Effect of Different Compatibilisers on Nanoclay Dispersion, Thermal Stability, and Burning Behavior of Polypropylene–Nanoclay Blends

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ABSTRACT: The dispersion of nanoclays in nonpolar polypropylene (PP) is difficult without the use of a small fraction (1–3%) of modified grafted PP as a compatibiliser. This work reports the effect of different graft-modified polypropylenes on the dispersion of nanoclays in PP, and thermal stability and flammability of the blends. PP has been compounded in a Brabender compounder with a selection of modified PP polymers as compatibilisers. The grafts include maleic anhydride, N-ethylmaleimide, diethylmaleate, diethyl-p-vinylbenzyl phosphonate, and acrylic acid-2-[(diethoxyphosphoryl)methylamino] ethyl ester. Films were cast from the blends by compression molding and the nanocomposite structures assessed using X-ray diffraction. Thermal characterization was performed using DSC and TGA, the burning behavior was observed using limiting oxygen index measurements, and cone calorimetry where samples were exposed to 35 kW/m^2 external heat flux. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 816–824, 2008

Key words: polypropylene; compatibilser; nanoclays; X-ray diffraction; scanning electron microscopy; thermal analysis; flammability

INTRODUCTION

The properties and low cost of polypropylene gives it the advantage over other polymers for use in engineering plastic and fiber applications. However, it burns easily giving rise to flaming drips with no char formation.[1] It has been found that the addition of layered silicates (nanoclay) to the polymer to yield a nanocomposite structure can have positive effects on both the flammability and physical properties of polypropylene and, in particular, modulus, strength, and heat resistance.[2] The most commonly used layered silicate is montmorillonite, which is made up of several stacked silicate layers with a regular gap or gallery between each. Nanocomposites can be either intercalated or exfoliated. Intercalation occurs when a small amount of polymer enters the gallery spacing and may separate the layers slightly but fails to separate the layers completely. Exfoliation (or delamination) happens when the clay platelets are pushed apart and distributed homogenously throughout the polymer matrix.[3] However, because the clay is hydrophilic, it makes exfoliation in a hydrophobic polymer such as PP difficult; therefore, the surfaces of the clay layers have to be modified with a surface treatment to make them similarly hydrophobic. The clay can be organically modified by ion-exchange reactions using cationic surfactants.[4,5] While the use of either a twin-screw or Brabender compounder may melt blend functionalised clays with polar polymers such as nylon (PA6), polymethyl methacrylate (PMMA), and polystyrene (PS), the low polarity of polypropylene makes a homogeneous dispersion of the nanoclay very difficult.

In our previous work, we have compounded polypropylene (PP) with nanoclays and melt extruded the products into fibers, but observed that to improve the dispersion of the clay in polymer matrix it is necessary to add a compatibiliser.[6] While the full exfoliation of clay platelets is not necessary for successful fiber production, it is important that the clay is well dispersed or production of melt spun fibers will not be possible. Dispersion can be improved with the addition of maleic anhydride-grafted polypropylene. It would appear

that the optimum levels for increasing the interlayer spacing are between 5 and 15% compatibiliser. Above 15% levels, no further significant increase in the interlayer spacing is observed.[4] However, high loadings of maleic anhydride-grafted PP are detrimental to the mechanical properties, especially in the case of filament formation; therefore it is necessary to find the lowest level that will give reasonable dispersion.[7] We have observed the optimal values between 1 and 3% for filament production.[6] Furthermore, the cyclic anhydride structures in PP grafted with maleic anhydride are prone to slow adventitious hydrolysis eventually leading to intramolecular crosslinking of the polymer chains. In the present work, we have tried a variety of alternate compatibilisers, some novel, which are more hydrolytically stable than maleic anhydride and optionally containing flame retardant groups.

The mechanisms involved in clay dispersion and intercalation would also appear to be dependent on type of clay used and the functionalised intercalant. If the thermal stability of the intercalant is not good, then thermal degradation occurring during melt processing can result in the collapse of any dispersed clay platelet structure which might appear in X-ray diffraction (XRD) patterns as an apparent exfoliated structure.[8] Much of the literature discussing the use of a compatibiliser discusses maleic anhydride-modified PP with nothing about the use of any other compatibiliser. Here, we discuss the use of maleic anhydride-modified PP and polypropylene modified with other grafting agents.

EXPERIMENTAL

Samples

Materials

Polypropylene. Fiber grade Polypropylene chips, Moplen HP561R, Basell Polyolefins.
Grafted polypropylene

1. Polybond 3200 (Pb), Chemtura Corp. (former Crompton Corp.), USA: maleic anhydride (MA) grafted polypropylene with a maleic anhydride graft level of 1% (w/w).
2. Four grafting agents were used to modify polypropylene in house, two of which were specially synthesized:
   i. *N*-ethylmaleimide (EMI), Sigma-Aldrich
   ii. Diethylmaleate (DEM), Sigma-Aldrich
   iii. Diethyl-*p*-vinylbenzyl phosphonate (DEP)
   iv. Acrylic acid-2-[(diethoxyphosphoryl)methylamino] ethyl ester (ADEP).

