

Polypropylene based Novel Flame Retardant Nanocomposite Compositions

by

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Introduction

Use of nanoparticles like layered silicate, silica, carbon nanotubes, as effective flame retardants [1, 2, 3] for variety of polymers has been known. Previous research attributed the flame retardant effect of those nanoparticles to char formation on top of burning polymer. The mechanism was proved to be in condense phase and purely physical in nature. Improvement in flame resistance of nanocomposite materials by char formation was obtained at low loadings of those nanoparticles. 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]. Those studies proved flame retardancy by nanoparticle in terms of reduction in heat release rates, but no literature talked about the effect of nanoparticles on the burning rate of very thin polymeric films.

Ammonium polyphosphate is conventionally used phosphorous based flame retardant. APP is used as an acid source for charring the "char forming agent" such as polyalcohol in flame retardant intumescent mastics and paints [6, 7]. APP is an effective flame retardant for polar polymers like nylon 6 [8], but is found to be ineffective as flame retardant for polypropylene because of purely hydrocarbon nature of polymer, when used alone[9]. However, addition of suitable charring agent like

Abstract

In this research we investigated chemical mode of flame retardant action of calcium carbonate nanoparticles (CC) along with ammonium polyphosphate (APP) on burning of polypropylene (PP). We prepared PP/ CC/ APP nanocomposites with five different percentage loadings of additives by melt mixing. In each nanocomposite, the weight ratio of APP to CC was kept 2:1 because of stoichiometry of the expected reaction between them. We studied the effect of the additives on flame spread rate of polypropylene films using standard horizontal flame spread test and observed reduction in burning rate without appreciable char formation up to 30 percent loading additives. But at higher percentage loading of additives, there was char formation at the flame front, which further reduced the burning rate significantly. Thermogravimetric analysis (TGA) of the mixture of CaCO_3 and APP showed that calcium carbonate nanoparticles react with APP prior to the degradation of the phosphate chains. TGA-FTIR studies were carried out on nanocomposite samples and powder mixture of the additives to confirm evolution of ammonia and carbon dioxide due to interaction between the additives. X-ray diffraction (XRD) analysis of chars, obtained after burning nanocomposite films, showed definite crystal pattern and diffraction peaks corresponding to that of calcium meta phosphate.

pentaerythritol along with APP into PP reduces its flammability significantly [9]. Calcium carbonate is commonly used fillers for polymers to reduce to cost of material and to improve the impact strength of polymers [10]. Studies have been carried out on effects of calcium nanoparticles on rheology, tensile strength and impact strength of polypropylene [11, 12]. A calcium carbonate nanoparticle has been found to be more effective HCl scavenger for PVC than to micron size particles. The reasons behind the effectiveness of nanoparticles were, the reduced size causing higher reactivity and better dispersion in polymer than that of micron size particles. [13]. 5 wt. percent calcium carbonate nanoparticles, along with 5 wt. percent montmorillonite, reduced heat release rate of polypropylene by 53 percent. [13], however specific role of CaCO_3 in reducing the flammability was not explained. We expected that only calcium carbonate particles, even in nano size, would not be effective because of their comparatively low specific surface area than other nano fillers and lack of high aspect ratio geometry.

One of the modes of flame retardancy is by promoting the inert gas formation around flame front and thus dilute the combustible mixtures to retard the flame spread. Many conventional flame retardants like ATH, magnesium hydroxide etc., work in this chemical mode of action [15]. In our approach we prepared CC/ APP/ PP films and tested their flame spread rate. APP, during fire,

degrades into polyphosphoric acid. CaCO_3 , because of its highly basic nature could react with polyphosphoric acid and evolve carbon dioxide and water vapors. Thus generation of inert gases while burning could lead to dilution of combustible fuel, reduction in oxygen concentration and hence reduction in burning rates. We expected to obtain better percentage reduction in burning rates of polypropylene when two additives were present together. The expected reaction between the two additives is shown in equation 1. From the expected chemical reactions shown above, it is clear that one calcium atom is consuming two phosphate groups. Therefore we kept weight ratio for APP to CaCO_3 as 2:1 in nanocomposites preparation.

Experimental

Materials

We used following materials for this research: Fiber grade isotactic polypropylene (MarlexTM) from Philip-Sumika Inc., Ammonium Polyphosphate (Exolit 423TM) from Clariant Inc., Calcium carbonate nanoparticles (Multiflex MMTM) from Specialty Minerals Inc. Calcium carbonate particles were of calcite crystals, rhombic in shape and had average individual particle size 70 nanometer. Polypropylene beads, powders of APP and CC were dried in the oven at 80 °C for 3 hours prior to melt mixing. The additives were mixed with polypropylene by melt mixing using Brabender IntelliTorque roller blade melt mixer. All the mixings were done at 180 °C, 70 rpm and under nitrogen flow. Table 1 shows the additive concentrations and conditions for preparation of all the samples. The samples were pressed into films of 0.5 mm thickness using Carver hot press under a pressure of 10000 psi at 180 °C for 5 min.

Horizontal flame spread testing (FMVSS 302)

The burning behavior and the flame spread rates of the nanocomposite films were assessed using “Atlas Horizontal Flame Spread Tester” and the standard test method FMVSS 302 (Federal Motor Vehicle Safety Standards-302). The ignition source used was Bunsen burner flame of 1 inch height and it was applied for 15 seconds. Burning times for 4.5 inch length of film were recorded. Visual observations were also recorded to characterize the burning behavior of films. The char residues left behind were collected and used for further analysis.

Thermogravimetric Analysis

We studied the decomposition behaviors of pure APP, CC and 2:1 mixture of APP and CC, as well as three nanocomposite film samples; PAC10:5, PAC20:10, PAC30:15 and neat polypropylene films under inert nitrogen atmosphere using TGAQ500 by TA

Instruments. All the samples were heated up to 750 °C and held isothermally for 20 min. under nitrogen atmosphere. The analysis on the powders was performed using 20 °C/ min. heating ramp while films of PAC10:5, PAC20:10 and PAC30:15 were heated with 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.

TGA-FTIR analysis

We carried out a combined TGA-FTIR analysis on pure APP powder, 2:1 powder mixture of APP and CC, and nanocomposite samples PAC10:5, PAC20:10, PAC30:15. TGA-FTIR was performed in nitrogen, at a flow rate of 60 ml/min and a heating rate of 20 °C/min on a Cahn TG 131 instrument connected to a Mattson Research grade FTIR. The evolved volatile products were sampled at a rate of 40 ml/min, using a 'sniffer' tube that extended to the sample cup. The evolved gases were carried through stainless steel tubing to the IR chamber, the temperature of the tubing and the sample cell was maintained at 250- 300°C. The sample size was ~ 40mg.

X-ray Diffraction Analysis of Char

Powder X-ray diffraction analysis on the char residues was performed using Scintag Model XDS 2000 diffractometer under the conditions 40kV and 35mA 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 FMVSS 302 are given in Table 2 and in terms of burning rates (quantitative) and visual observations (qualitative) respectively. Readings for average burning time for each sample were obtained after testing 10 films of each sample. The standard deviation in burning time readings was around 1 second (specific values tabulated), which shows good consistency in the readings. Difficulties in visual observation of flame front and recording of time could lead to variation in measured burning time by +/- 2 seconds.

