Thermal degradation analysis and XRD characterisation of fibre-forming synthetic polypropylene containing nanoclay

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Abstract: Flammability of synthetic fibres is significantly worse than that of bulk polymers because of the high surface area to volume ratio and the low tolerance to high filler loadings in the fibre production process. Introducing nanocomposite structures has the potential to enhance the char formation at relatively low loadings and hence can reduce their flammability.

This paper reports thermal degradation analysis results in conjunction with TG and DSC under different atmospheres and further studies of X-ray diffraction characterization of fibre-forming polypropylene containing selected dispersed nanoclays.

The concentrations of hydrocarbons, carbon monoxide and carbon dioxide released during the TG analysis have been monitored and analysed by using a combined electrochemical infrared analyser. The intensity changes of the crystallinity peaks and nanoclay peaks in the polymer and composites are discussed.

Key words: polypropylene, nanocomposites, thermal degradation, evolved gas, x-ray diffraction.

Introduction: Polypropylene fibres have been one of the fastest growing synthetic fibres of recent years with increasing usage in technical products including those requiring improved flame retardancy, such as contract furnishings and automotive upholstery [1]. However, generating improved levels of fire performance is challenged by the low melting point (circa 165°C), the high inherent flammability (LOI is around 19%) and the need for high levels of flame retardant additive which compromise fibre production processes [1].

A potential solution lies in the use of nanocomposites which has attracted considerable interest of the flame retardant (FR) polymer community since 1997 due to their reported improved fire properties [2-6]. It has been suggested that the presence of clay in a polymer can enhance the char formation, thus providing a transient protective barrier and hence slowing down the degradation of the matrix [2, 3]. The incorporation of nanoclays with the correct level of nanodispersion and possibly orientation in the drawn polypropylene fibre has the potential to both reinforce and contribute to fire retardancy while allowing the possibility of lower overall FR loadings. We have shown that this is indeed possible by combining nanoclays with certain phosphorus-containing retardants in polyamide 6 and 6.6 films [7, 8]. However, if such a concept is to be applied to fibres, it is essential to understand the effect that introduction of nanoclays has on polymer thermal behaviour and also fibre fine or nanophysical structure.

Our initial studies of the flammability, thermal degradation and X-ray diffraction characterization of polypropylene containing dispersed layered silicates has demonstrated that nanoclays at low concentrations ($\leq$ 5%) of selected flame retardants introduced into polypropylene can reduce flammability and modify thermal degradation properties [9].

This work extends these studies and investigates the effect of introducing selected nanoclays into graft-modified polypropylene films on polymer physical structure and thermal degradation behaviour.

2. Materials and Experimental

2.1. Materials

The fibre-grade, isotactic polypropylene suitable for technical yarns was provided by a UK fibre extrusion company**.** Two potentially nanoparticulate flame retardant species

were introduced to the polymer: Bentone HC, functionalised nanoclay Bentone 107 (one of the Bentonite clays) and Cloisite 30B, were provided **by** Southern Clay Products Inc. having the generic quaternary methyl, bis(dihydroxyethyl), hydrogenated tallow ammonium cation as functionalising species. In order to improve polymer-clay potential compatibility, the compatibiliser Polybond 3200 (a 1% wt maleic anhydride grafted polypropylene), was provided by Chemtura Corporation (former Crompton Corporation), USA.

As an example of a conventional flame retardant, ammonium polyphosphate, APPe (Antiblaze MCM) was provided by Albemarle, UK. This is a phase I APP having a degree of polymerisation of about 290 and average particle diameter of 30μm.

All chemicals, reagents and solvents were obtained from the Aldrich Chemical company, and they were all at analytical grade.

