

Calcium Carbonate and Ammonium Polyphosphate-Based Flame Retardant Composition for Polypropylene

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ABSTRACT: The chemical mode of action as a flame retardant of calcium carbonate nanoparticles combined with ammonium polyphosphate in polypropylene was investigated. Reduction in burning rates for 0.5 mm thick samples were observed without appreciable char formation up to 30 wt % loading of additives. Thermogravimetric analysis (TGA) of the mixture of CaCO₃ and ammonium polyphosphate (APP) showed that calcium carbonate nanoparticles react with ammonium polyphosphate before the degradation of the phosphate chains. TGA–FTIR studies of the polymer composite samples and powder mixtures of the additives

confirmed the evolution of ammonia and carbon dioxide due to interaction between the additives. X-ray diffraction (XRD) analysis of chars, obtained after burning the films, showed definite diffraction peaks corresponding to that of calcium metaphosphate. The inert gasses produced by the interaction of the additives hindered the advancing flame and, thus, reduces the burning rates, at times even without char formation. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1866–1873, 2011

Key words: flame retardance; additives; nanoparticles

INTRODUCTION

The use of nanoparticles, e.g., layered silicate, silica, carbon nanotubes, as flame retardants for a variety of polymers has been studied.^{1–3} The flame retardant effect of those nanoparticles is attributed to char formation on top of the burning polymer. These fillers act via a condensed phase flame retardation mechanism, which is purely physical in nature. Improvements in flame retardation, due to the presence of these nanodimensional materials by char formation was observed at low loadings. The primary reason behind the effectiveness of those nanoparticles as flame retardant is their platelet geometry, high aspect ratio, and very high specific surface area.^{4,5} Flame retardancy by nanoparticles has usually been reported in terms of reduction in the peak heat release rates, and the effect of nanoparticles on the burning rate of thin polymeric films have not been well explored.⁶

Ammonium polyphosphate (APP) is used as an acid source along with charring agents, such as polyalcohols, in flame retardant intumescent mastics and paints.^{7,8} APP is an effective flame retardant by itself

for polar polymers like polyamide-6,⁹ but it is ineffective as a flame retardant for polypropylene (PP). However, the addition of a suitable charring agent, like pentaerythritol, along with APP, to PP significantly reduces the flammability of the polymer.¹⁰

Calcium carbonate (CC) is used as a filler for polymers to reduce the cost of materials and to improve the impact strength. Studies have been carried out on the effects of calcium carbonate nanoparticles on rheology, tensile strength, and impact strength of polypropylene.^{11,12} Calcium carbonate nanoparticles have been found to be more effective as HCl scavengers for PVC than are micron size particles. The suggested reason behind the effectiveness of the nanoparticles was the reduced size causing higher reactivity and better dispersion in polymer than that of micron size particle.¹³ Calcium carbonate nanoparticles, along with 5 wt % montmorillonite, reduced the heat release rate of polypropylene by 53%. However, the specific role of CaCO₃ in reducing the flammability was not explained.¹⁴ It was expected that calcium carbonate particles, even of nanodimensional size, would not be effective because lack of a high aspect ratio geometry and hence comparatively low specific surface area, compared to other nano fillers.

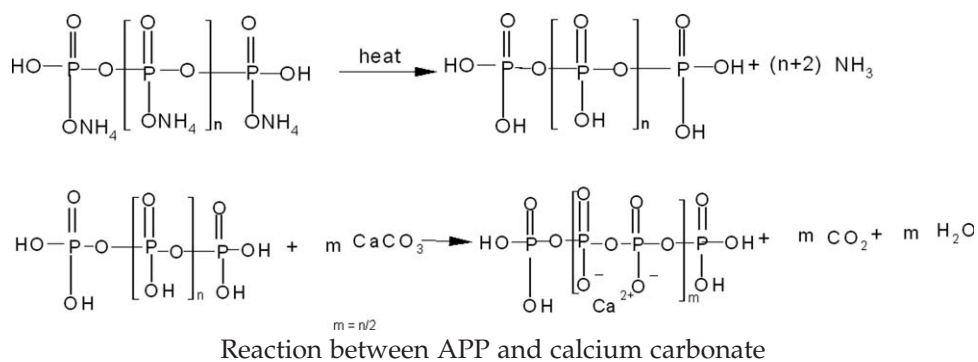
One of the modes of flame retardancy is by promoting inert gas formation around the flame front and thus diluting the combustible mixture to retard the flame

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spread. Many conventional flame retardants, like alumina trihydrate (ATH), magnesium hydroxide, etc., are effective flame retardants via this chemical mode of action. In addition to releasing water, they also endothermically decompose to remove heat from the polymer.¹⁵

