fibers

PP composite fibers were prepared by using a melt-spinning method. As-spun fiber was cooled in water, then drawn through a glycerol bath at 105°C and a water tank at room temperature to various draw ratios. All composites as-spun can be drawn to a maximum draw ratio of 7x under these conditions.

In Figure 5, the crystallographic structure of 7x drawn fibers shows diffraction peaks of both IFR particles and PP crystals. The XRD patterns of composite fibers show three strong diffraction peaks at 2θ = 14.01, 16.83, and 18.48° which correspond to the diffraction planes (110), (040), and (130) for the α–form PP crystal (Karger-Kocsis, 1994), similar to a pristine PP fiber.

Mechanical properties (Table 3) show that the drawn fibers with less IFR particles (PP/25IFR_D and PP/mod-25IFR_M-1) exhibited higher tensile strength at break, elongation at break, and modulus, compared to the high-IFR PP/30IFR_D. This improvement is attributed to reduced IFR loading, which minimizes stress concentrations and maintains structural integrity. This reduction in filler content is inherently beneficial for mechanical properties, as a high filler loading can disrupt the polymer matrix, reduce chain mobility, and introduce stress concentration points, leading to decreased strength and ductility. As a significant practical advantage, the potential to develop PP composites

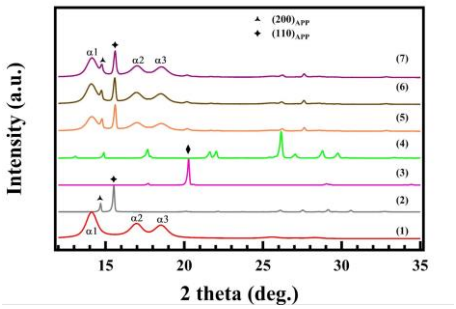

Figure 5. XRD curves for drawn fiber at draw ratio of 7x. (1) PP, (2) APP, (3) PER, (4) MEL, (5) PP/30IFR_D, (6) PP/25IFR_D, and (7) PP/mod-25IFR_M-1

that are both highly fire-resistant and mechanically robust opens up new possibilities for their use in demanding applications.

Flame retardancy testing (NFPA 705, Table 3, Figure 6) showed that PP fabric failed due to sustained flaming and dripping. In contrast, PP/30IFR_D, PP/25IFR_D, and PP/mod-25IFR_M-1 composites passed, exhibiting char formation and no flaming drip. Pyrolysis-Combustion Flow Calorimeter (PCFC) testing confirmed enhanced flame retardancy in the drawn composite fibers, with lower peak heat release rates (pHRR) and total heat release (THR) compared to 7x drawn PP fiber, indicating reduced oxygen demand during pyrolysis and combustion. This demonstrates the thermal stability of both IFR and mod-IFR particles after melt spinning and drawing.

Thermal and Gaseous Phase Analysis using TGA/FTIR under nitrogen (Figure 7) revealed that PP/mod-25IFR_M-1 fibers released the lowest gas concentration at 450°C, indicating improved thermal stability due to silane-modified IFR. FTIR spectra at 40°C, 250°C, and 450°C (Figures 7b, 7c, and 7d) showed no gas at 40°C. At 250°C, ammonia and water were detected (wavenumbers 3330, 1625, 1500, 956, 926 cm^{-1} for ammonia; 3730, 3600, 1080 cm^{-1} for water; Wang, Lv, Hu, & Hu, 2009), corresponding to the reaction between APP and PER (Camino, Costa, Trossarelli, Costanzi, & Landoni, 1984; Camino, Costa, Trossarelli, Costanzi, & Pagliari, 1985). At 450°C, C-H groups of PP and PP/IFR composites were observed, with PP/mod-25IFR_M-1 showing much lower intensity, suggesting that MEL particles in the composites sublimate during heating.

4. Conclusions

A silane-modified intumescent fire retardant has been presented for polypropylene. This modified intumescent fire retardant allows the lower loading of 25% with still acceptable flame-retardance properties (UL94-V0). However, for the system to be effective, it is important that a proper mixing sequence is used, i.e. APP and silanes have to be added to the molten PP before adding PER and MEL. Under reactive blending as in the multi-step mixing, the APP particles show more thermal stability due to some silane strongly covering the APP particles. For drawn composite fiber with flame retardant property, the intumescent fire retardant still shows thermal stability after melt spinning and drawing.