2.2 Preparation of grafting agents:

Diethyl-p-vinylbenzyl phosphonate (DEpVBP) and acrylic acid-2-[(diethoxyphosphoryl)methylamino] ethyl ester (ADEPMAE) were obtained according to the detailed synthetic procedures reported elsewhere [10-12]
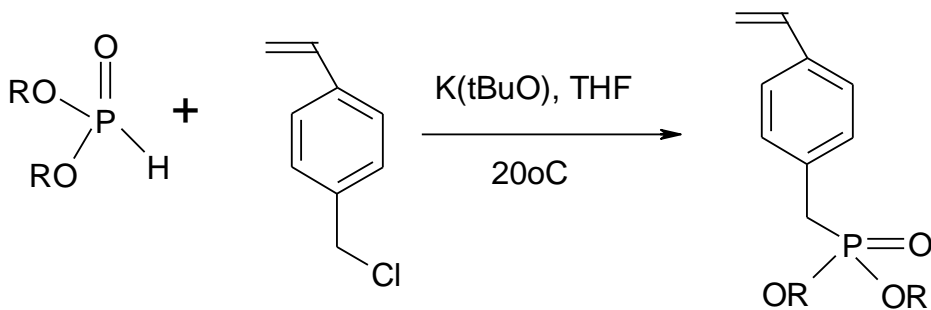
Diethyl-p-vinylbenzyl phosphonate (DEpVBP)
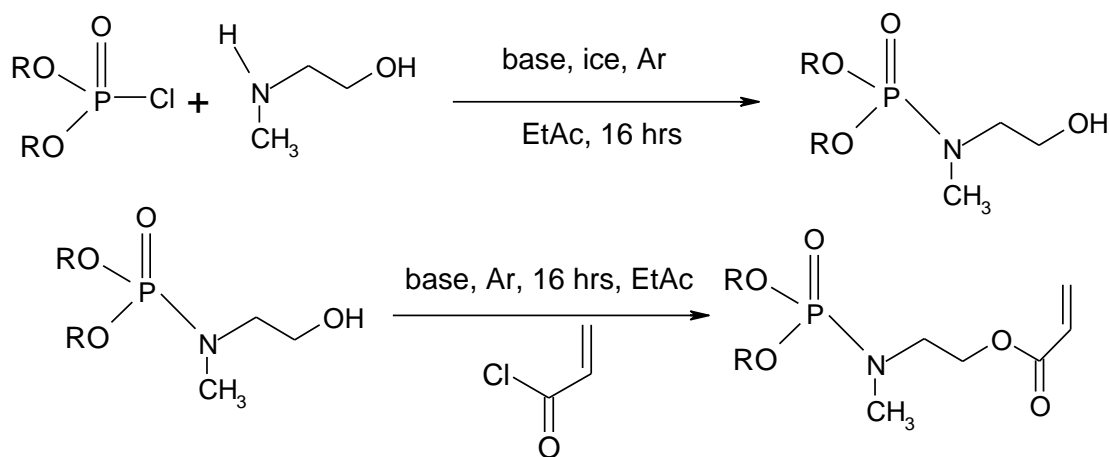
Acrylic acid-2-[(diethoxyphosphoryl)methylamino] ethyl ester (ADEPMAE)

2.3. Grafting procedure

The substrate (PP chips) and the solvent o-DCB (*o*-dichlorobenzene) were accurately weighed into a three-necked round-bottomed flask fitted with a double-walled water condenser and a gas bubbler. The contents of the flask were purged with argon and were brought to the reaction temperature with stirring. The grafting monomers were then added followed by the dropwise addition of the initiator DTBPO (di-*tert*-butylperoxide). The grafting reactions were undertaken at a fixed temperature for *ca.* 1.5 hrs under a blanket of argon. The grafted polypropylene was recovered by precipitating the reaction contents (while hot) into acetone, washed with acetone, and dried in a vacuum oven at 60 ºC for several hours before further examination. The initiator was diluted with the solvent (*o*-DCB) prior to introducing it into the reaction mixture in order to control the initial exotherm of the grafting reaction. Experimental conditions and yields for various grafting reactions are given in Table 1.

2.4. PP nanocomposite compounding

Polypropylene and additives with various percentages were hand mixed in a 200 mL plastic container prior to compounding. The samples were compounded by using a Betol

BTS30 twin screw extruder with a temperature profile over six heating zones from 179 to 190^{0}C.

2.5. PP film formation by compression moulding

Films (ca. 0.3mm thickness) were prepared from the blends (around 5g blend was used for each film) by compression moulding with spacer plates, between aluminium foil-covered steel plates at a set plate temperature of 190°C. A pure PP control with equivalent thermal history to the filled samples was also produced.

2.6. Flammability testing:

Limiting oxygen index (LOI) values were determined on selected PP nanocomposite film samples with thickness of around 0.3~1.5 mm by using a standard procedure [13].

2.7. Thermo gravimetric analysis

The TGA curves were obtained by using a Polymer Laboratories TG 1000 instrument under flowing air (10 cm^3/min.) with a heating rate of 20^{0}C/min. Approximately 6 mg samples were used in each case.

2.8. Gas analysis

The concentrations of carbon monoxide and carbon dioxide evolved from TG furnace were monitored by using a non-dispersive infrared gas analyser and the concentration of oxygen was monitored by using an electrochemical cell oxygen sensor.