In this investigation, CC/APP/PP films were prepared and tested for flame spread rate. APP, under fire conditions, degrades into polyphosphoric acid. Calcium carbonate, because of its basic nature, could react with polyphosphoric acid and release carbon dioxide and water vapors. Thus, generation of inert gasses during burning could lead to dilution of the combustible fuel, reduction in oxygen concentration, and hence reduction in burning rates. A reduction in the burning rates of

polypropylene was expected if the two additives are present together. From the expected reaction between the two additives shown in eq. (1), it is clear that one calcium atom reacts with two phosphate groups, therefore, the weight ratio of APP to CaCO₃ was kept 2 : 1 in all specimens. Melt mixing is an efficient method to obtain well-dispersed particles in the matrix and good mixing will promote reaction of the additives upon burning. The use of CaCO₃ nanoparticles was preferred because the reduced particle size enhances the possibility of reaction with APP during short burning periods. The focus of the research was to investigate the potential reaction between these components and its effect in reducing the polypropylene burning rate.



EXPERIMENTAL

Materials

Materials used for this research: fiber grade isotactic polypropylene (MarlexTM) from Philip-Sumika, Ammonium polyphosphate (Exolit 423TM) from Clariant, calcium carbonate nanoparticles (Multiflex MMTM) from Specialty Minerals. Calcium carbonate particles were calcite crystals, rhombic in shape and had an average individual particle size of 70 nm. The additives were mixed with polypropylene by melt mixing using Brabender IntelliTorque roller blade melt mixer. Polypropylene beads, powders of APP and calcium carbonate, were dried in the oven at 80°C for 3 h prior to melt mixing. All mixing was done at 180°C at 70 rpm under nitrogen flow. Table I shows the additive concentrations and conditions for preparation of all samples. The samples were pressed into composite films of ~ 0.5 mm thickness using Carver hot press under a pressure of 1.38 MPa at 180°C for 5 min.

Characterization

Horizontal flame spread testing (FMVSS 302)

The burning behavior and the burning rates of the films were assessed using Atlas Horizontal Flame

Spread Tester and the standard test method FMVSS 302 (Federal Motor Vehicle Safety Standards-302). Figure 1 shows the experimental configuration for this test. The ignition source was a Bunsen burner flame with a height of 2.5 cm, which was applied for 15 s. The burning times for an 11.4 cm length of film were recorded. Visual observations were also

TABLE I
Total Number of Samples

No.	Sample	APP (wt %)	CaCO ₃ (wt %)	PP (wt %)	Mixing time (min)
1	PP	0	0	100	20
2	AC10 : 5	10	5	85	20
3	AC15 : 7.5	15	7.5	77.5	20
4	AC20 : 10	10	20	70	20
5	AC25 : 12.5	25	12.5	63.5	30
6	AC30 : 15	30	15	55	30
7	A10	10	0	90	20
8	A20	20	0	80	20
9	A30	30	0	70	30
11	C10	0	10	90	20
12	C20	0	20	80	20
13	C30	0	30	70	30

AC20 : 10 indicates polypropylene composite with 20 wt % of APP and 10 wt % CC, C20 indicates 20 wt % loading of only CC, and A20 stands for sample with 20 wt % of only APP.

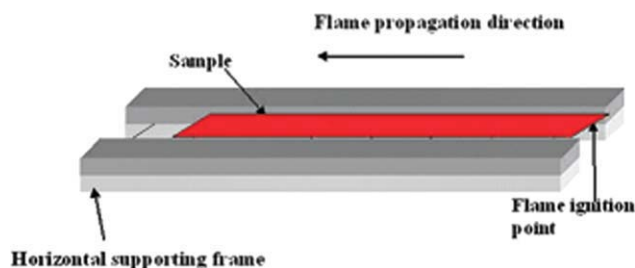


Figure 1 Schematic of FMVSS 302 test. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

made to characterize the burning behavior of the films and the char residues were collected and subjected to further analysis.

Thermogravimetric analysis

The decomposition behavior of pure APP, calcium carbonate, and a 2 : 1 mixture of APP and calcium carbonate powders, as well as three composite films, AC10 : 5, AC20 : 10, AC30 : 15, and neat polypropylene films were studied under an inert nitrogen atmosphere using a TGA Q500 from TA Instruments. The sample weight was about 20 mg and all the samples were heated to 750°C and held at that temperature for 20 min under a nitrogen atmosphere. Analysis on the additive powders and their 2 : 1 mixture was performed using 20°C/min heating ramp, whereas films of AC10 : 5, AC20 : 10, AC30 : 15, and PP were heated at a rate of 90°C/min. This study was useful to identify the chemical interaction between two additives as well as to observe the effect of those additives on polypropylene pyrolysis. The mass reproducibility of the TGA was $\pm 3\%$.