The syntheses of DEP and ADEP are reported in detail elsewhere.[9–11] The chemical structures of the grafting agents are given in Figure 1.
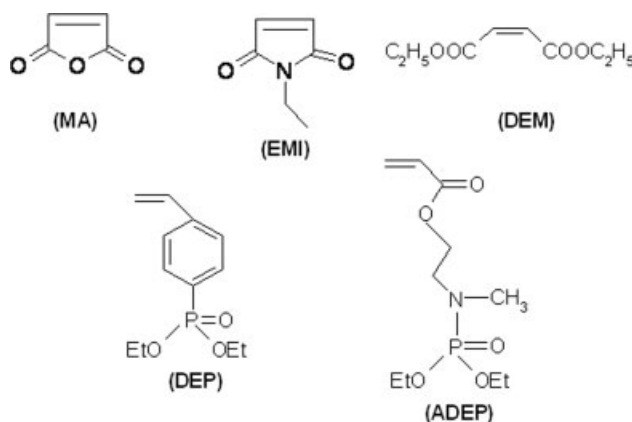

Figure 1 Chemical structures of the grafts used for modifying polypropylene.

Grafting procedure. The full procedure has been described in our previous paper[12] and is summarized here. The substrate (PP chips) and the solvent *o*-dichlorobenzene (*o*-DCB) were reacted with monomer and the initiator, di-*tert*-butylperoxide (DTBPO) under argon and reflux at a fixed temperature of 150 or 160°C for 1.5 h. 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°C for several hours before further examination. Experimental conditions and yields for various grafting reactions are given in our previous publication.[12]

Charactrerization of grafted polypropylene. NMR: [1]H, ^{13}C, and ^{31}P spectra of starting materials, various reagents and monomers were recorded in deuterated solvents (CDCl$_3$ and $_{d6}$-DMSO) on Bruker spectrometers, operating at 250 or at 400 MHz, at ambient probe conditions. For polypropylene based polymers, $_{d2}$-1,1,2,2-tetrachloroethane was used as the solvent and the spectra were recorded at elevated temperatures (ca. 80–100°C). The spectra were processed using WIN-NMR software after being calibrated using standard residual signals for proton or the main solvent signals for carbon spectra. For ^{31}P spectra, an external calibrant was employed (85% orthophosphoric acid).

The chemical structure and purity of small molecules and monomers were mainly inferred from ^{1}H and ^{31}P spectra. For grafted polymers, the chemical compositions (i.e., mole fractions of the grafted units present) were deduced from proton spectra by comparing the integral areas of appropriately assigned signals.

FT-IR: Infra red spectra were recorded using a Perkin–Elmer Paragon 1000 spectrometer (absorbance mode). Liquids were used as such, whereas solids were made into KBr pellets for spectral measurements. For polypropylene samples, films made by hot pressing (temperature ∼ 180°C, and at a pressure of

Grafted PP	N (wt %)	P (wt %)	Graft units (mol fraction)	Graft units (wt %)
PP/gEMI	0.40	0.00	0.01[a]	3.86
			0.01[b]	3.86
PP/gDEM	0.00	0.00	0.01[b]	4.89
PP/gDEP	0.00	1.91	0.03[c]	17.90
PP/gADEP	–	4.80	0.10[c]	42.11

[a] From nitrogen analysis (combustion method).
[b] From NMR.
[c] From phosphorus analysis (ICP/OES).

about 10 tons for ca. 3 min) were used to obtain the spectra. An appropriate proprietary software was employed for detailed analysis and plotting of spectra.
Elemental analysis. Combustion method: Elemental analyses for C, H and N were done on a Perkin–Elmer 2400 CHNS/0 series II elemental analyzer that uses a combustion method in a pure oxygen environment to oxidize the elements to their respective oxides. After reduction by passing over pure copper, the mixture of gases were separated by a chromatographic column and the amounts estimated using a thermal conductivity detector (a tolerance of 0.3% is set for organic samples). For most of the samples, the analysis was done in duplicate.

Inductively coupled plasma/optical emission spectroscopy (ICP/OES): The phosphorus contents of grafted PPs were obtained by this method employing a ICP-OES-Spectro Ciros Plasma spectrometer. The polymeric samples were first digested with a mixture of conc. HNO_3 and conc. $HClO_4$ for about 4 h to facilitate the conversion of P into aqueous phosphates, and then made up to a known volume, before analysis.

The characterization data of all grafted polypropylene samples is given in Table I.
Nanoclays. The following two commercial clays modified with dimethyl, dehydrogenated tallow quaternary ammonium ions have been used:

1. Cloisite 20A (20A), Southern Clay Products, USA
2. Elementis Bentone 107 (E107), Elementis Specialities.

and the different formulations used are given in Table II.

Compounding

The polypropylene and other additives were hand mixed in a plastic container prior to compounding. A Brabender W50E chamber fitted with cam blades was used to compound the polypropylene with grafted polypropylene and nanoclays at a rotor speed of 60 rpm, a set temperature of 190°C and with a 6 min mixing time.