2.9. X-ray diffraction

X-ray diffraction analysis of compounded samples was carried out with a Siemens D500 X-ray Diffractometer with Cu-Kα radiation. The diffractometer was equipped with a diffracted beam graphite monochromator, tuned to Cu-K$_\alpha$ radiation, and a scintillation detector. Diffraction patterns were collected in reflection-mode geometry from 2° to 20° 2θ at a rate of 2° 2θ/min. The XRD samples were cut from the film samples with similar thickness of 0.3mm.

2.9. Optical microscopy

Optical microscopy may used to characterize the dispersion of nanoclay at the micro-level and was used here in order to estimate this level in each of the compounded samples.

Film samples with thicknesses of around 0.2mm were examines using a Nikon optical microscope.

3. Results and Discussion

3.1. Thermal stability of clays

Figure 1 shows the TGA curves of three clays: Bentone HC, Bentone 107 and Cloisite 30B. The onset of mass loss for all three clays occurs below 100°C. However, while for Bentone HC and Cloisite 30B the mass loss is only of a few percent and so may be due to loss of volatiles such as water, the 8% mass loss seen for Bentone HC occurring above 70°C is also considered to be associated with water volatilisation. Serious mass loss and hence decomposition temperatures are evident for Bentone 107 at 225°C and for Cloisite 30B at 218°C, indicating that both Bentone 107 and 30B are able to withstand the temperature of the extrusion process at 190°C for polypropylene. Since no further significant mass loss occurs from Bentone HC up to 500°C, it may be considered to be the most stable for extrusion and this may reflect the absence of any functionalising groups. Mass loss for Bentone 107 sample at 700°C is up to 34%, higher than for 30B (28%), suggesting that Bentone 107 has more surfactant content than 30B.

Figure 2 shows the XRD patterns of Bentone 107 before and after heating at 190°C for 30min. The intensity of heated sample is less than that of unheated sample and this drop of counts of heated samples may indicate some loss of excess surfactants. After heating the clay peak position has not been changed, which means the functionalising groups in nanoclay have not been degraded or oxidised at 190°C.

3.2. Structural characterisation of compounded polypropylene/clay samples by XRD and optical microscopy

Fig. 3 shows the XRD results of PP control, Bentone 107 clay itself and ungrafted and grafted PP with Bentone 107 samples. All the samples are films with similar thickness of 0.3 mm. No peak has been observed for the control sample as expected since PP polymer crystal diffraction does not occur at $2\theta < 10^{\circ}$. The peaks between $3\sim4^{\circ}$ (2θ) are correspondent to the clay characteristic peak. There is no shift for the PP/Bentone107 sample peak compared with the Bentone 107 clay itself, indicating there is no obvious intercalation between the silicate layers. However, all other samples with each grafted PP involved have obvious shifts to the left, indicating the possibility of intercalated

structures having been achieved between the layered silicates. The decrease in peak height of the sample with 1%DEpVBP grafted polypropylene and 3%Bentone suggests exfoliation, but could also result from deformation of the clay layer.

The optical microscopic images of PP control and PP with nanoclay samples have been shown in figure 5. Greater inhomogeneity for the sample of PP with Bentone clay compared with pure PP is seen at the micro level indicating that there are considerable micro-level particles still present. However, better dispersion is apparent in the sample with grafted PP, indicating the addition of grafted polypropylene could improve the compatibility of the substrate polymer and Bentone 107 clay.

3.3 TG analysis

Figure 5 shows the TG curves in air for the PP control sample and PP clay-containing samples. The onset of degradation temperature for PP control sample is around 232°C, and it is not significantly different from values for the samples containing Bentone 107 clays (see below and Table 2). However, the rates of degradation are influenced by the introduction of clays. The slowest degradation rates are observed for the samples with ADEPMAE grafted and DEpVBP grafted polypropylene.

The char residues in air at 500ºC and onset and final decomposition temperatures are shown in Table 2. The char residues at 500ºC for samples containing Bentone 107 clay are all around 4.0% and there is no char left for the control PP sample. Considering the fact that Bentone 107 contains 34% organic surfactant (Figure1), 3% Bentone 107 is equivalent to 2.04% clay. This suggests that the addition of Bentone 107 has some char enhancement effect on polypropylene samples. The onset decomposition temperature for control polypropylene is 232ºC, while the onset temperatures for samples containing clay are about 15ºC higher. The final decomposition temperatures for sample-containing clays are much higher than the control (385ºC), and the highest value is 430ºC for DEpVBP grafted sample. Thus it appears that Bentone 107 lowers the rate of PP decomposition and extends the decomposition process over a larger temperature range..