TGA-FTIR analysis

TGA-FTIR analysis was carried out on pure APP powder, a 2 : 1 powder mixture of APP and calcium

carbonate, and composite samples AC10 : 5, AC20 : 10, AC30 : 15 in nitrogen at a flow rate of 60 mL/min and a heating rate of 20°C/min on a Cahn TG 131 thermogravimetric analyzer connected to a Mattson Research grade FTIR spectrometer. The evolved volatile products were sampled at a rate of 40 mL/min, using a “sniffer” tube that extended into the sample cup and then carried the vapors through stainless steel tubing to the IR chamber; the temperature of the tubing and the sample cell was maintained at 250–300°C.

X-ray diffraction analysis of char

Powder X-ray diffraction analysis on the char residues was performed using a Scintag Model XDS 2000 diffractometer. The conditions were 40 kV and 35 mA with a scanning angle range from 10 to 60° at scanning rate of 2°/min.

RESULTS AND DISCUSSION

Horizontal flame spread test (FMVSS 302)

The results of the horizontal flame spread test (FMVSS 302) are given in Tables II and III, in terms of quantitative burning rates and qualitative visual observations, respectively. Values for the average burning time for each sample were obtained by testing 10 films of each sample. The standard deviation in burning time was around 1 s (specific values tabulated), which shows good consistency. Visual observation of flame front and recording of time could lead to variation in measured burning time by ± 2 s. The values for burning rates and percentage reduction in burning rates of polypropylene clearly showed that better results in lowering the burning rates of the composite films were obtained when APP and calcium carbonate were both present. The use of either APP or calcium carbonate up to 30 wt % in polypropylene did not significantly modify the

TABLE II
Results for Burning Rates by FMVSS-302

Sample	Avg. burning time (s) for 4.5"	Burning rate (Inch/min)	Standard deviation (s)	% Reduction in burning rate
Neat PP	29.90	9.03	1.03	–
AC10 : 5	39.13	6.80	1.12	24.70
AC15 : 7.5	44.80	6.02	1.11	33.33
AC20 : 10	52.50	5.10	1.23	43.23
AC25 : 12.5	75.80	3.60	1.02	60.15
AC30 : 15	97.30	2.78	1.15	69.23
C10	31.50	8.30	1.20	8.12
C20	33.20	7.70	1.34	14.67
C30	39.20	6.70	1.23	25.83
A10	32.90	8.20	1.01	9.23
A20	35.23	7.70	1.34	14.76
A30	42.23	6.40	1.12	29.15

TABLE III
Visual Observations for FMVSS-302

Sample	Visual observations
Neat PP	Intense burning with high flames, wax like dripping, dripping beads did not extinguished
AC10 : 5	Reduced dripping, less intense burning with low flame heights, no char formation
AC15 : 7.5	Reduced dripping, less intense burning with low flame heights, no char formation
AC20 : 10	Reduced dripping, less intense burning with low flame heights, no char formation
AC25 : 12.5	Continuous char layer formation, steady and slow burning with flame heights
AC30 : 15	Continuous char layer formation, steady and slow burning with flame heights
C10	Intense burning with high flames, dripping, no char formation
C20	Intense burning with high flames, dripping, no char formation
C30	Continuous burning without any char formation, reduced dripping
A10	Intense burning with high flames, dripping, no char formation
A20	Intense burning with high flames, dripping, no char formation
A30	Continuous burning and dripping

burning behavior of polypropylene. Neither of those additives was able to form char at the flame front to resist the advancing flame.

Burning rates for the films containing both additives showed improved flame resistance as the burning rates were gradually reduced with an increase in the concentration of additives. In the case of PP/APP/CC films, AC10 : 5, AC15 : 7.5, and AC20 : 10, the burning rates were reduced without any char formation at the flame front. Visual observations also confirmed that the intense burning of polypropylene was suppressed as the films burned with low flame heights. However, both AC25 : 12.5 and AC30 : 15 film samples showed continuous char layer formation as the flame advanced. This char layer acted as a physical barrier for flow of polymer towards flame as well as for outside oxygen to come in contact with flammable mass and, thus, reduced the burning rates and burning intensity.