Film formation by compression molding

Films (∼ 0.3 mm thickness) were cast from the blends by compression molding with spacer plates, between aluminum foil-coated steel plates at a set plate temperature of 190°C.

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 2θ = 2° to 20°, at a rate of 2° per min. The samples for XRD analysis were cut from the film samples and had a thickness of 0.3 mm.

Scanning electron microscopy

Scanning electron microscopic (SEM) images were obtained using a Cambridge Stereoscan 200 SEM having a tungsten electron gun with accelerating voltage capacity 0.5–30 kV and magnification ranges between 30× and 300,000× at 30 kV, providing resolution down to 60Å. All images were obtained at 10 kV. Films were etched with chromic acid before gold sputtering to attempt to develop any underlying structural texture.

Thermal analysis

Differential scanning calorimetric (DSC) experiments were conducted using a Polymer Laboratories (PL-

TABLE II
Formulation Compositions, Film Thickness, and XRD Data

Sample No.	Sample ID	Nanoclay (3%, w/w)	Graft (1%, w/w)	Film thickness (mm)	XRD peaks, 2θ
PP	PP	–	–	0.38 ± 0.04	
1	PP + 20A	20A	–	0.36 ± 0.06	3.65
2	PP + Pb + 20A	20A	Pb	0.43 ± 0.10	3.4
3	PP + E107	E 107	–	0.43 ± 0.09	3.3
4	PP + Pb + E107	E 107	Pb	0.40 ± 0.05	3.0
5	PP + EMI + E107	E 107	EMI	0.36 ± 0.08	2.95
6	PP + DEM + E107	E 107	DEM	0.40 ± 0.07	2.95
7	PP + DEP + E107	E 107	DEP	0.45 ± 0.09	3.0
8	PP + ADEP + E107	E 107	ADEP	0.35 ± 0.05	2.95

DSC) instrument, under flowing nitrogen (10 mL/min) and a heating rate of 10°C/min from room temperature to 350°C. About 2.5 mg of sample was taken in each case and all the thermograms were then normalized to 1.0 mg for comparison. Thermogravimetric analyses were undertaken using a Polymer Laboratories TG 1000 instrument under flowing air (10 mL/min) with a heating rate of 20°C/min. Approximately 6 mg of sample was used in each case.

Flammability testing

Limiting oxygen index (LOI) values were determined on selected samples using a standard procedure.[13]

Cone calorimetric tests were carried out on a Fire Testing Technology (UK) cone calorimeter, and all the tests were conducted according to the test methods defined in ISO 5660[14] using an incident heat flux of 35 kW/m^2. Samples were supported by aluminum foil to contain molten polymer during testing.

RESULTS AND DISCUSSION

To enhance the compatibility of PP and clays, the base polymer was chemically modified with polar groups. This was achieved through grafting reactions of carefully chosen grafting agents with PP, in solution at elevated temperatures, under radical initiation. The grafting agents employed in the present study include maleic anhydride [MA in commercially available sample, Polybond 3200 (Pb)], N-ethyl maleimide (EMI), diethyl maleate (DEM), and P-containing unsaturated compounds such as diethyl-p-vinylbenzyl phosphonate (DEP) and acrylic acid-2-[(diethoxyphosphoryl)-methylamino] ethyl ester), (ADEP). The choice of the grafting agents was primarily based on the grafting efficiency (i.e., the reactivity of the olefinic group), polarity, hydrolytic stability (especially of EMI and DEM as compared to MA), flame retardant properties[10,11] (e.g., in the case of DEP and ADEP). All grafting reactions were found to be quite straight forward resulting in appreciable yields of the products. The yields, quoted as weight percentages,[12] were based on weights of the recovered products after thorough purification (by washing several times with acetone, a good solvent for the unreacted grafting agents, and through drying of the washed products, in a vacuum oven kept at 60°C, to constant weight).

It is fairly well established fact that in the case of PP, under similar experimental conditions, the grafting reactions primarily occur at the tertiary carbon atoms of PP backbone. Furthermore, in the case of 1,2-unsaturated cylic anhydride (MA) and its derivatives (EMI and DEM), the grafts consist of predominantly monomeric units. However, the P-containing agents (DEP and ADEP), owing to their strong tendency to homopolymerize, the possibility of formation of oligomeric grafts cannot be completely ruled out. The detailed analyses of the exact position(s) of attachment or the true chemical nature of the grafts onto the PP chains were not attempted in the present study. However, ^{1}H and ^{13}C-NMR of the purified products, recorded at both 250 and 400 MHz in $_{d2}$-1,1,2,2-tetrachloroethane at elevated temperatures (ca. 80–100°C), furnished unequivocal evidence for the presence of grafted units in the PP chains. This was also supported by the examination of the corresponding FT-IR spectra recorded on films of the modified polymers (indicative signals from the carbonyl and phosphonate ester groups resulting from the grafts were prominent in the spectra). Quantitative information regarding the amount of grafted units was obtained from ^{1}H-NMR and/or through microelemental analyses (for N and/or P as the case may be). The results obtained by both methods compared favorably as can be seen from Table I.