3.4 Evolved gas analysis

Table 3 gives CO_2 values, CO values and the CO_2/CO ratio values for different formulation samples at various temperatures. All the CO peak values of samples containing Bentone107 clay except the one with Bentone 107 only are higher than that of the control sample, while the CO_2 peak values of samples containing Bentone 107 clay are much less than that of the control sample. Furthermore, all the CO_2/CO ratio values of samples containing Bentone 107 clay are much less than that of the control sample, this is an indication of less heat release for the samples with nanoclays because less CO_2 gas release means less sample has been fully oxidized and hence less heat released.

 Figure 7 show the maximum evolution value of CO_2/CO ratio values versus temperature for Bentone 107/PP samples. The graph suggests there is some links between CO_2/CO ratio and T_{CO2} peak. It has been reported that CO2 is usually formed by surface oxidation of condensed phase-released species [12], and this suggests that a reduction in reactivity of the surface with presence of clay. The PP/3%Bentone 107 sample is less quite well dispersed (see Fig 4) suggesting that surface blocking by clay may have an influence on the condensed phase, surface oxidation and hence CO_2 formation. A significant portion of the polymer has been lost at T_{CO2} peak, indicating it is reasonable to assume that there are more clay platelets on the surface of the well dispersed materials. If this is true, the CO_2/CO ratio would be expected to fall when sufficient clay layers have built up assuming that CO levels are constant. This may be used as an indication of the critical concentration of clay that has been reached during decomposition. However, the results in table 3 show that the higher the peak temperature, the less CO_2 seems to be formed. CO peaks at around 400°C for PP/clay samples result from evolution of fuel to gas phase which oxides to CO because of the oxygen-deficient atmosphere caused by the presence of clay and/or the low temperature for conversion to CO_2.

3.5 Flammability testing results

The LOI test result for the PP control sample and PP containing nanoclays Bentone107 and Cloisite 30B for films having various thicknesses are shown in Figure 8. All the samples with clay have higher LOI values than that of PP control sample. For Bentone 107-containing samples, the sample with Bentone 107 only has an average LOI value of

20.5 despite its poor dispersion (see Figures 1 and 4), while the addition of DEP can further increase the LOI value to 20.7.

For the samples containing 30B clay, the presence of nanoclay 30B only increase the LOI value to 20.7.

4. Conclusions

The dispersion of Bentone 107 clay can be greatly improved by the addition of grafted polypropylene. Some degree of exfoliation could be achieved for the sample containing Diethyl-p-vinylbenzyl phosphonate (DEpVBP) grafted polypropylene.

The fire performance of polypropylene can be effectively improved by the addition of nanoclay in conjunction with conventional phosphorus flame retardant and phosphorus containing grafting monomers. Fire performance is being talked about here on the basis only of small scale TGA and LOI tests. Further investigation is required for a better understanding to the degradation mechanism of the nanocomposites with improved fire performance. All this will come up in our recent discussions.

A better dispersion of nanoclay in the composite does not necessarily increase its fire performance due to the negative effect to the degradation caused by the addition of grafting monomers.

Acknowledgements

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Tables and Figures

Table 1 Experimental data for grafting reactions on PP (medium-scale ~20g)

Sample No.	substrate (g)	grafting reagent (g)	solvent o-DCB (g)	initiator DTBPO (g)	temp. (^{o}C)	time (hrs)	yield (wt%)
1	PP, 17.52	DEM[a], 3.500	200	1.7865	150	1.5	82
2	PP, 17.55	EMI[b], 3.652	200	1.7865	150	1.5	85
3	PP, 10.02	ADEPMAE, 2.023	131	1.02	160	1.5	82
4	PP, 10.01	DEpVBP, 2.038	131	1.02	160	1.5	83

a DEM = diethyl maleate

b EMI = N-ethyl malemide

Table 2 Char residue and starting and finishing decomposition temperatures

Sample	T_{onset} (^{o}C)	T_{final}(^{o}C)	Char residue at 500°C
PP control	232	385	0.00
3%Bentone 107	246	413	4.02
1%PB+3%Bentone 107	243	426	4.05
1%EMI+3%Bentone 107	245	415	4.03
1%DEM+3%Bentone 107	244	418	4.06
1% ADEPMAE +3%Bentone 107	245	417	4.02
1% DEpVBP +3%Bentone 107	246	430	4.03