The values for burning rates and percentage reduction in burning rates of polypropylene clearly showed that better results were obtained when APP and CC were present together. Use of either APP or CC up to 30 wt. percent with polypropylene did not modify the burning behavior of polypropylene much. Neither of those additives was able to form char at the flame front to resist the advancing flame. Figure 1 Figure 2 Figure 3 show the digital images of burning of polypropylene films with either APP or CC in it.

Flame spread rates for the films, containing both additives, showed improved flame resistance as burning rates were gradually reduced with increase in the

concentration of additives. PAC10:5, PAC15:7.5 and PAC20:10 burning rates reduced without any char formation at flame front. A visual observation also showed the intense burning of polypropylene was suppressed as film burned with low flame heights. However, PAC25:12.5, PAC30:15 nanocomposite samples showed continuous char layer formation as the flame was advancing. This char layer provided the physical barrier for flow of polymer towards flame and thus reduced the burning rates and burning intensity. Figure 4 Figure 5 show the burning of various films containing these two additives. The images clearly indicated the reduction in burning intensity of polypropylene by these two additives, with or without char formation. Inability of CaCO_3 nanoparticles, even used up to 30 wt. percent, to reduce the burning rates significantly may be attributed to the lack of high aspect ratio and lack of high specific surface area. These particles are of rhombic in shape and have $17\text{m}^2/\text{g}$ specific surface area. These factors give poor covering power to CaCO_3 to form continuous char network and hinder flame spread. The studies have shown the ineffectiveness of only APP as a flame retardant for polypropylene [9]. However, when those two additives were present together, we observed higher reduction in burning rates. This synergism between APP and CC could be through the chemical interaction between them. Evolution of inert gases like ammonia, water and carbon dioxide from the reaction between APP and CC could dilute the combustible fuel and reduce flame spread rate and intensity of burning. We performed char analysis to investigate the interaction between the additives.

TGA and TGA-FTIR analysis

We performed TGA on powder mixtures of two additives as well as on nanocomposite films to study the interaction between the additives and their effects on thermal stability of polypropylene.

Figure 6 Figure 7 Figure 8 illustrate the TGA and DTG curves for APP, CaCO_3 and 2:1 by weight mixture of APP and CaCO_3 respectively. APP showed two degradation steps. The first step around 311°C was due to ammonia and water evolution from APP to form polyphosphoric acid. Second weight loss step observed around 570°C was due to degradation of polyphosphate network [16]. TGA-FTIR analysis of APP showed the ammonia doublet (966 cm^{-1}) in the FTIR spectrums (Figure 9) recorded around 330°C . CaCO_3 started decomposing around 550°C and showed only one decomposition step, as indicated by DTG curve. This decomposition must be due to conversion of CaCO_3 into CaO. We constantly observed around 56 percent of residue after CaCO_3 decomposition.

TGA on 2: 1 powder mixture of APP and CaCO_3 was performed to analyze the interaction between them. TGA curve clearly showed that there is interaction between the two compounds, as we did not observe the

three different weight loss steps for the mixture. Instead the mixture showed only one weight loss step as indicated by single broad peak on DTG curve. The mixture started showing weight loss around 250°C and 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 nanoparticles. Calcium carbonate, on reacting with polyphosphoric acid evolves CO_2 and H_2O 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 prior to polyphosphate network degradation. We did not observe any major weight loss step above 550°C corresponding to CaCO_3 degradation.

We observed FTIR spectrums obtained on heating the mixture of APP and CaCO_3 . Figure 10 shows FTIR spectrums at various temperatures and percentage weight loss. It shows absorbance signals for ammonia (966 cm^{-1}) and carbon dioxide (2310 cm^{-1}), revealing that weight loss occurred in APP and CC mixture was due to evolution of NH_3 and CO_2 . Evolution of water could not be detected by FTIR. Evolution of carbon dioxide could not be from degradation of CaCO_3 since that degradation occurred above 550°C .

We held the sample at 750°C for 15 min. and did not observe any weight loss. Those observations indicated that there was formation of thermally stable compound from APP and CC. The compound could be calcium phosphate. The percent residue left after the TGA run could be useful to determine the stoichiometry of the reaction and hence the amount of inert gas evolution during the reaction.

Equation 1 shows the expected net reaction between APP and CaCO_3 . Formation of polyphosphoric acid from APP with ammonia evolution is an intermediate step. From the reaction, we found out that reacting 194 g of APP with 100 g of CaCO_3 should produce 198g of $\text{Ca}(\text{PO}_3)_2$, which is ~ 67 percent of original amount. We constantly observed around 65 percent residue at the end of each experiment for APP/CC mixture. These observations further supported our proposed mode of reaction between the two additives.

Overlay of TGA curves for PAC10:5, PAC20:10 and PAC30:15 with that of neat PP are shown in Figure 11 Figure 12 Figure 13. The nanocomposite films were heated with $90^\circ\text{C}/\text{min}$. to understand their behavior under high heating rates. All the three nanocomposite samples showed early weight losses than that off neat polypropylene. PAC20:10 and PAC30:15 showed very similar decomposition behavior with 5 percent weight loss and 10 percent weight loss temperatures around 350°C and 440°C respectively. The corresponding 5 percent weight loss and 10 percent weight loss temperatures for neat polypropylene were 443°C and 459°C . The early onset of weight loss for

nanocomposite films could be due to degradation of APP to polyphosphoric acid followed by reaction of CaCO_3 with it. We observed weight loss step around same temperatures in case of APP/CC mixture. Polypropylene and all three nanocomposite samples showed maximum weight loss rate around 530-535 °C. The peak could be attributed to weight loss by PP degradation. The concentration of additives did not show any effect on peak decomposition temperature. However TG curves showed that polypropylene degradation was delayed due to presence of additives. Nanocomposite TGA curves were always leading to that of neat PP at higher temperatures indicating delay in PP degradation. In case of PAC 20:10 and PAC 30:15, the weight loss curve showed higher temperatures for higher weight losses than those for pure PP e.g. in the case of neat PP 20 percent wt. loss occurred around 408 °C while the temperatures for 20 percent weight loss on PAC20:10 and PAC30:15 curve were around 508 °C. We observed the same trend in case of PAC10:5 nanocomposites. We could say that presence of additives improved the thermal stability of PP in inert atmosphere.

TGA-FTIR analysis of PAC20:10 and PAC30:15 revealed that ammonia and carbon dioxide evolution occurred prior to polypropylene degradation. Figure 14 and Figure 15 show TGA-FTIR spectrums for PAC20:10 and PAC30:15 samples. Broad FTIR peak at 2950cm^{-1} was due to evolution of hydrocarbons, indicating onset of polypropylene degradation. We observed this peak from 430 °C onwards. The peaks for CO_2 and NH_3 disappeared once polypropylene started degrading and we obtained messy spectrums containing peaks of hydrocarbons.