Effect of grafts on structural properties of polypropylene–nanoclay blends

X-ray diffraction

Figure 2 shows the XRD results for films of PP control, ungrafted and grafted PP with 20A and E107 samples. The peaks between 3 and ~ 4° (2θ) are characteristic of the clay. No diffraction peaks are observed for the control sample [see Fig. 2(a)] as expected since PP polymer crystal diffraction does not occur at 2θ < 10°.

The data recorded in Table II show significant changes in the XRD peak at 2θ of the nanoclay in the presence of the compatibiliser. There is a reduction in peak angle from 3.65° in Sample 1 (ungrafted) to 3.4° for Sample 2 (Pb-grafted) compounded with Cloisite 20A [see Fig. 2(a)]. Sample 3 with E107 clay with no compatibiliser, shows a peak at 3.3° but on addition of compatibiliser to the mix, the XRD peak shifts to the lower angle of 3.0° for Sample 4 [Fig. 2(b)]. This shows that Pb-grafted polypropylene's effect on both 20A and E 107 in terms of shifting the angle to lower 2θ is similar. The shift in peak to a lower angle indicates an increase in interlayer spacing, which is evidence of, at least, an intercalated structure if not a fully exfoliated structure.[4,15] Compared to Pb graft, the DEP graft has similar effect, with 2θ angle at 3.0° in Sample 7 [Fig. 2(c)], whereas, EMI, DEM, and ADEP have shifted it to 2.95° in Samples 5, 6, and 8 [Fig. 2(c)]. The decrease in peak height of the sample with 1% DEP grafted polypropylene (Sample 7) and 3% E107 suggests exfoliation, but could also result from deformation of the clay layers. These results indicate that grafts EMI, DEM, DEP, ADEP can be used similar to maleic anhydride in improving dispersion of the nanoclays. This can be attributed to the strong polar effects exerted by the imide functionality (of EMI) and by the ester
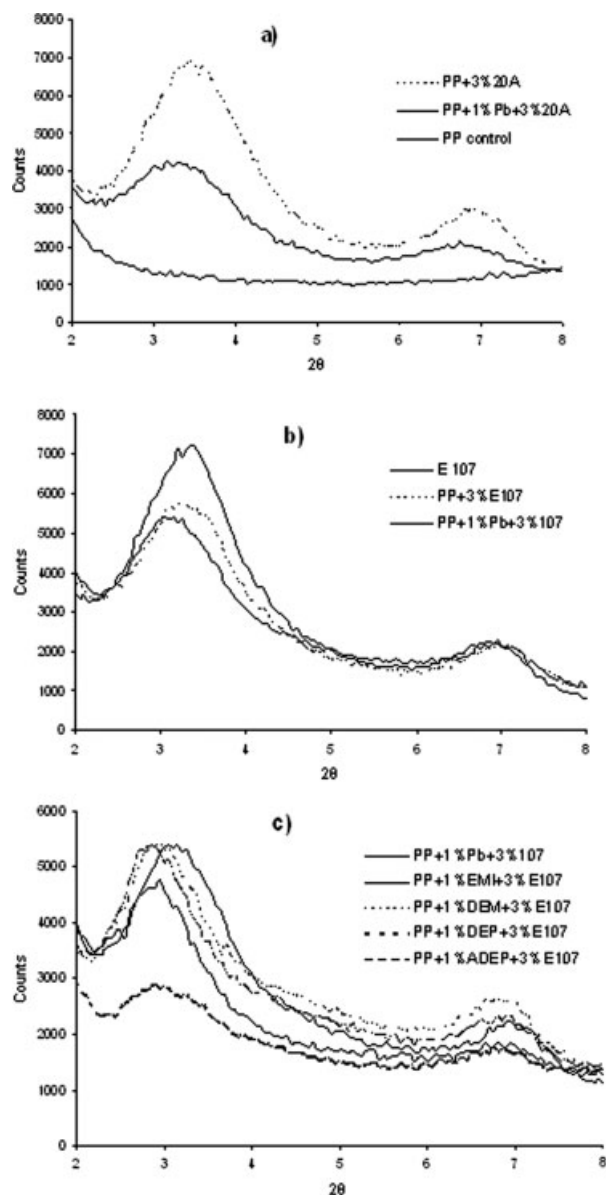
Figure 2 XRD curves of (a) PP control, ungrafted and grafted PP with 20A, (b) E107 clay, ungrafted and maleic-anhydride grafted PP with E107, and (c) grafted PP with different grafts and E107 clay.

groups (in DEM, DEP, and ADEP) in the base polymer matrix. The strongly polar phosphonate ester groups (in DEP and ADEP) could also greatly facilitate exfoliation of the clay layers.