Table 3 CO_2 and CO peak values and ratios of CO_2/CO

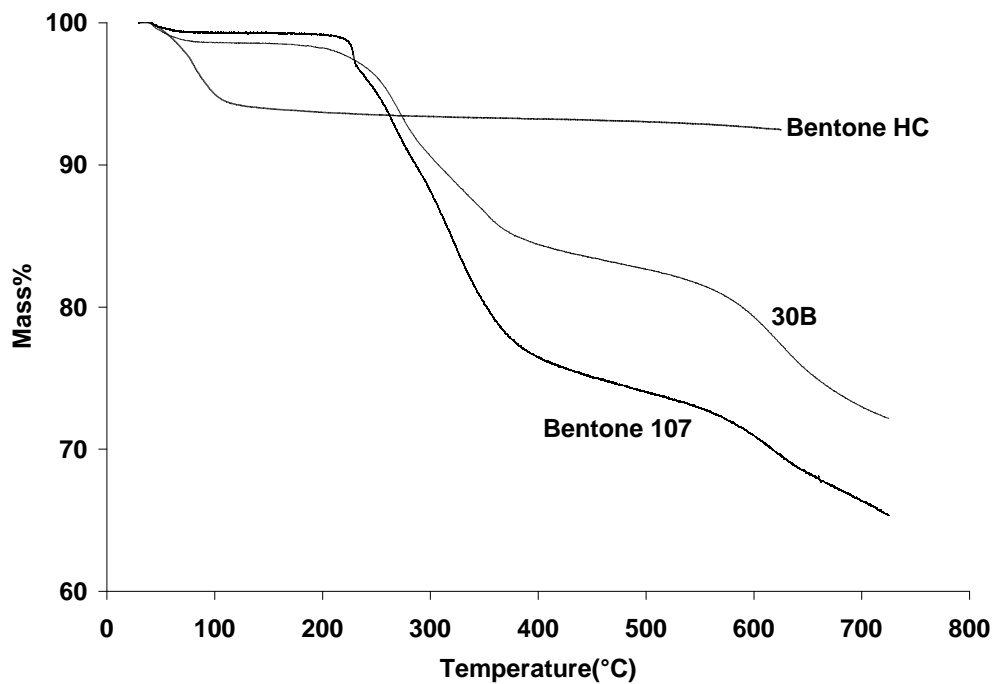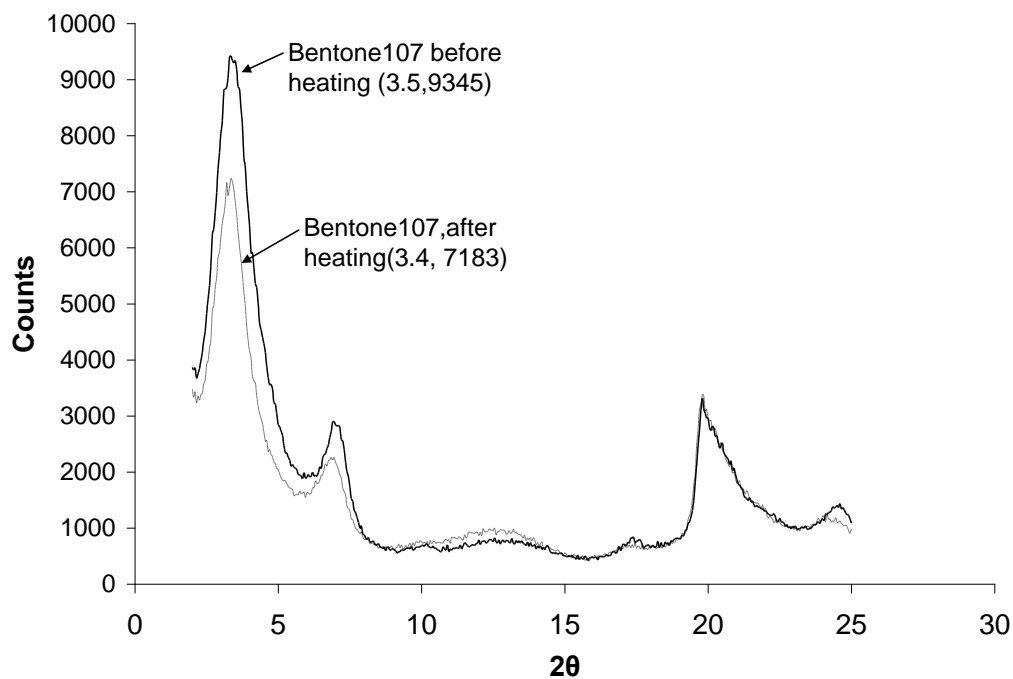| Sample	CO Peak	CO_2 Peak	Ratio of CO_2/CO	TCO_2 Peak
PP control	0.43	1.77	4.12	369
3%Bentone 107	0.31	0.78	2.52	416
1%PB+3%Bentone 107	0.90	0.78	1.48	446
1%EMI+3%Bentone 107	0.86	0.79	0.91	435
1%DEM+3%Bentone 107	0.67	0.77	1.15	447
1% ADEPMAE +3%Bentone 107	0.73	0.93	1.27	440
1% DEpVBP +3%Bentone 107	0.94	0.66	0.70	454