We analyzed the amount of residues obtained at the end of TGA experiments. Polypropylene was completely degraded and did not leave any significant amount of residue. Based on our TGA analysis for APP/CC mixture, we expected that the additives would react with each other even in presence of polypropylene and leave behind around 67 percent of their original concentration. PAC10:5, PAC20:10 and PAC30:15 left 9.5 percent, 20 percent and 29 percent residue at end of each test. Each nanocomposite sample left nearly 67 percent of original additive concentration in the form of residue which could led to conclusion that the two additives reacted in similar way as they did in case of their pure powder mixtures and the residue could be of $\text{Ca}(\text{PO}_3)_2$. Comparison between TGA curves of nanocomposite films and neat PP showed that the reaction between the additives started prior to onset of polypropylene degradation. Formation of thermally stable calcium phosphate, which could protect the molten polymer by forming protective layer on top, could be the reason behind improved thermal stability of polypropylene.

XRD analysis of char

We performed X-ray diffraction analysis on char residue obtained after burning nanocomposite films of

PAC10:5, PAC20:10 and PAC30:15 to identify the inorganic compound, formed by reaction between APP and CC, during burning. We also performed the same analysis on char residues obtained after burning off the residual carbon by heating at 750 °C to obtain strong and sharp signal for the analysis.

Figure 16, Figure 17 and Figure 18 show overlay of XRD patterns for PAC10:5, PAC20:10 and PAC30:15 chars obtained after burning the films and after treating at 750 °C. We observed three major, high intensity diffraction peaks for all the six samples at angles (2θ) 25.28°, 28.50° and 31.76°. The peak positions did not alter even after heating the chars at 750 °C, indication that inorganic compound formed during burning did not undergo any structural alterations. However, the absolute intensities were higher in case of 750 °C residues as the traces of unburned polymer in the char must have been oxidized at 750 °C. We observed that char residues gave higher intensities and broad diffraction pattern in the range of 10° to 25° than that of for 750 °C residues. The reasons behind it can be due to presence of amorphous carbon residues in the chars. Thus the inorganic residue and corresponding diffraction patterns could be of calcium phosphate formed, by the reaction between APP and CC, during burning of polymer nanocomposite films.

Since there was no change in diffraction pattern for the residues obtained after burning and after heating at 750 °C, we used diffraction patterns of 750 °C residues for further peak analysis and determination of compound. Table 4 shows 2θ values, corresponding relative intensities and d spacing, of 4 strong peaks.

We expected that the residue should contain some form of calcium phosphate, so we compared XRD data with the published literature by McIntosh et al. [17] on crystal structures and XRD patterns of various calcium phosphates. We found that above mentioned peaks and the XRD pattern resemble with the one shown by β -calcium meta phosphate. The literature also reported that β -calcium meta phosphate and β -calcium polyphosphate show almost identical diffraction patterns and they have almost identical crystal cell structures and dimensions. β -calcium meta phosphate has molecular formula $[\text{Ca}(\text{PO}_3)_2]_n$, and it is linear chain calcium phosphate [18]. The chains are connected through the PO_4 tetrahedron. So we concluded that the nanocomposite char residue obtained in flame spread test also contained calcium meta phosphate. XRD analysis proved complete conversion of CaCO_3 into calcium meta phosphate during burning. This conversion must have been accompanied by evolution of ammonia, water and CO_2 .

Conclusions

We observed gradual reduction in flame spread rate of polypropylene between 24 – 69 % with increase in concentration of APP and CC together. Maximum reductions in burning rates, with the use of either of the additives at 30% loadings, were by 25% for CC and 29% for APP. There was no apparent char formation up to 30

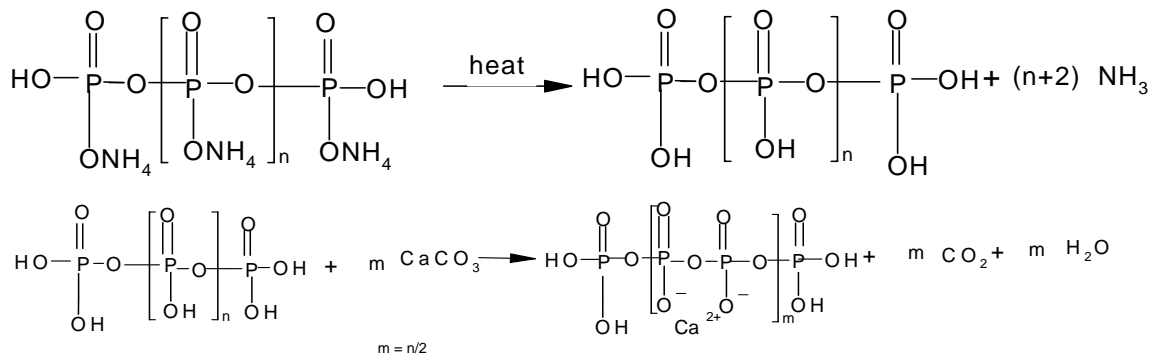
wt. % addition of two additives. Formation of char in case of PAC25:12.5 and PAC30:15 further enhanced the suppression of burning rates by providing the physical hindrance to advancing flame front. Burning intensity and dripping were also reduced by these additives. We concluded that the two additives acted as synergist for each other and the synergism could be due to chemical interaction between them. TGA analysis of 2:1 powder mixture of APP and CC showed that CaCO₃ nanoparticles had higher reactivity towards polyphosphoric acid, formed from APP degradation. We obtained around 65% residue from 2:1 mixture which could be because of formation of Ca(PO₃)₂. We obtained the same amount of residues for nanocomposite films as well, indicating that APP and CC had maintained their reactivity even in presence of polymer. The formation of inorganic residue from APP and CC delayed polypropylene degradation. TGA-FTIR analysis supported the explanation for various weight loss steps shown by TGA studies. We obtained FTIR peaks for CO₂ and NH₃ at around 270 °C onwards for powder mixture of two additives indicating the proposed interaction between the two additives. We observed the same peaks, prior to polypropylene degradation, for

nanocomposite samples. XRD analysis of char of combustion was very conclusive as we obtained diffraction peaks, resembling to those shown by β-calcium meta phosphate. XRD analysis confirmed the chemical reaction between the two additives occurred while burning.

The synergism between APP and CC in reducing the flammability of polypropylene must be because of chemical reaction between them. The interaction between the additives resulted into evolution of inert gases; carbon dioxide, water, ammonia, which caused the dilution of combustible fuel and reduction in oxygen concentration around flame front. Those effects resulted in hindering the advancing flame front prior to char formation. CaCO₃ nanoparticles, because of their reduced size, offered more surface area to absorb polyphosphoric acid and convert into calcium meta phosphate during short period of time. Thus flame retardant effect of APP and CC based nanocomposite could be perceived as chemical mode of action through condense phase mechanism. The flame retardant effect was further enhanced at higher concentrations of two additives since there was char formation, which provided physical barrier to advancing flame.

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Equation 1 Reaction between APP and CaCO₃

No.	Sample Name	Wt. % APP	Wt. % CaCO ₃	Wt. % PP	Mixing Time (min.)
1	PP	0	0	100	20
2	PAC10:5	10	5	85	20
3	PAC15:7.5	15	7.5	77.5	20
4	PAC20:10	10	20	70	20
5	PAC25:12.5	25	12.5	63.5	30
6	PAC30:15	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

Table 1 Number of samples (PAC20:10 indicates polypropylene nanocomposite with 20 wt. % of APP and 10 wt. % CC, C20 indicates 20 wt. % loading of only CC and A20 stands for sample with 20wt. % of only APP.)