Table 3. Flame-retardant properties and mechanical properties of composites

Sample	Flame retardant properties					Mechanical Properties		
	Sheet		Fibers at draw ratio of 7x					
	UL94-V	NFPA 705	PCFC			Modulus (GPa)	Tensile strength at break (MPa)	Elongation at break (%)
			HR capacity (J/gK)	Peak HRR (W/g)	Total HR (kJ/g)			
PP	FAIL	FAIL	1221.5 ± 34.5	1191.5 ± 30.5	44.1 ± 0.9	5.9 ± 0.4	459.1 ± 25.7	17.2 ± 1.5
PP/30IFR_D	V0	PASS	-	-	-	3.3 ± 0.1	205.5 ± 3.6	14.0 ± 0.4
PP/25IFR_D	FAIL	PASS	914.5 ± 0.5	829.7 ± 60.3	33.0 ± 1.8	3.9 ± 0.1	253.0 ± 9.4	13.4 ± 0.9
PP/mod-25IFR_M-1	V0	PASS	904.0 ± 16.0	883.1 ± 18.6	33.0 ± 0.7	3.2 ± 0.1	217.1 ± 6.6	14.9 ± 0.6

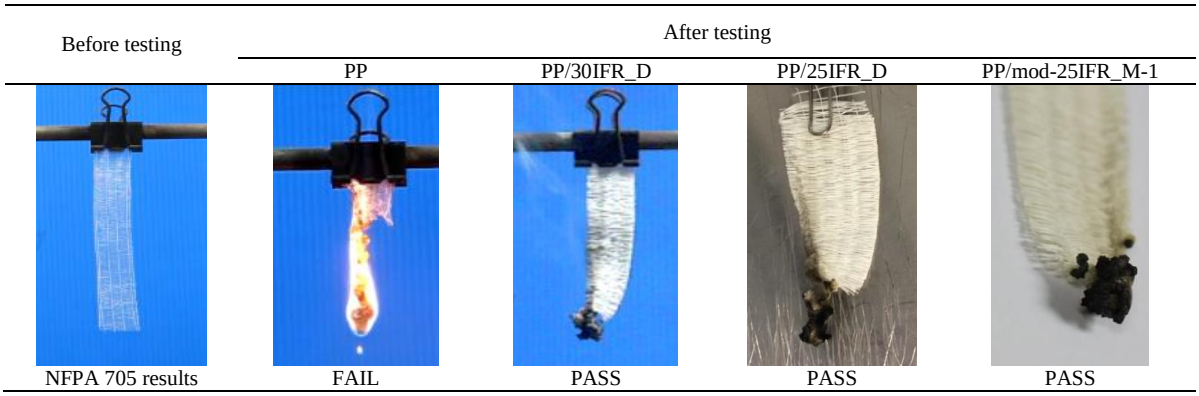

Figure 6. NFPA 705 results of PP and composite fibers at draw ratio of 7x

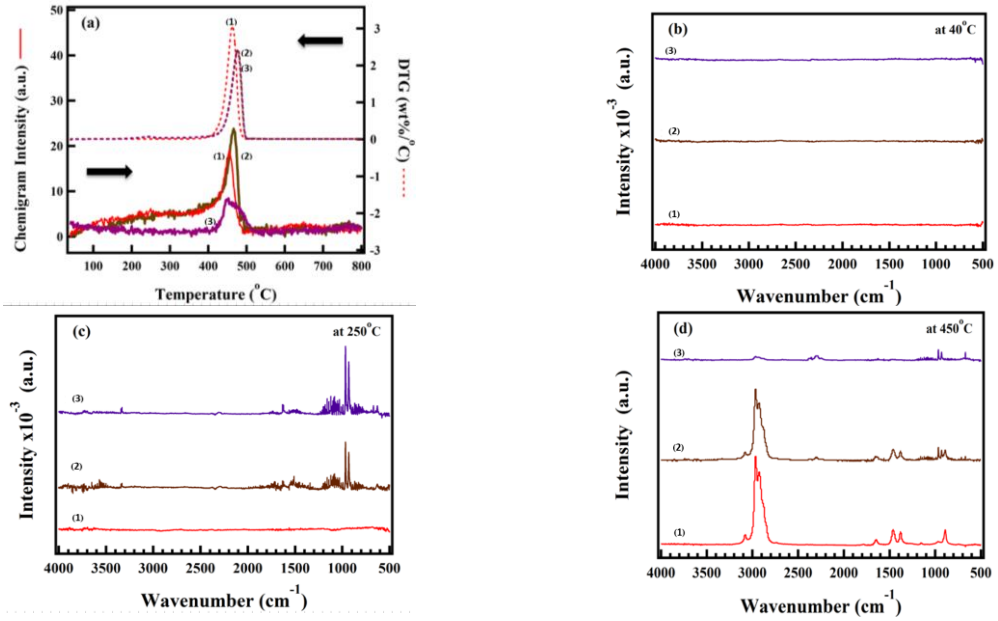

Figure 7. TGA/FTIR analysis under nitrogen atmosphere of PP fiber (1), PP/25IFR_D fiber (2), and PP/mod-25IFR_M-1 fiber (3) at draw ratio of 7x; (a) gaseous phase analysis compared with DTG curves, (b) FTIR spectra at 40 °C, (c) FTIR spectra at 250 °C, and (d) FTIR spectra at 450 °C.

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