Figure 1 TGA curves for the clay samples

Figure 2 XRD patterns of Bentone 107 before and after heating at 190ºC（the values in brackets are the peak values for each curve）
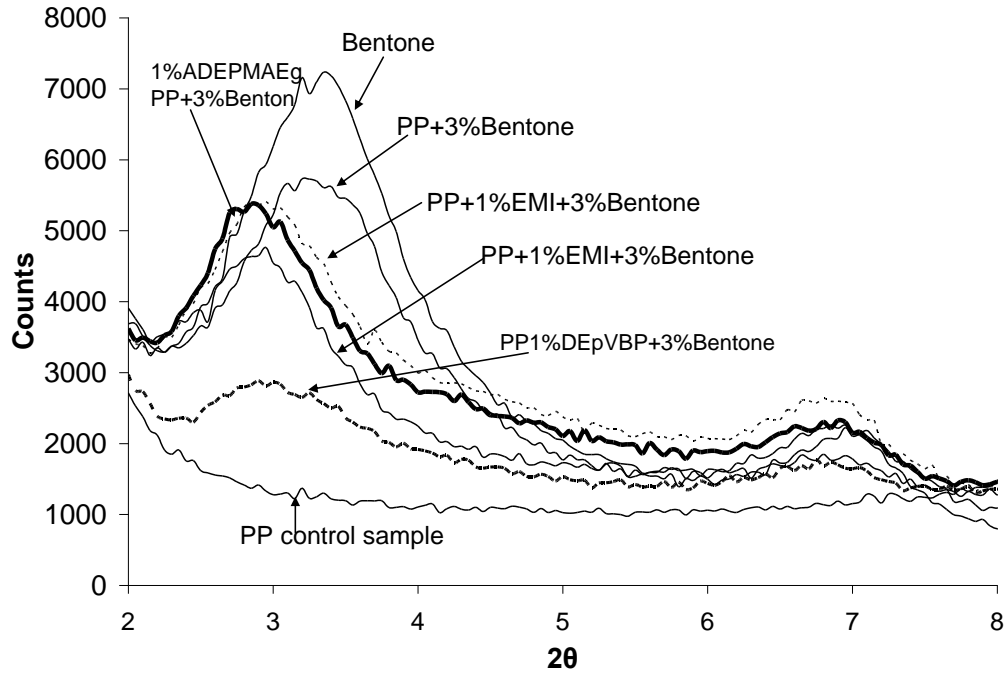
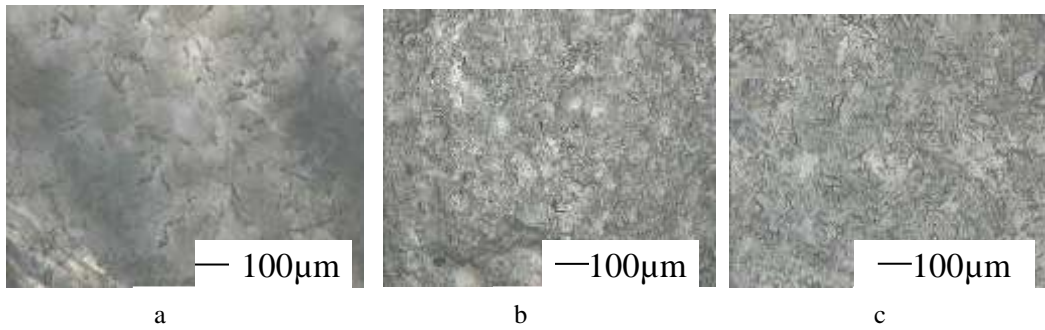Figure 3 XRD patterns for PP with Bentone 107 and N-ethyl maleimide (EMI) grafted PP