Sample	Avg. Burning Time(s) for 4.5"	Burning Rate Inch/min.	Standard Deviation (s)	% Reduction in Burning Rate
Neat PP	29.9	9.03	1.03	----
PAC10:5	39.13	6.8	1.12	24.70
PAC15:7.5	44.8	6.02	1.11	33.33
PAC20:10	52.5	5.1	1.23	43.23
PAC25:12.5	75.8	3.6	1.02	60.15
PAC30:15	97.3	2.78	1.15	69.23
C10	31.5	8.3	1.2	8.12
C20	33.2	7.7	1.34	14.67
C30	39.2	6.7	1.23	25.83
A10	32.9	8.2	1.01	9.23
A20	35.23	7.7	1.34	14.76
A30	42.23	6.4	1.12	29.15

Table 2 Results for burning rates by FMVSS-302

Sample	Visual Observations
Neat PP	Intense burning with high flames, Wax like dripping, Dripping beads did not extinguished
PAC10:5	Reduced dripping, less intense burning with low flame heights, no char formation
PAC15:7.5	Reduced dripping, less intense burning with low flame heights, no char formation
PAC20:10	Reduced dripping, less intense burning with low flame heights, no char formation
PAC25:12.5	Continuous char layer formation, steady and slow burning with flame heights.
PAC30:15	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

Table 3 Visual observations for FMVSS 302



Figure 1 Burning of C20 nanocomposite film



Figure 2 Burning of A20 film



Figure 3 Burning of A30 film



Figure 4 Burning of PAC20:10 film

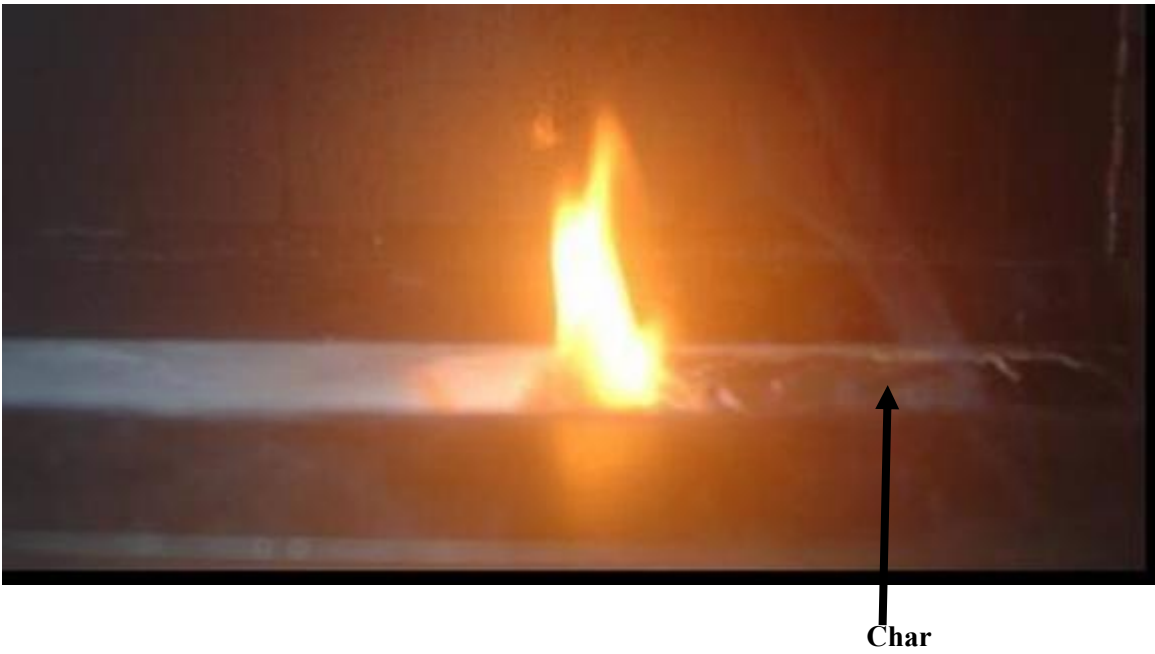


Figure 5 Burning of PAC30:15 film (Note char formation)