The inability of CaCO₃ nanoparticles by itself, even when used at a loading of 30 wt %, to significantly reduce the burning rates may be attributed to the lack of high aspect ratio and high specific surface area. These particles are rhombic in shape and have 17 m²/g specific surface area. Because of this morphology, these particles are unable to form a continuous char network and hinder flame spread. There have been reports pertaining to the ineffectiveness of APP alone as a flame retardant for polypropylene.¹⁰ This work shows that the combination of the two additives is effective and a large reduction

in burning rate was observed. The effectiveness of the combination of two additives in reducing the burning rates of polypropylene could be because of their chemical interaction. The evolution of inert gases, like ammonia, water, and carbon dioxide, from the reaction between APP and calcium carbonate could dilute the combustible fuel and reduce the burning rates and intensity of burning. The identity of the gasses evolved was probed using TGA–FTIR techniques and char analysis, using powder X-ray diffraction, was performed to fully investigate the interaction between the additives during burning.

TGA and TGA–FTIR analysis

TGA on powder mixtures of APP and calcium carbonate, as well as on composite films, was performed to study the interaction between the additives and their effects on the thermal stability of polypropylene.

Figure 2(a–c) illustrate the TGA and DTG curves for APP, CaCO₃, and a 2 : 1 weight mixture of APP and CaCO₃, respectively. APP shows two degradation steps. The first step around 310°C is due to ammonia and water evolution from APP to form polyphosphoric acid. The second weight loss step observed around 570°C is due to the degradation of polyphosphate network.¹⁶ TGA–FTIR analysis of APP showed the ammonia doublet (930 cm⁻¹ and 966 cm⁻¹; Fig. 3) around 330°C. CaCO₃ starts to decompose around 550°C and shows only one decomposition step, as indicated by the DTG curve. This decomposition must be due to conversion of CaCO₃ into CaO; 56 wt % of residue was constantly observed after CaCO₃ decomposition.

TGA on 2 : 1 powder mixture of APP and calcium carbonate was performed to observe the interaction between them. The TGA curve clearly shows that there is an interaction between the two compounds, as three different weight loss steps are not observed for the mixture, as would be expected by summing the TGA curves of the individual components. Instead, the mixture showed only one weight loss step, indicated by single broad peak in the DTG curve. The mixture began to lose weight around 250°C and this continued until the end of the run. The weight loss curve was almost linear and it showed the maximum weight loss rate around 370°C. This could be due to the reaction between polyphosphoric acid, formed from APP and calcium carbonate particles. Calcium carbonate, upon reaction with polyphosphoric acid, evolves CO₂ and H₂O, causing further weight loss. It was clear from the absence of the degradation peaks at 577°C that calcium carbonate could have reacted with polyphosphoric acid before the degradation of the polyphosphate network. No