Figure 4 Optical microscopic images of PP control (a), PP+3%Bentone(b) and PP + 3%Bentone + 1% ADEPMAE grafted PP (c)
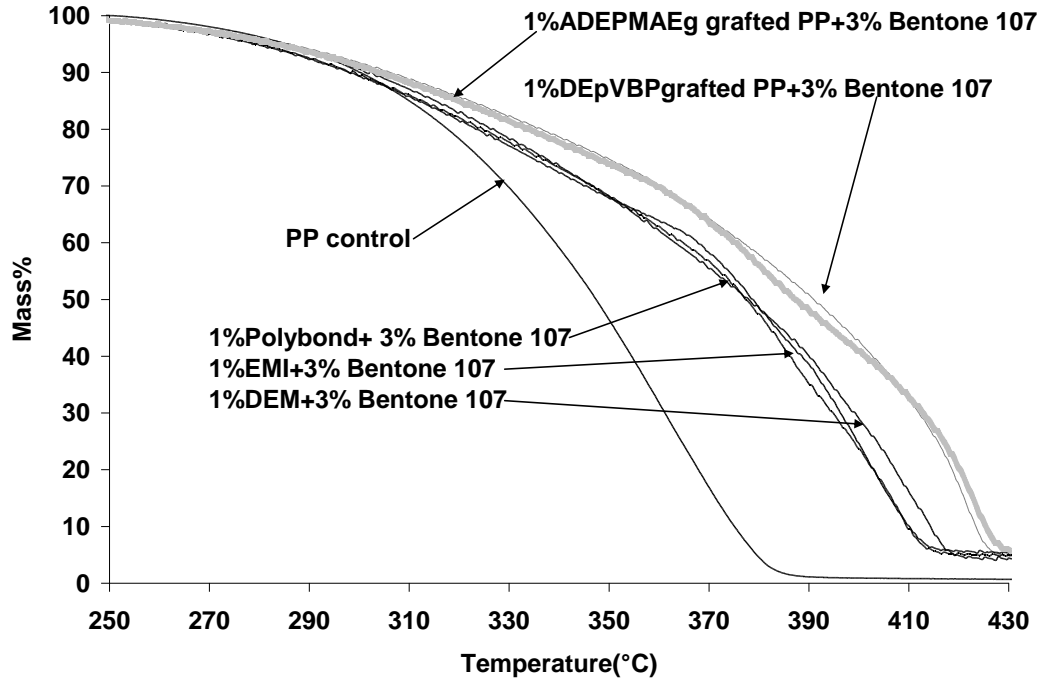
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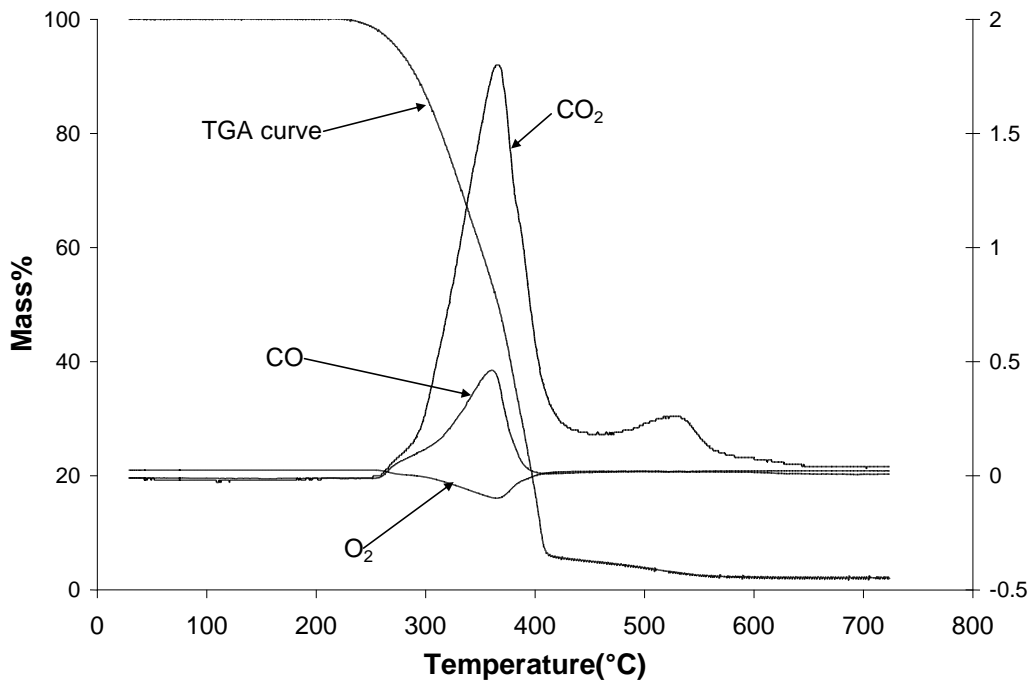Figure 5 TGA curves for control and grafted PP samples containing Bentone 107 clay