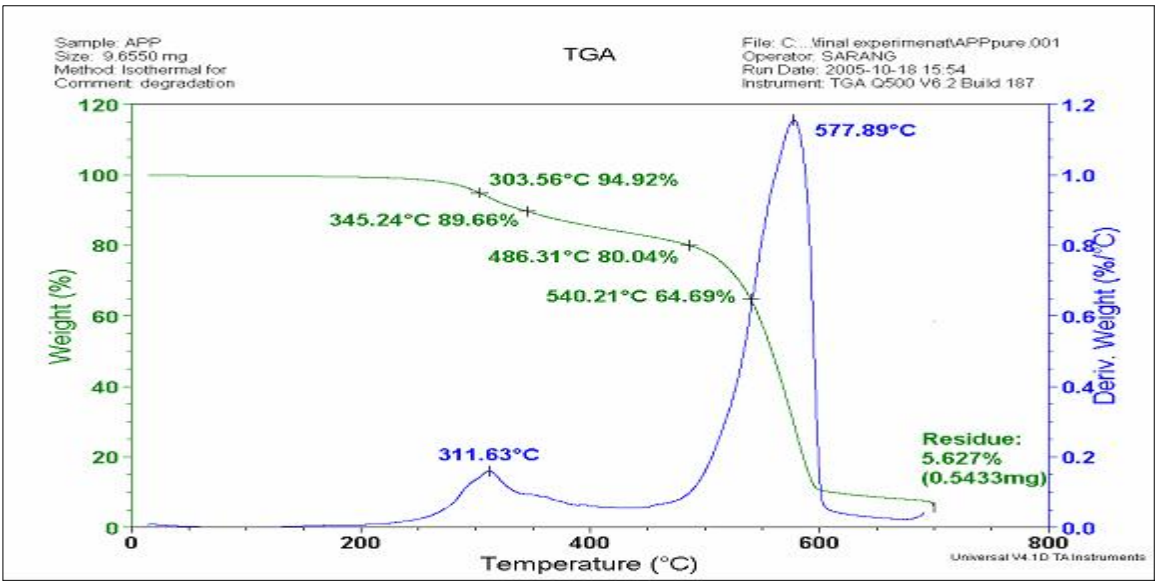


Figure 6 TGA and DTG curves for pure APP

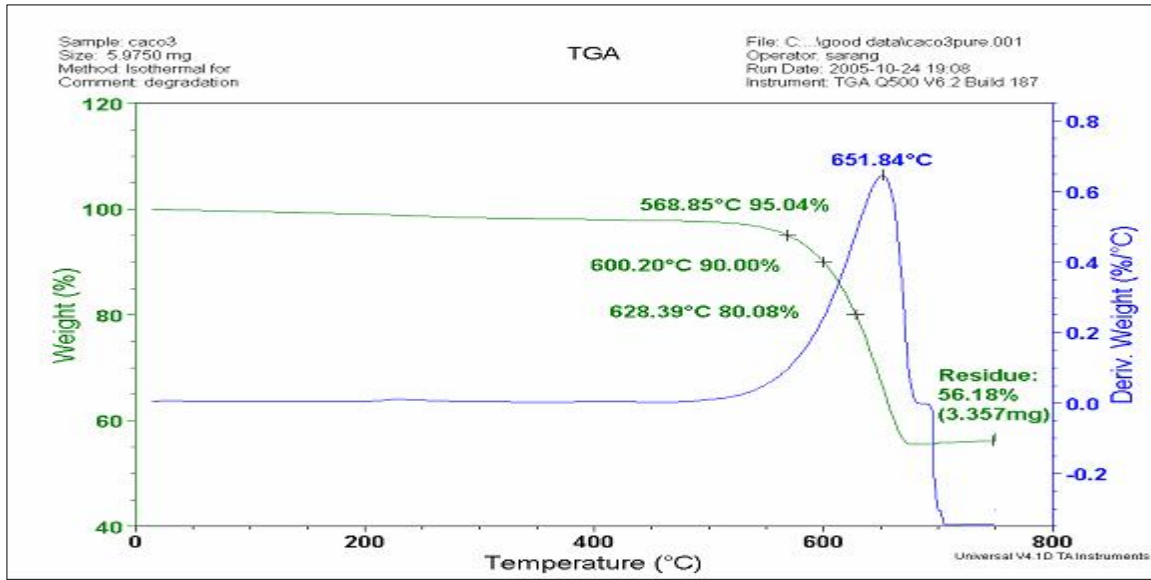


Figure 7 TGA and DTG curves for pure CaCO₃

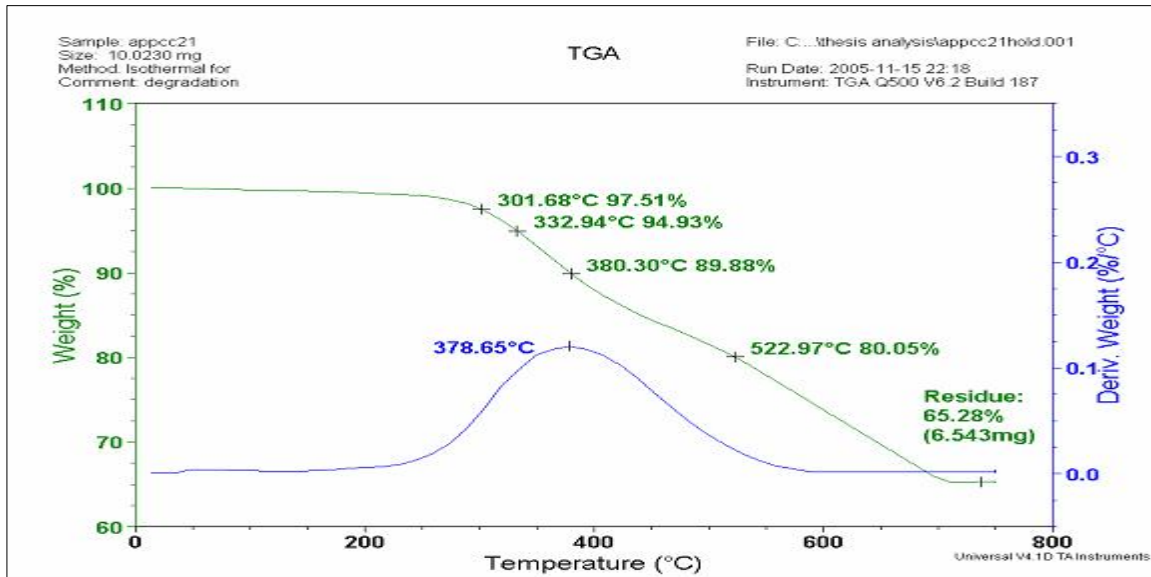


Figure 8 TGA and DTG curves for 2:1 mixture of APP and CaCO₃

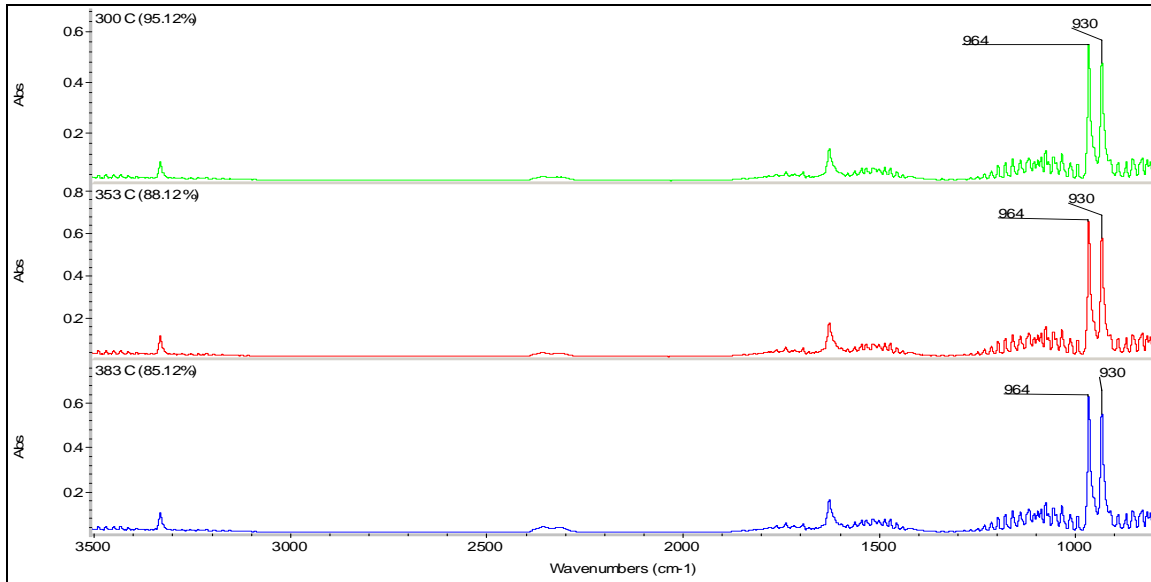


Figure 9 TGA-FTIR of pure APP