Scanning electron microscopy

The scanning electron microscopic images of PP with nanoclay and different compatabilisers are shown in Figure 3. Generally it can be seen that the relatively coarse surface texture of Sample 1 which contains dispersed clay alone reduces with the addition of compatibiliser [Fig. 3(b)]. A similar reduced texture occurs

when Polybond (containing MA) compatibiliser is added to a E107 clay-containing PP in Figure 3(d). In both Figure 3(a) and Figure 3(c), clay particles are evident whereas in all other micrographs in which a grafted PP matrix is present, generally these are less clear. Hence, the addition of the laboratory-synthesized grafted polypropylenes has generally reduced the coarseness of surface texture in the presence of this same clay [Fig. 3(e–g)] thereby corroborating other evidence that clay particle dispersion has been improved following PP grafting.

Effect of grafts on thermal stability of polypropylene–nanoclay blends

Table III lists the fusion minima temperature or the melting temperatures. It can be seen that addition of clay and graft has minimal effect on the melting point of the polypropylene.

TGA results shown in Figure 4 and listed in Table III show that onset temperature for decomposition (temperature where the mass loss starts, measured from DTG curves (not shown here)) is 232°C for PP, which is not changed by presence of Cloisite 20A clay in Samples 1 and 2. E 107 clay has increased this temperature to 246°C in Sample 3. The grafts have minimal additional effect on the onset temperature with values ranging from 243 to 246°C in Samples 4–8. Although the addition of comaptibiliser seems to have no effect on the onset temperatures, there is an effect on the thermal degradation behavior of the samples in that while the clay increases the mass residue at any particular temperature, including the compatibiliser in the mix raises it even further. This can be seen from Figure 3 and also from mass residue values at different temperatures given in Table III. The results show that Polybond (MA graft) has increased thermal stability with both clays. Using EMI (Sample 5), DEM (Sample 6), or ADEP (Sample 8) the effect on mass loss and hence, the rate of decomposition is less than Polybond (Sample 4), whereas with DEP (Sample 7), the increase is similar to that of Polybond. In general, the presence of graft increases the final decomposition temperatures for all samples, slows down the rate of decomposition, and extends the decomposition temperature over a larger temperature range, with best results shown for Pb and DEP grafts with E 107 clay. From this study, it can be anticipated that samples containing E107 clay and compatibilser Pb (Sample 4) and DEP (Sample 7) should show lower flammability than other samples.

Effect of grafts on flammability of polypropylene–nanoclay blends

Limiting Oxygen Index

The LOI test results for the PP control sample and for films of PP containing nanoclays 20A and E107 are

given in Table III. The results indicate that LOI values are very similar and within the experimental error range. However, some generic trends can be seen. All the samples with clay have slightly higher LOI values than that of the PP control sample. For 20A-containing samples, the poorly dispersed sample with 20A has an LOI value of 17.2, which with addition of Polybond-grafted PP has increased to 17.6 in Sample 2. For E107-containing samples, the sample with clay only has an LOI value of 17.2; while the addition of DEP, DEM and Pb increases it to 17.4–17.7, introduction of EMI and ADEP grafts produced no effect. The results
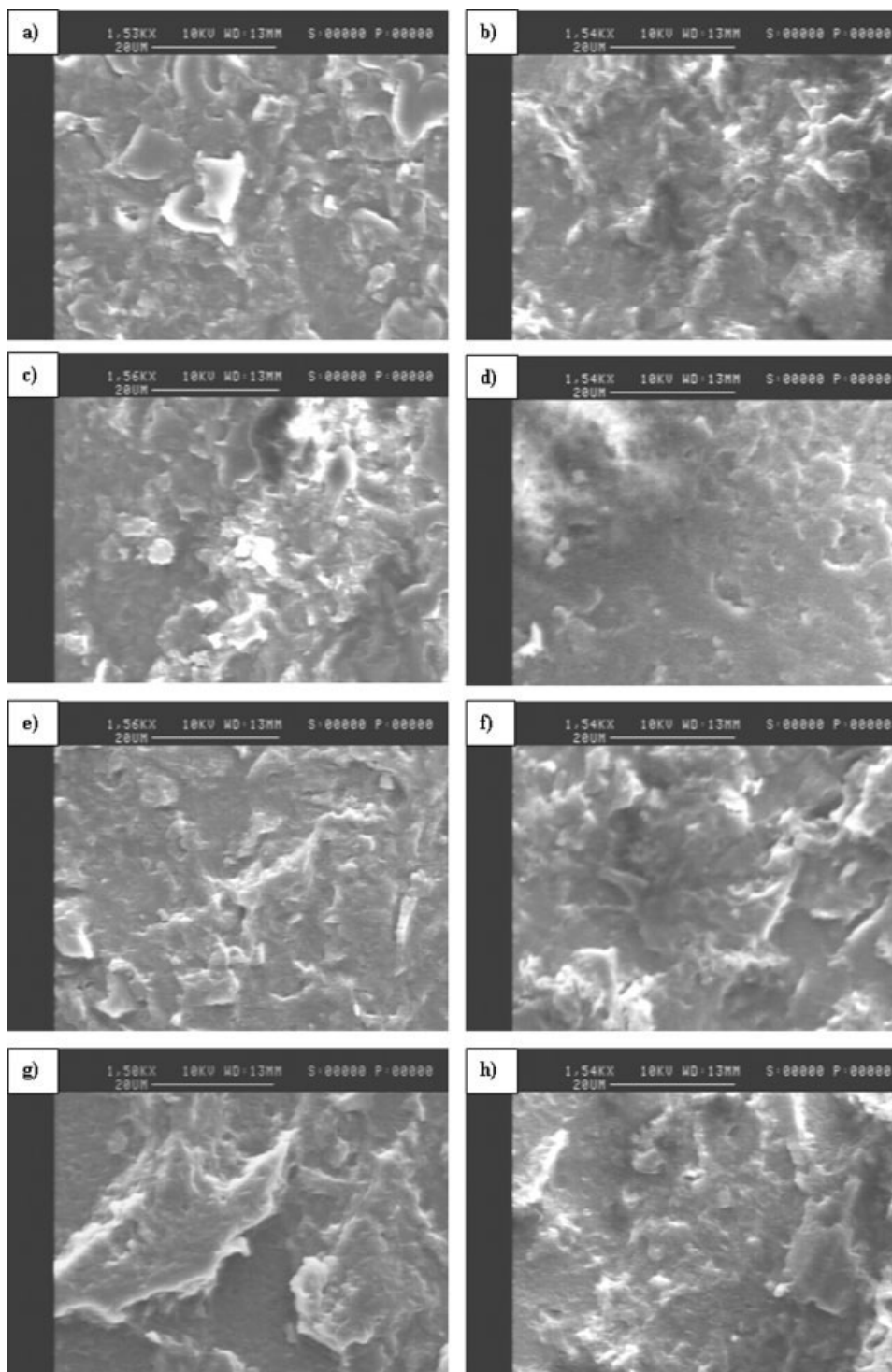