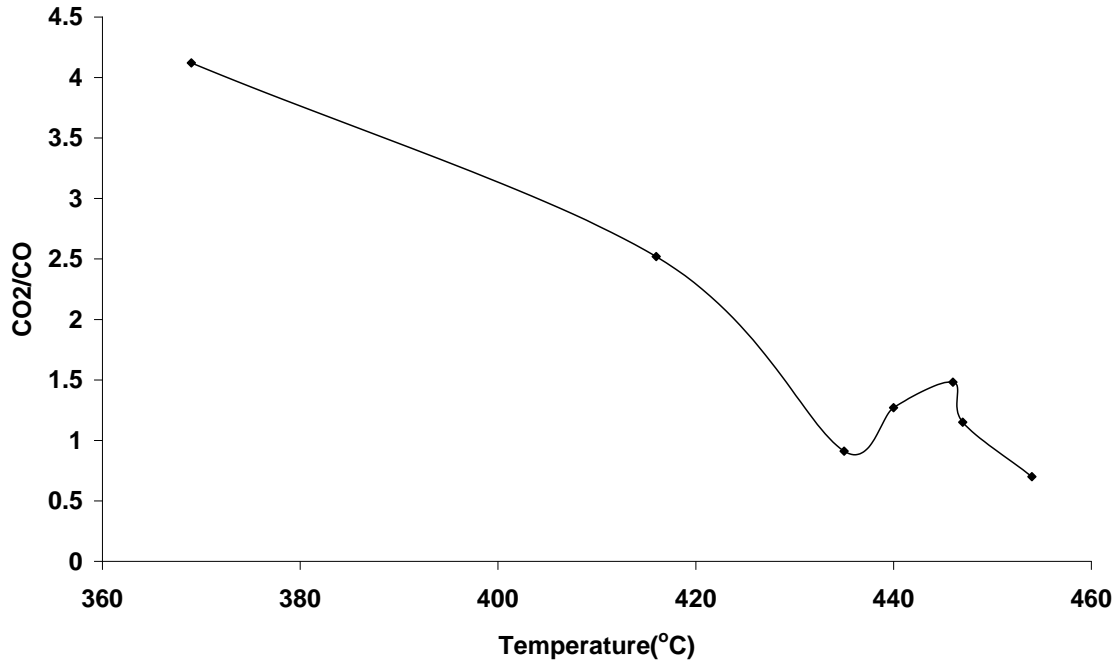Figure 6 TGA-EGA curves for PP control sample

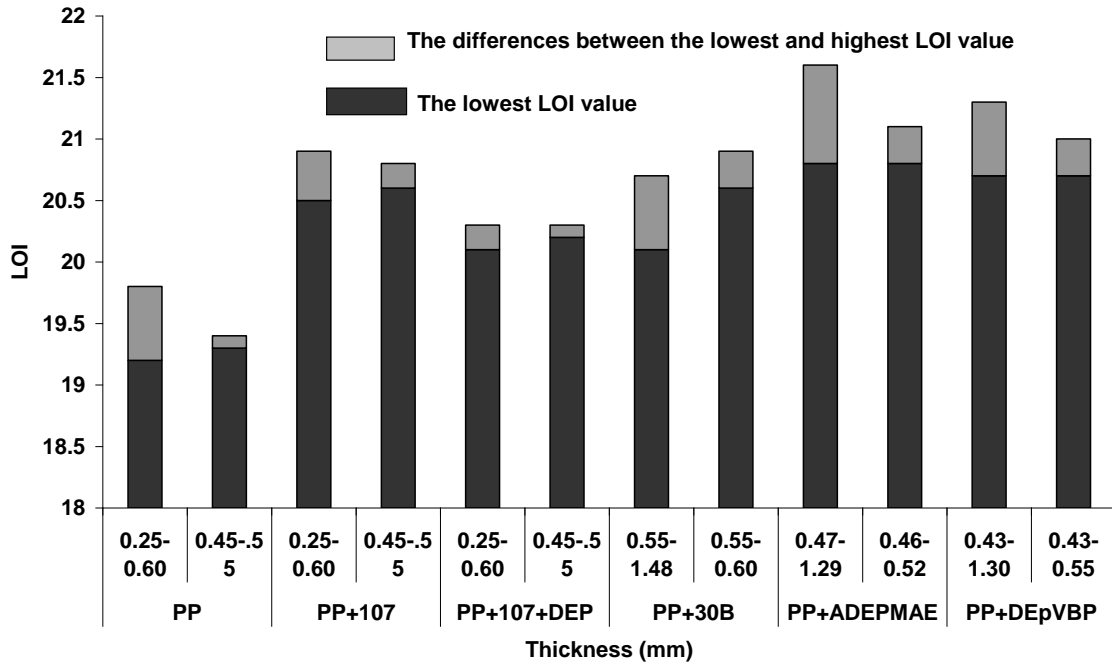Figure 7 CO2/CO ratio vs Temperature for Bentone 107 containing samples

Figure 8 LOI values for PP film samples with different thicknesses