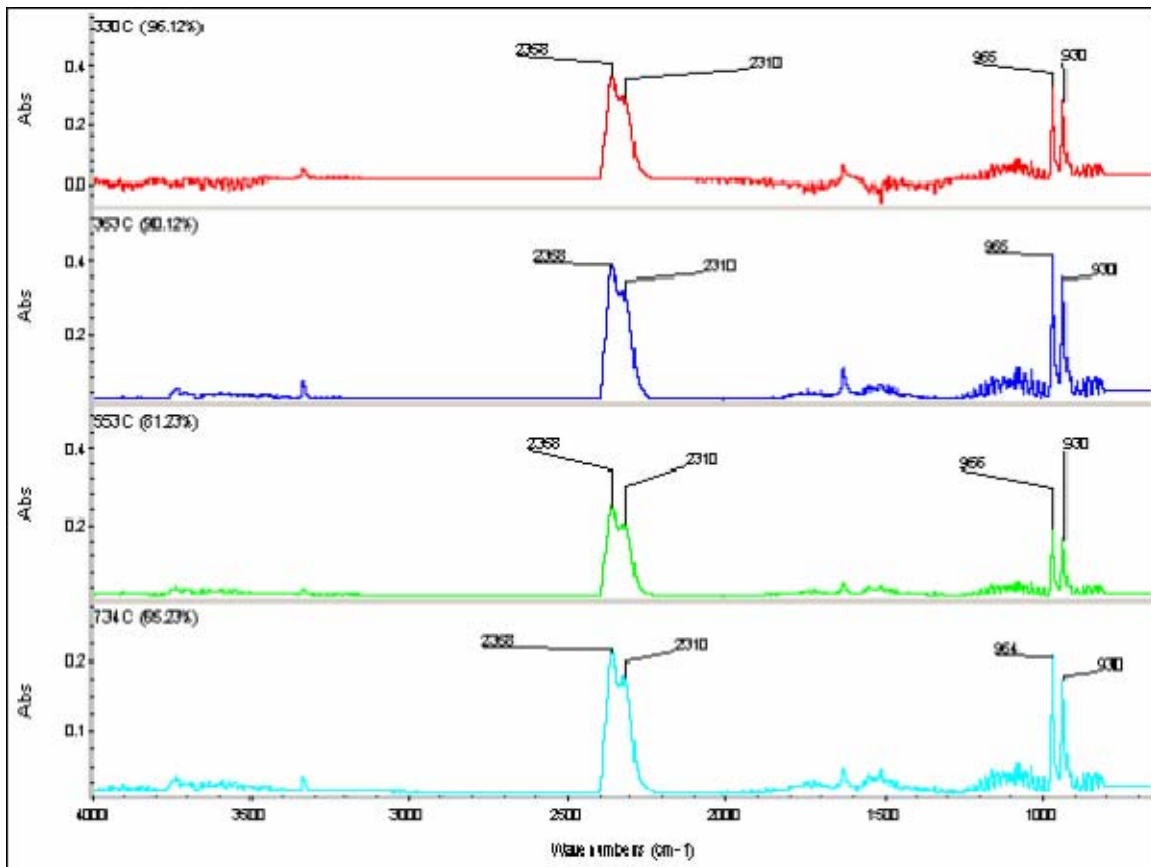


Figure 10 TGA-FTIR of 2:1 mixture of APP and CC

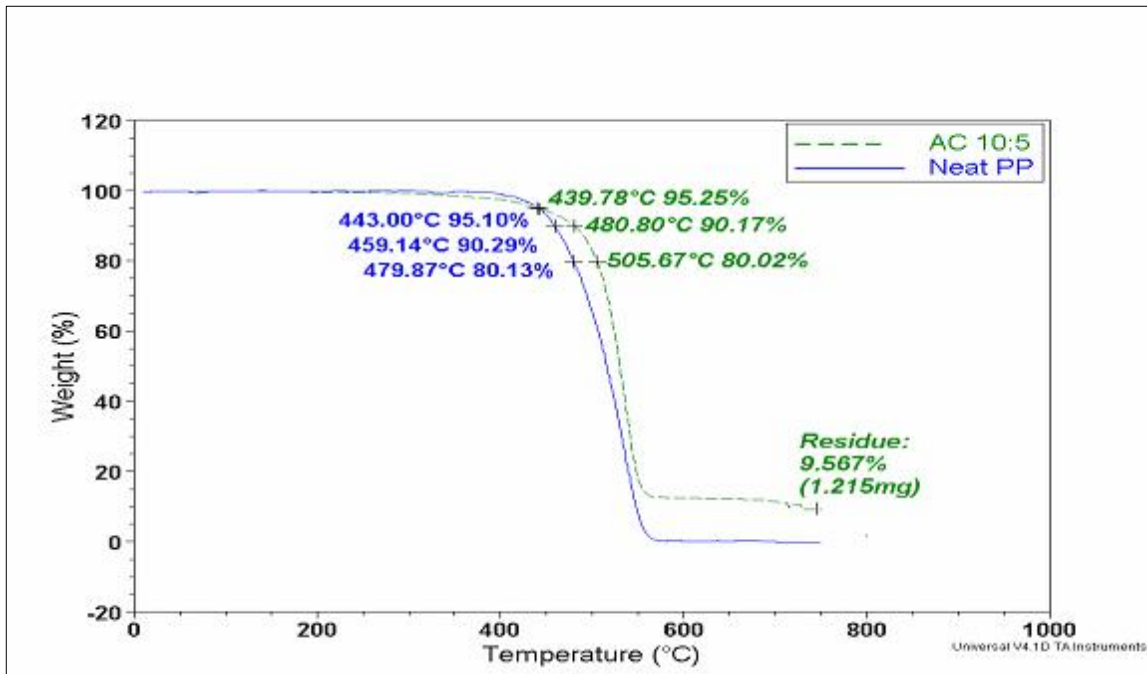


Figure 11 Overlaid TGA curves of neat PP and PAC 10:5 films

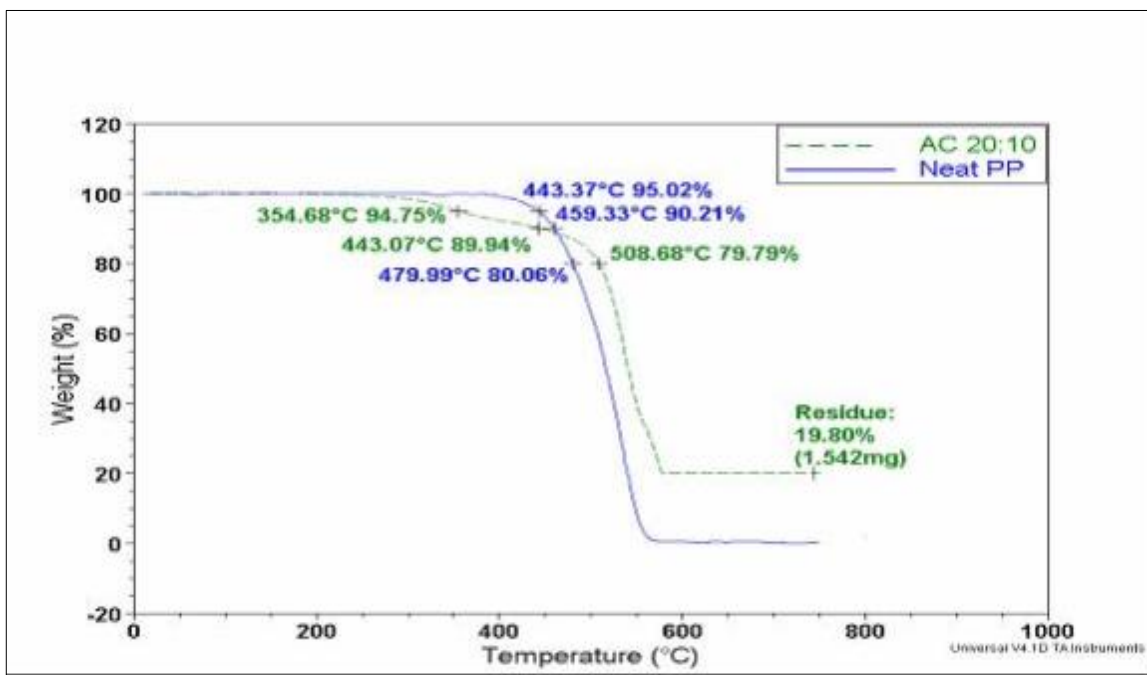


Figure 12 Overlaid TGA curves of neat PP and PAC20:10 nanocomposite film

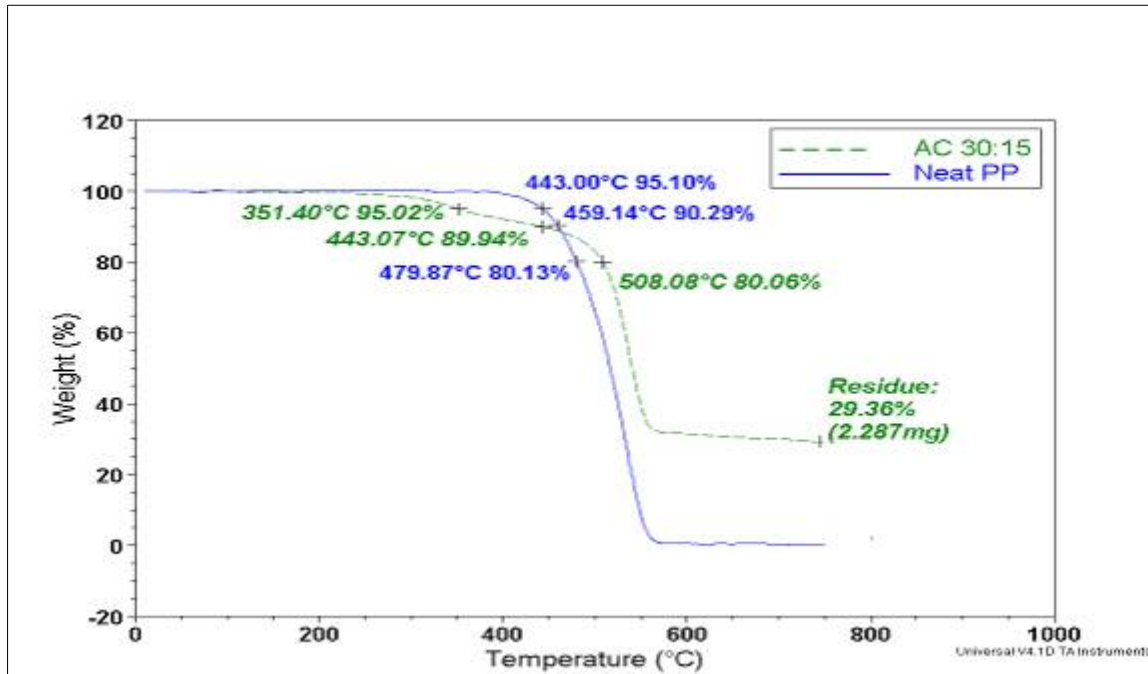