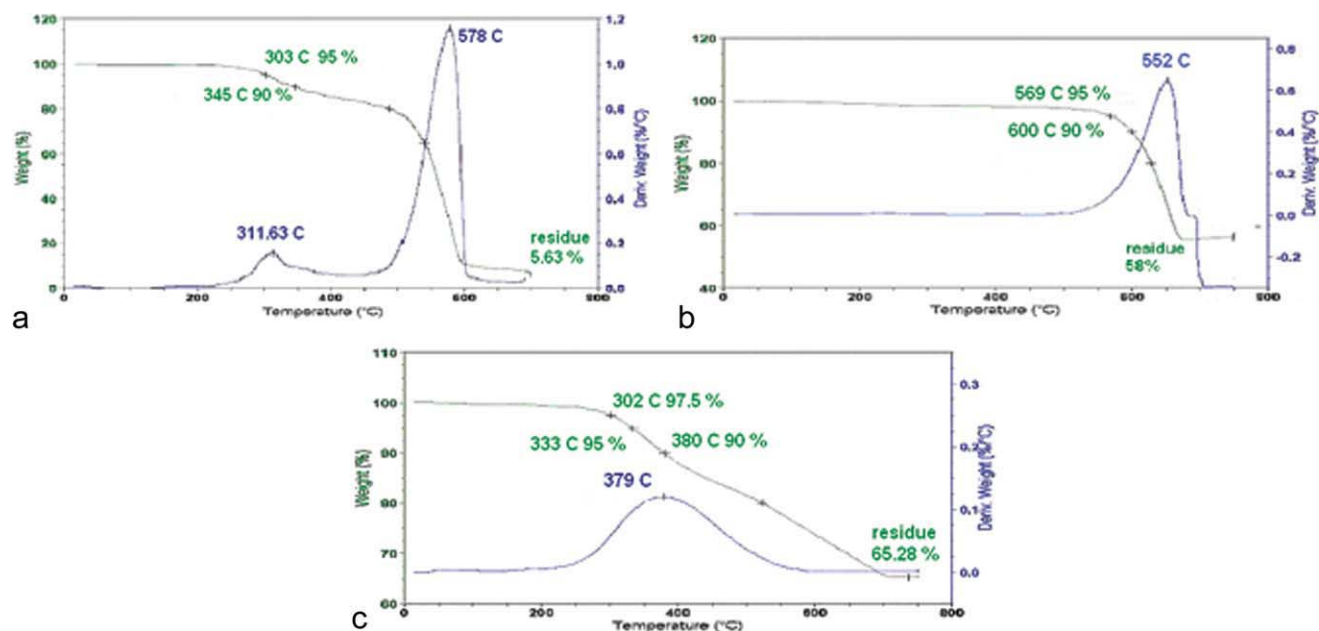


Figure 2 (a) TGA curve of APP, (b) TGA curve of calcium carbonate, and (c) TGA curve of 2 : 1 mixture of APP and calcium carbonate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

major weight loss step above 550°C, corresponding to CaCO₃ degradation, was observed.

The FTIR spectra obtained on heating the mixture of APP and calcium carbonate to 300°C are shown in Figure 4. There are peaks for ammonia (966 cm⁻¹) and carbon dioxide (2310 cm⁻¹), revealing that the weight loss occurred in APP and CC mixture was due to evolution of NH₃ and CO₂. The evolution of water could not be detected by FTIR. Evolution of carbon dioxide could not be from degradation of CaCO₃, since that degradation occurred above 550°C.

The mixture of additives was held at 750°C for 15 min. In the TGA no further weight loss was seen. These results indicate that a thermally stable compound from APP and calcium carbonate was

formed. This compound could be some form of calcium phosphate.

Equation (1) shows the expected net reaction between APP and CaCO₃. Formation of polyphosphoric acid from APP with ammonia evolution is an intermediate step. From the reaction, it is observed that reacting 194 g of APP with 100 g of CaCO₃ should produce 198 g of Ca(PO₃)₂, which is 67 wt % of the original weight of reactants. Around 65 wt % residue at the end of each experiment with the APP/CC mixture is constantly observed. These observations further support the proposed mode of reaction between the two additives.

The overlays of TGA curves of AC10 : 5, AC20 : 10, and AC30 : 15 with that of neat PP are shown in

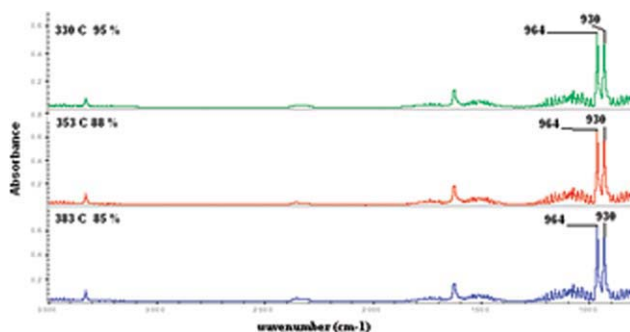


Figure 3 TGA-FTIR spectrum of APP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

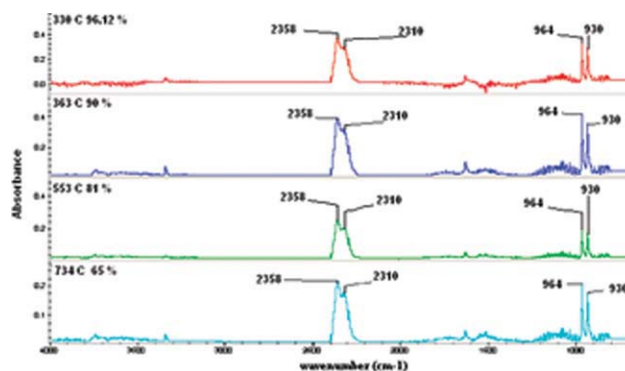


Figure 4 TGA-FTIR spectra of 2 : 1 mixture of APP and calcium carbonate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

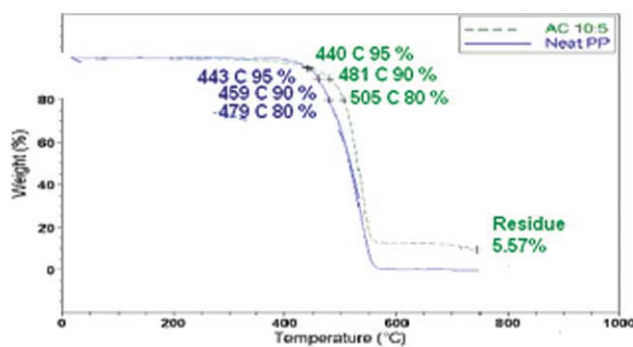


Figure 5 TGA curves of neat PP and AC10 : 5 film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