Figure 3 SEM images of etched films at similar magnification levels: (a) Sample 1, PP + 20A; (b) Sample 2, PP + Pb + 20A; (c) Sample 3, PP + E107; (d) Sample 4, PP + Pb + E107; (e) Sample 5, PP + EMI + E107; (f) Sample 6, PP + DEM + E107; (g) Sample 7, PP + DEP + E107; (h) Sample 8, PP + ADEP + E107.

TABLE III
Thermal and Flammability Data

Sample No.	Sample ID	DSC Peak maxima (°C)	Onset decomp temp (°C)	TGA results					LOI (%)
				Mass residue, % at temp					
				300°C	350°C	400°C	450°C	500°C	
PP	PP	169	232	84.9	62.2	18.9	5.0	3.9	17.0
1	PP + 20A	168	233	84.8	61.5	16.2	5.5	4.5	17.2
2	PP + Pb + 20A	170	232	89.3	74.3	38.5	5.2	3.9	17.6
3	PP + E107	169	246	90.1	66.2	36.2	3.3	2.5	17.2
4	PP + Pb + E107	168	243	90.7	76.0	44.0	4.3	3.6	17.7
5	PP + EMI + E107	167	245	88.0	69.5	27.2	5.1	3.8	17.2
6	PP + DEM + E107	171	244	89.4	70.2	30.6	3.8	3.3	17.6
7	PP + DEP + E107	166	246	89.8	75.3	42.2	5.0	4.4	17.2
8	PP + ADEP + E107	170	245	88.1	69.9	25.9	4.5	3.5	17.4

are in accordance with thermal analytical results, where best results were shown with Pb and DEP grafts. This suggests that the type of graft used can influence the burning behavior of the blend.

Cone calorimetry

The cone results of all the samples are reported in Table IV and selected results are shown in Figure 4. Previously reported work has shown that when sample masses are below 5g, errors in cone results are rarely less than ±10%.[16] Furthermore, observation of the polypropylene film samples as they burned showed considerable bubbling and flowing of the polymer during burning which, although contained by aluminum foil, still caused anomalies in the weight losses recorded by the mass balance. As a consequence, in the data shown in Table IV, while there are significant variations in each set of replicate samples, a general trend can still be discerned. It can be seen that there is no significant effect on time-to-ignition (TTI) with addition of grafted polypropylene with nanoclay although a slight increase is recorded for Samples 2 and 4 containing Polybond (MA graft) and Sample 7 containing DEP grafted PP compared to the respective ungrafted samples (Samples 1 and 3). It is well known that the nanoclays in general do not effect the TTI and in some cases even lower it compared to polymer only.[17] The slight increase in TTI for Samples 2, 4, and 7 samples indicates the positive effect of Pb and DEP grafts, which was also observed by TGA and LOI studies. The burning time varies for different samples and is especially noteworthy in Figure 3(a).