Figure 13 Overlaid TGA curves of neat PP and PAC30:15 nanocomposite films

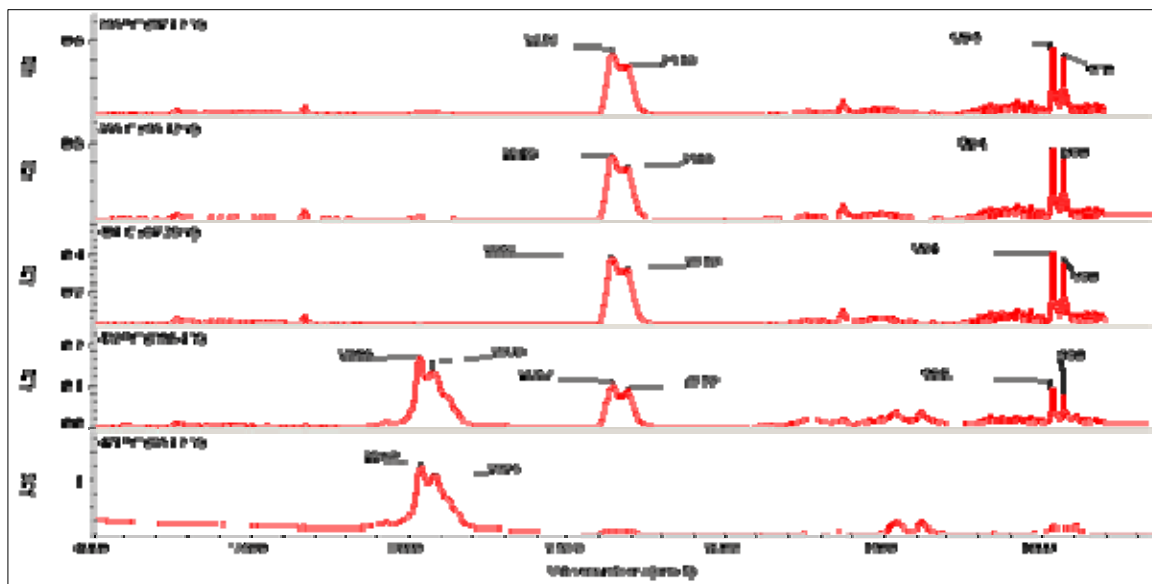


Figure 14 TGA-FTIR of PAC20:10 nanocomposite film

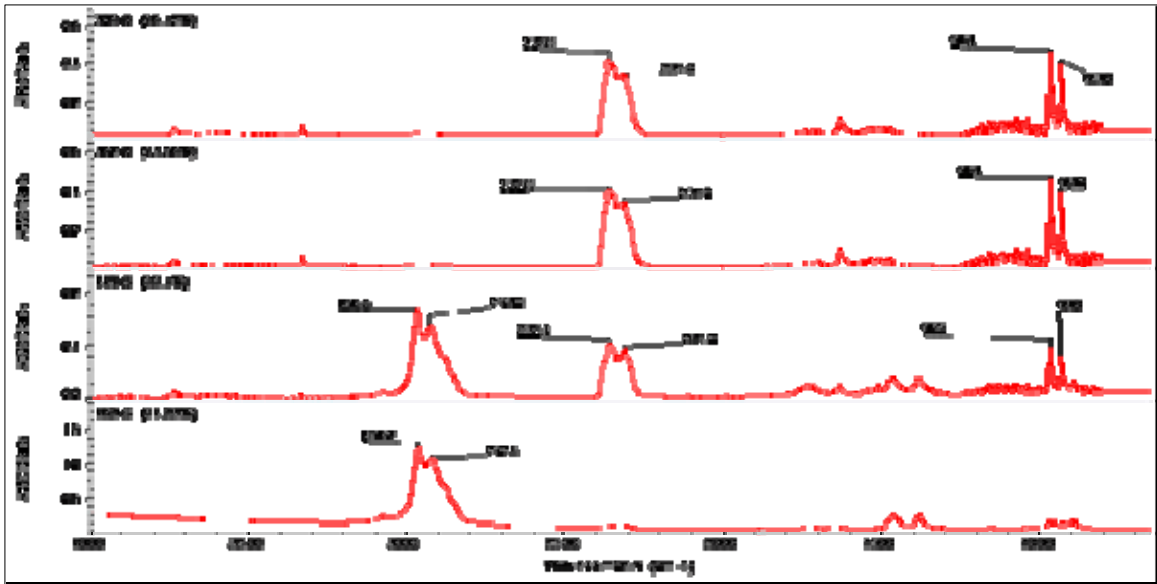


Figure 15 TGA-FTIR of PAC30:15 nanocomposite film

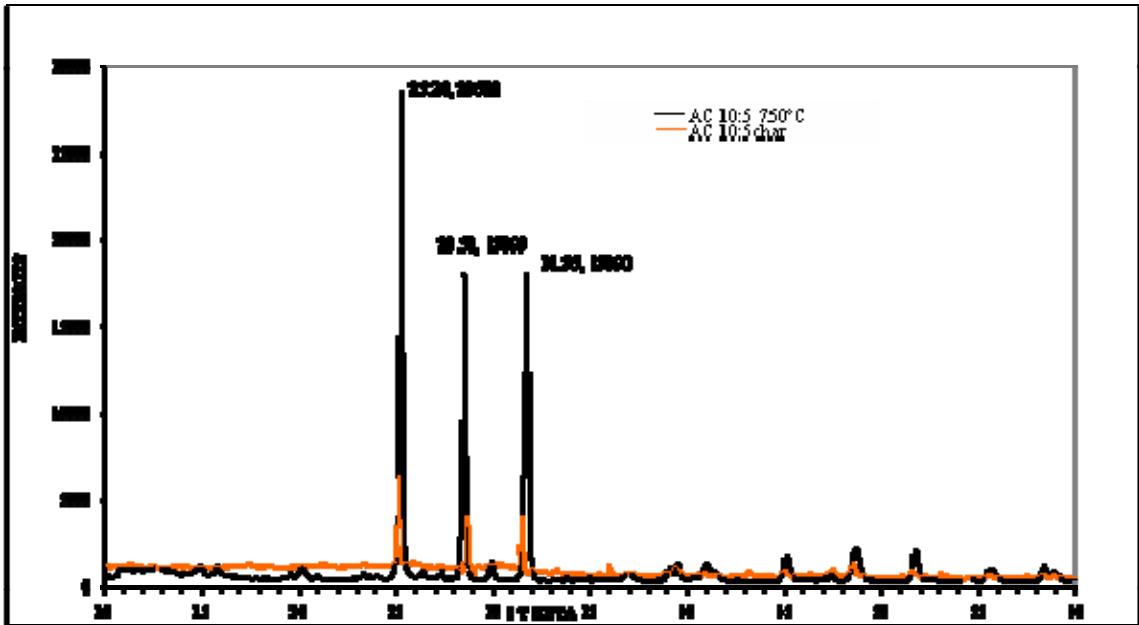


Figure 16 XRD patterns for PAC10:5 char before and after 750 °C treatment