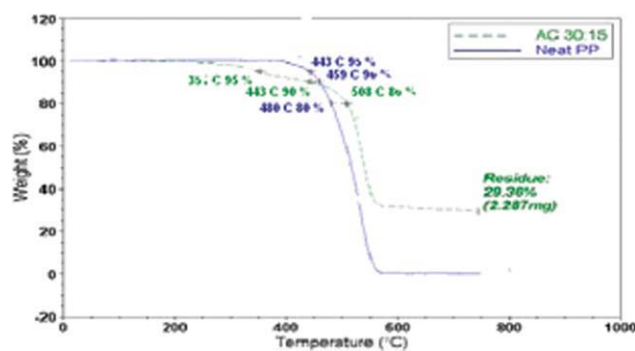


Figure 7 TGA curves of neat PP and AC30 : 15 films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figures 5–7, respectively. The composite films were heated at 90°C/min to determine their behavior under high heating rates. All the three composite samples showed early weight losses compared to that of neat PP. AC20 : 10 and AC30 : 15 showed very similar decomposition behavior with 5% weight loss and 10% weight loss temperatures around 350°C and 440°C, respectively. The corresponding 5% weight loss and 10% weight loss temperatures for neat PP were 443°C and 459°C, respectively. The early onset of weight loss for composite films could be due to the degradation of APP to polyphosphoric acid followed by reaction with calcium carbonate. A weight loss step was observed around the same temperatures in the case of the APP/CC mixture. Polypropylene and all three AC samples showed the maximum weight loss rate around 530–535°C, likely due to PP degradation. The concentration of additives in films did not have any effect on peak decomposition temperature. The TGA curves of the AC composite films indicate a delay in PP degradation at higher temperatures. In the case of AC20 : 10 and AC30 : 15, the weight loss curve show higher temperatures for higher weight losses than those for neat PP, e.g., in the case of neat PP 20 wt % loss occurred around 408°C whereas the temperatures

for 20% weigh loss of AC20 : 10 and AC30 : 15 curve were around 508°C. The same trends were observed in the case of AC10 : 5 films. The presence of additives improved the thermal stability of PP in an inert atmosphere.

TGA–FTIR analysis of AC20 : 10 and AC30 : 15 revealed that ammonia and carbon dioxide evolution occurred before polypropylene degradation. Figures 8 and 9 show the IR spectra for AC20 : 10 and AC30 : 15 samples as a function of temperature. The broad FTIR peak at 2950 cm⁻¹ is due to the evolution of hydrocarbons, indicating the onset of polypropylene degradation. This peak was observed from 430°C onwards. The peaks for CO₂ and NH₃ disappear once polypropylene starts to degrade and complex spectra containing peaks of hydrocarbons are observed.

Neat polypropylene undergoes complete degradation and no significant amount of residue remains. On the basis of TGA analysis for APP/CC mixture, it was expected that the additives would react with each other, even in the presence of polypropylene, and leave ~ 67 wt % of their original weight. AC10 : 5, AC20 : 10, and AC30 : 15 left 9.5%, 20%, and 29% residue at end of each test, respectively. Each composite sample left nearly 67% of original additive weight in the form of residue which led to the

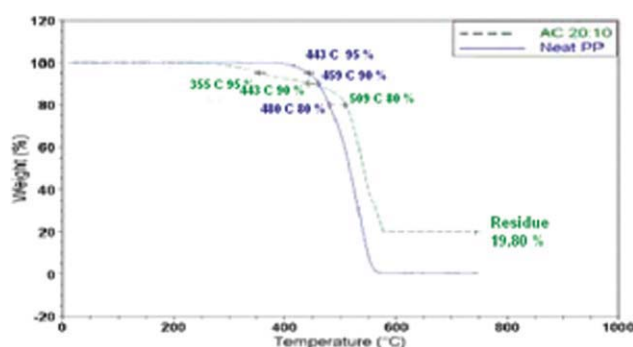


Figure 6 TGA curves of neat PP and AC20 : 10 films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

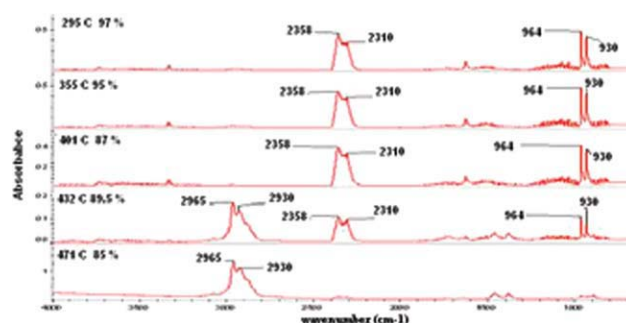


Figure 8 TGA–FTIR spectra of AC20 : 10 film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