Heat release rate is the heat generated per unit time by the burning sample divided by the surface area of the sample. Hence, it is a measure of the heat release rate to the surroundings per unit surface area of the burning material. The important parameters for assessing the fire performance of a material are the maximum or peak heat release (PHRR) and total heat release rates (THR). HRR curves as a function of time

for all samples are given in Figure 5(a,b). As can be seen from the curves and the values reported in Table IV, the peak heat release rate (PHRR) is unaffected in some samples; however, Sample 4 containing E107 and polybond, and Sample 7, containing E107 and DEP grafted polypropylene, show comparatively low values. Total heat release for Sample 7 is also lower compared to those of the other samples. This again indicates that DEP graft contributes in reducing the flammability of the polypropylene-nanoclay blend,
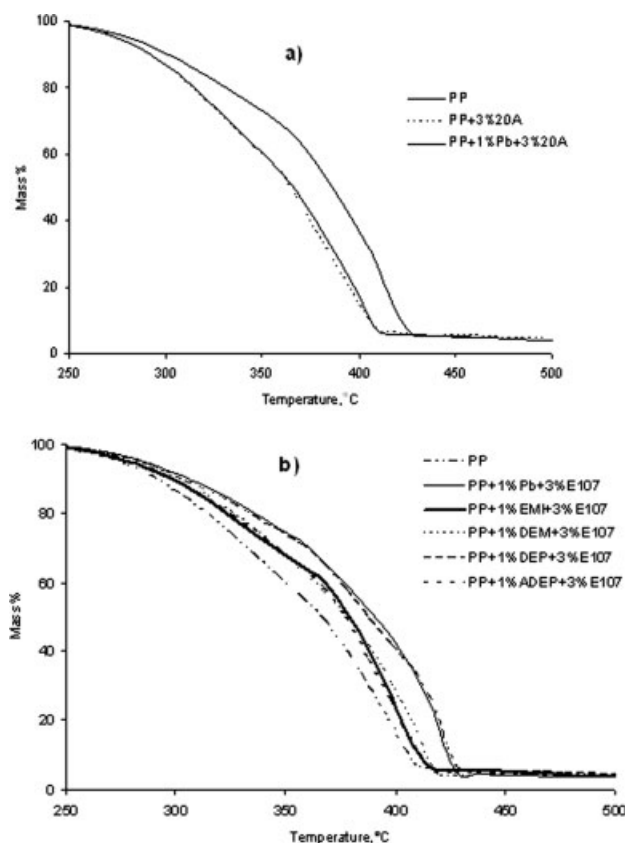

Figure 4 TGA curves in air for control and grafted PP samples containing (a) 20A and (b) E107 clay.

TABLE IV
Cone Calorimetric Results

S. No	Sample ID	Mass (g)	TTI (s)	FO (s)	PHRR (kW/m²)	THR (MJ/m²)	Mass residue (%)	Smoke (m²/m²)
1	PP + 20A	2.9	15	81	499	11.1	1.9	223
2	PP + Pb + 20A	3.5	23	121	498	12.1	4.8	257
3	PP + E107[a]	3.08	16	82				
4	PP + Pb + E107	4.0	22	95	392	12.9	4.7	350
5	PP + EMI + E107	3	16	85	512	11.5	2.2	250
6	PP + DEM + E107	3.1	17	90	504	12	1.2	216
7	PP + DEP + E107	3.4	23	96	463	10.9	3.8	222
8	PP + ADEP + E107	3.1	10	86	494	12.8	3.2	196

[a] Data could not be saved for certain parameters due to software problem.

which is expected since DEP contains a phosphonate group and the presence of phosphorus, even in small amounts in the polymer structure, can influence its flammability.

Because the char retained after burning a polymer is also a measure of its flammability, the mass loss curves give insight into the fire performance of the samples. The mass loss curves for all samples and their residual char retained after completion of the test are given in Figure 5(c,d) and Table IV, respectively. Mass loss behavior of Sample 2 containing 1%