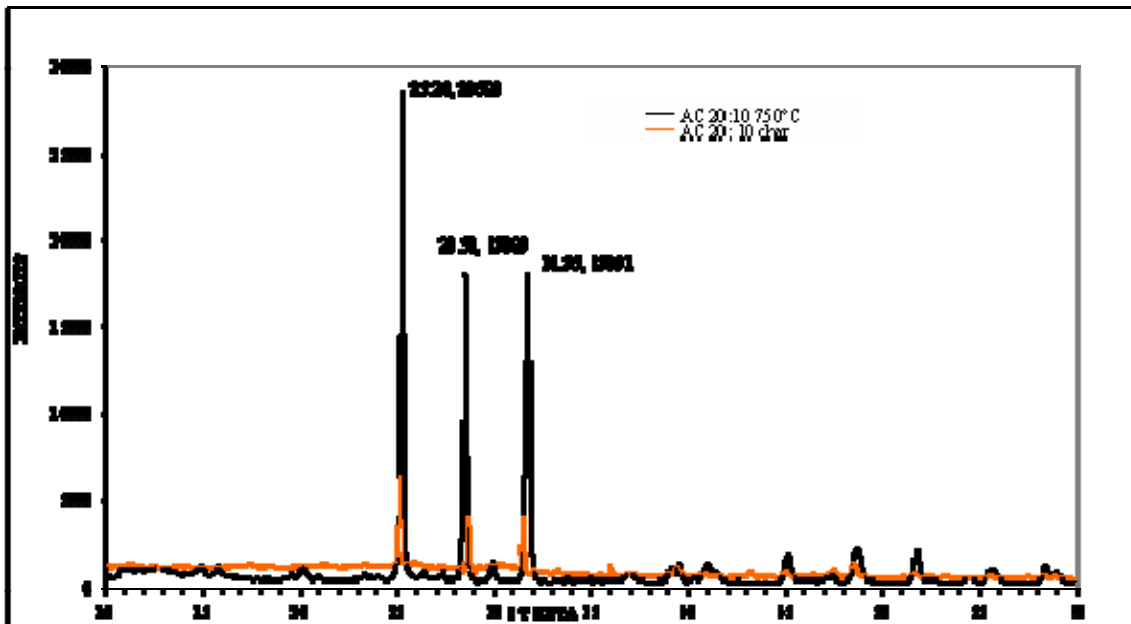


Figure 17 XRD patterns for PAC20:10 char before and after 750 °C treatment.

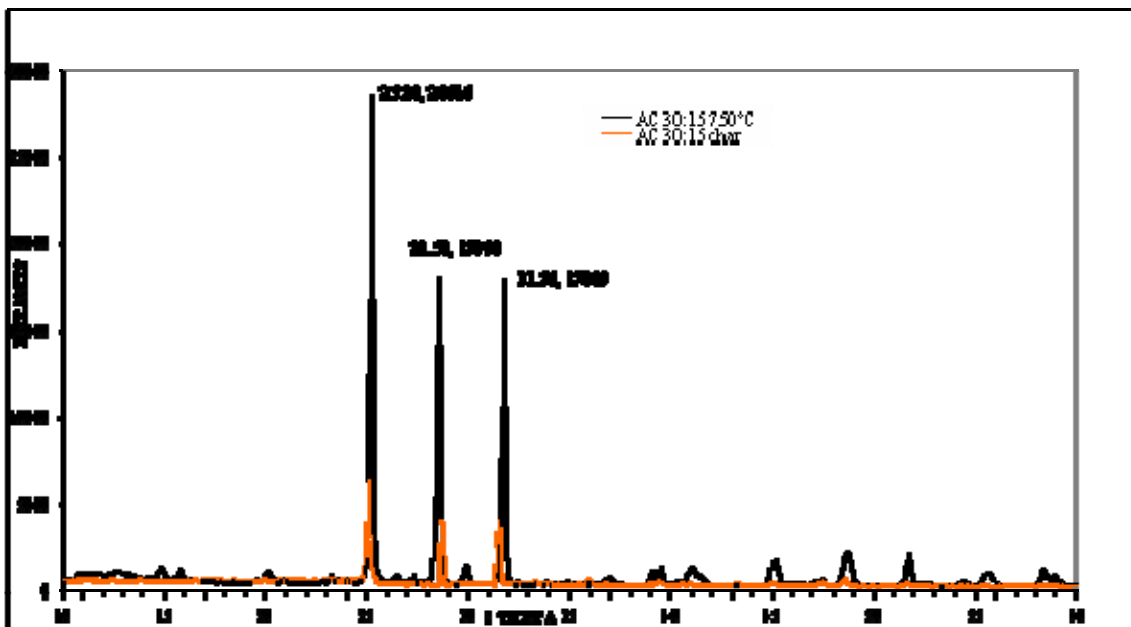


Figure 18 XRD patterns for PAC30:15 char before and after 750 °C treatment

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

Table 4 X-ray data for char residues after 750°C treatment.