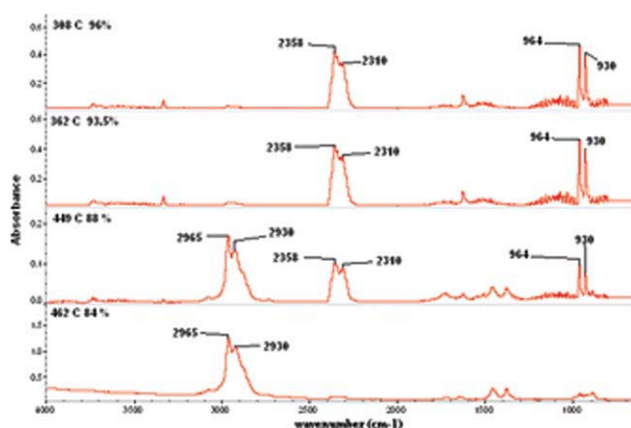


Figure 9 TGA-FTIR spectra of AC30 : 15 film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conclusion that the two additives react in a similar way as they did in the pure powder mixtures and the residue could be $\text{Ca}(\text{PO}_3)_2$.

XRD analysis of char

X-ray diffraction analysis was performed on the char residues obtained after burning films of AC10 : 5, AC20 : 10, and AC30 : 15 to identify the inorganic compound formed by reaction between APP and CC, during burning. The same analysis was performed after heating the chars at 750°C , to obtain strong and sharp peaks. Figures 10–12 show overlays of XRD patterns for AC10 : 5, AC20 : 10, and AC30 : 15 chars, obtained after burning the films and after heat treating at 750°C . Three high intensity diffraction peaks at 2θ values of 25.28° , 28.50° , and 31.76° were observed in all six samples. The peak positions did not change after heating at 750°C , suggesting that the inorganic compound, formed during burning, did not undergo any structural alterations. However, the absolute intensities were higher in the

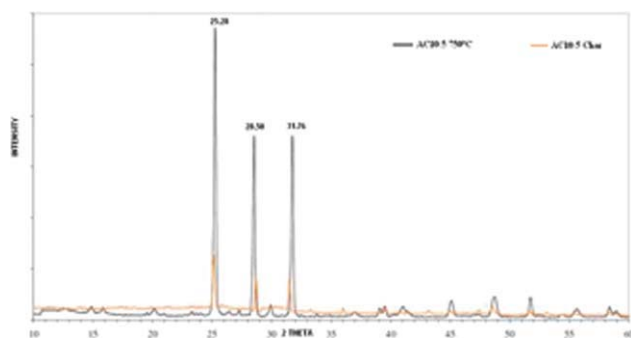


Figure 10 XRD patterns of AC10 : 5 char (before and after heating at 750°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

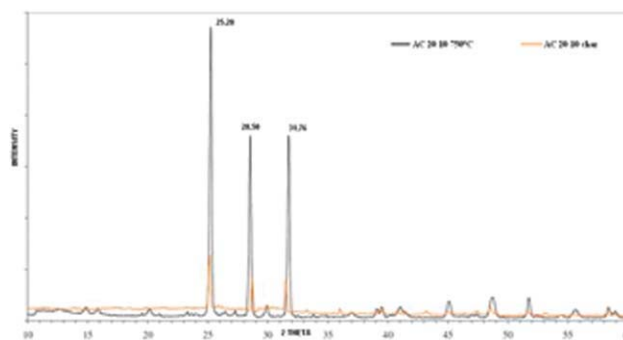


Figure 11 XRD patterns of AC20 : 10 char (before and after heating at 750°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

case of the heat treated residues as traces of unburned polymer in the char may have been oxidized and/or the heat treatment may improve the crystallinity. Char residues after burning gave broader diffraction patterns in the range of $10\text{--}25^\circ$ compared to the heat treated residue.

As there was no change in diffraction pattern for the residues obtained after burning and after heat treating at 750°C , the diffraction patterns of the heat treated residues were used for further identification. Table IV shows the 2θ values and relative intensities of the three peaks in the XRD trace.