Pb and 20A clay is quite different than Sample 1 with clay only [see Fig. 5(c)]. For samples containing E107 clay, grafts Pb (Sample 4), and DEP (Sample 7) show slower mass loss rate [see Fig. 5(d)] and higher charred residue (see Table IV) compared to those containing EMI (Sample 5), DEM (Sample 6), and ADEP (Sample 8). Results for smoke production, expressed as m²/m² in Table IV show much variation and no real trend. In conclusion, maleic-anhydride (Pb) and DEP grafts, which indicated better performance by thermal analytical and LOI results, are seen to be
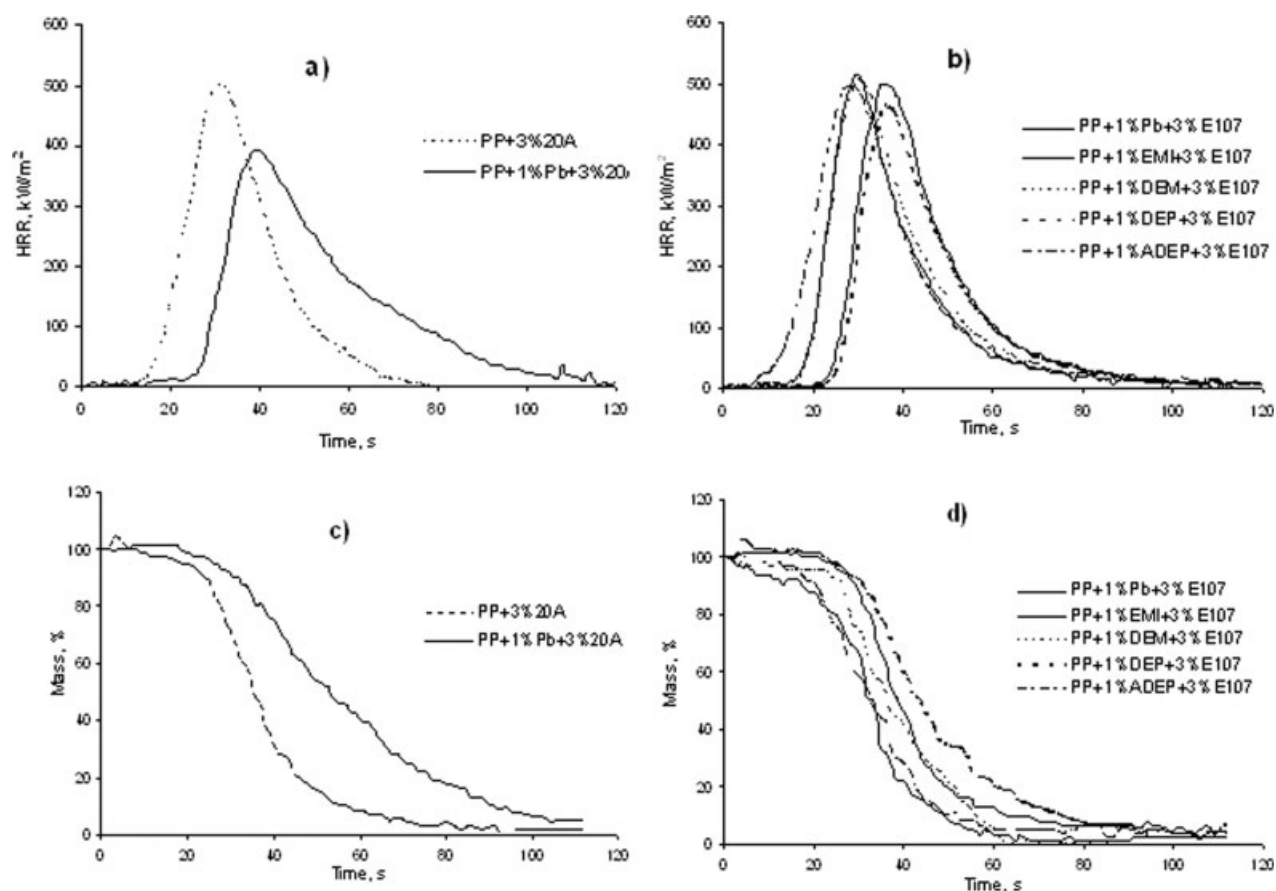

Figure 5 Cone calorimetric results for PP samples containing grafted PP and 20A and E107 clay: (a) and (b) HRR versus time; (c) and (d) mass loss versus time at 35 kW/m² heat flux.

effective in reducing the flammability of the polypropylene-nanoclay blends as observed by cone calorimetry by improving their dispersion and also contributing to the charring of the burning polypropylene.

This discussion shows that although nanoclays in presence of compatibilisers are effective in reducing flammability of polypropylene, but they do not do so to the same extent as seen for other polymer-nanocomposites systems. It must also be noted that these are thermally and physically thin samples and behave differently than bulk polymers, which are tested as thick plaques. It is believed that in polymer–nanoclay nano/micro composites, a carbonaceous-silicate char builds up on the polymer surface during burning, which insulates the underlying material and slows the mass loss rate of decomposition products, hence conferring flame retardant property to the polymer.[17] The poor performance of the thinner samples may be explained in terms of a competition between the formation of a surface carbonaceous-silica shield and the volatilization to fuel of surrounding polymer. In thicker polymer-nancomposite samples, the competition favors ceramic barrier formation while for thin composites, volatilization dominates. This can be considered as the difference between so-called thick and thin thermal behavior[17] and so in similarly "thin" films or textile fabrics it is possible that the "shield-forming" mechanism observed for bulk polymer nanocomposites may be too slow for effective improvement in fire performance.

CONCLUSIONS

The dispersion of clay in PP can be improved by the addition of grafted polypropylene. Some degree of exfoliation was achieved for the sample containing diethyl-p-vinylbenzyl phosphonate (DEP) grafted polypropylene. The grafts have minimal effect on melting points of the polymer but slightly enhance the thermal stability of the polymer below $400°C$. Grafted polypropylene containing samples have slightly lower flammability than ungrafted polypropylene and the results shown by maleic anhydride (Pb) and diethyl-p-vinylbenzyl phosphonate (DEP) grafted polypropylene are particularly encouraging.

On the basis of the results of the work reported here, combinations of samples containing 20A and E107 with maleic anhydride (Polybond) and DEP grafted polypropylene have been selected for further study. These will be compounded using a twin-screw extruder and then melt spun into filaments with an overall aim of producing flame retardant synthetic nanocomposite fibers.

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