The XRD data were compared with published literature by McIntosh et al.¹⁷ on crystal structures and XRD patterns of the various calcium phosphates; the XRD pattern closely resembles that shown by β -calcium meta phosphate. β -Calcium meta phosphate has molecular formula $[\text{Ca}(\text{PO}_3)_2]_n$, and is a linear chain calcium phosphate.¹⁸ The chains are connected through the PO_3 tetrahedra. Thus, the char residues obtained in flame spread tests also contain β -calcium meta phosphate and XRD analysis shows conversion

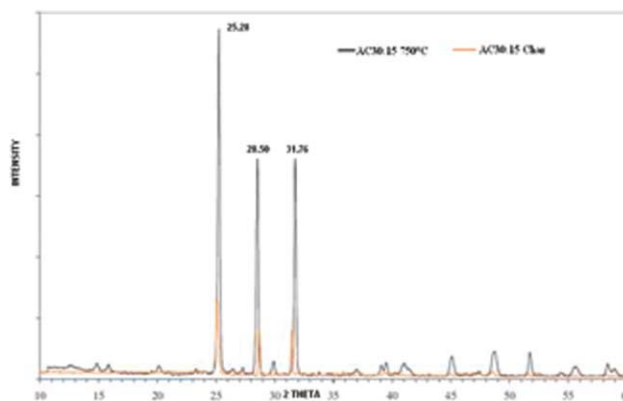


Figure 12 XRD patterns of AC30 : 15 char (before and after heating at 750°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV
X-ray Peaks Data for Char Residues After 750°C Heat Treatment

2θ	Relative intensity (%)	d spacing (°A)
25.28	100	3.52
28.50	63	3.13
31.76	63	2.83

of calcium carbonate into β -calcium meta phosphate during burning and the conversion is accompanied by the evolution of ammonia, water, and CO_2 .

CONCLUSIONS

A gradual reduction (between 24% and 69%) in the burning rates of polypropylene was observed with an increase in concentration of APP and calcium carbonate in PP. The two additives react to form β -calcium metaphosphate with the evolution of ammonia, water, and carbon dioxide. TGA and TGA-FTIR studies confirmed ammonia and CO_2 evolution and reaction mechanism in inert atmosphere, whereas XRD analysis confirmed reaction between additives in real fire situation. Degradation of polypropylene is delayed due to the presence of the barrier from the metaphosphate and the presence of the noncombustible gasses dilute the flammable gasses and hinder efficient burning of the polymer.

References

- Beyer, G. *Int Polym Sci Technol* 2003, 30, 1.
- Kashiwagi, T.; Gilman, J. W.; Butler, K. M.; Harris, R. H.; Shields, J. R.; Asano, A. *Fire Mater* 2000, 24, 277.
- Manias, E. FRCA; Lancaster: PA, 2002; p 8.
- Gilman, J. W. *Appl Clay Sci* 1999, 15, 31.
- Gilman, J. W.; Jackson, C. L.; Morgan, A. B.; Harris, R.; Manias, E.; Giannelis, E. P.; Wuthenow, M.; Hilton, D.; Phillips, S. H. *Chem Mater* 2000, 12, 1866.
- Shanmuganathan, K.; Deodhar, S.; Dembsey, N.; Fan, Q. G.; Calvert, P. D.; Warner, S. B.; Patra, P. K. *J Appl Polym Sci* 2007, 104, 1540.
- Joseph, P.; Ebdon, J. In *Fire Retardant Materials*; Horrocks, A., Price, D., Eds.; Woodhead publishing Limited: Cambridge, 2000; Chapter 7.
- Lynos, J. *The Chemistry and Uses of Fire Retardants*; John Wiley & Sons: New York, 1970.
- Camino, G.; Lomakin, S. In *Fire Retardant Materials*; Horrocks, A., Price, D., Eds.; Woodhead publishing Limited: Cambridge, 2000; Chapter 10.
- Zhang, S.; Horrocks, A. R. *Prog Polym Sci* 2003, 28, 1517.
- Chan, C. M.; Wu, J. S.; Li, J. X.; Cheung, Y. K. *Polymer* 2002, 43, 2981.
- Dangtungee, R.; Yun, J.; Supaphol, P. *Polym Test* 2005, 24, 2.
- Zhu, S.; Zhang, Y.; Zhang, Y.; Zhang, C. *Polym Test* 2003, 22, 539.
- Tang, Y.; Hu, Y.; Zhang, R.; Wang, Z. Z.; Gui, Z.; Chen, Z. Y.; Fan, W. C. *Macromol Mater Eng* 2004, 289, 191.
- Lewin, M.; Weil, E. In *Fire Retardant Materials*; Horrocks, A., Price, D., Eds.; Woodhead Publishing Limited: Cambridge, 2000; Chapter 2.
- Riva, A.; Camino, G.; Fomperie, L.; Amigouet, P. *Polym Degrad Stab* 2003, 82, 341.
- Mcintosh, A. O.; Jablonski, W. L. *Anal Chem* 1956, 28, 1424.
- Guo, L. H.; Li, H.; Gao, X. H. *J Mater Sci* 2004, 39, 7041.