

Polypropylene Fibers Containing Dispersed Clays Having Improved Fire Performance. I. Effect of Nanoclays on Processing Parameters and Fiber Properties

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ABSTRACT: While the present interest in the use of functionalized nanoclays as additives for improving tensile properties and fire performance in polypropylene thermoplastics has led to a considerable literature, little attention has been given to this polymer in fiber form. In this article, we report the conditions necessary for and the characteristics of filaments and tapes comprising dispersions of functionalized clay in polypropylene–clay prepared by melt compounding polypropylene in a twin screw extruder. A small fraction (1–3% w/w) of modified grafted polypropylene has also been included to improve dispersion of the clay. X-ray diffraction of hot-pressed films, coupled with transmission electron microscopic investigation has been used to assess the degree of dispersion of the clay. Clay dispersion at the nanolevel was observed by TEM, but intercalation was not evident from X-ray study. Compounded samples were melt-extruded into filaments using

a single screw extruder and drawn prior to wind up. The physical properties of the clay-containing polypropylene filaments showed that presence of dispersed clay increased filament modulus and was supportive of having achieved some degree of nanodispersion. Selected filament samples had sufficiently acceptable textile properties to enable their knitting into fabric samples. The burning behavior of fabric and film samples were observed by limiting oxygen index and cone calorimetry at 35 kW/m² external heat flux. While the clay presence did not confer flame retardancy, it did change the burning character and encouraged some char formation. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1707–1717, 2007

Key words: polypropylene fibers; nanoclays; compatibilizer; X-ray diffraction; transmission electron microscopy; flammability

INTRODUCTION

The low cost of polypropylene coupled with its excellent mechanical properties determines its suitability for the end-uses including, tapes, films, injection-moulded products, and important to this study, fibers. Although polypropylene fibers are rarely used in apparel fabrics, they are commonly used for both domestic, contract and automotive upholstery fabrics. However, when subjected to heat, once the melting temperature is reached, polypropylene drips and when the ignition temperature is reached, rapid burning occurs, with no char produced. High levels of flame retardants, typically >20% w/w, often antimony–bromine based, are needed to make polypropylene materials conform to the necessary standards for use in textiles or composites for the automotive and aero industries.¹ However, such high levels render the processing of compounded polymer into

fibers difficult and the resulting fiber properties unsuitable for textile applications.

As early as the 1950s, the use of silicates was first reported in the literature but it was not until 1990s that their potential as fillers for polymer–nanocomposites was brought to the fore by academic and industrial research.² It has been observed that the addition of just a small quantity of clay to a polymer matrix could enhance many of the properties of that polymer, including the fire performance, notably via a lowering in peak heat release rate.³ One of the difficulties of incorporating the clay platelets into polypropylene is the lack of polar groups in the polymer chain which makes direct intercalation or exfoliation almost impossible. A recent analysis of over 40 polypropylene composites has confirmed this to be the case and concludes that exfoliation can be seldom achieved.⁴ Early studies reported on the use of maleic anhydride-grafted polypropylene as a compatibilizer, which enhances the interaction between the clay and polymer with strong hydrogen bonding between OH or COOH and the oxygen groups of clay.^{2,5,6} Presence of such compatibilizers usually has adverse effects on fiber properties, however.¹

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Although good dispersion within the polymer is very important for further processing into fibers, it has been demonstrated that improved fire performance can be obtained where the clay structure is at best only intercalated forming a microcomposite instead of a true nanocomposite.⁷ However, clay platelets need to be fully exfoliated to form a true nanocomposite and it has been shown that increasing shear stress, mixing time, and decreasing mixing temperature, when compounding in the twin screw extruder, can improve clay platelet exfoliation.⁸

Much of the previous work on nanocomposites has been on injection and compression moulded thermoplastics, with very little recorded literature on the production of textile fibers. Some polypropylene fibers containing nanodispersed particles have been developed but they contain silver particles to improve the antimicrobial properties.⁹ However, the mechanical and fire behavior of fibers or fabrics is probably quite different from that of a solid nanocomposite plaque. Thus, while the addition of up to 5% w/w nanoclays into plaques brings an improvement in mechanical properties,^{10,11} our recent review shows that improved tensile properties of fibers may be achieved also at 1–5% clay-inclusion levels.¹² Deterioration in properties, however, usually occurs at clay levels >5%.^{10–12}

The present study is the first part of a larger project, investigating the possibility of creating fire retardant synthetic fibers based on nanocomposite structures. This part examines the challenges involved in generating polypropylene fibers comprising dispersed nanoclay and compatibilizing copolymer.

EXPERIMENTAL

Samples

Materials

Polypropylene. Fiber grade polypropylene chips, Moplen HP516R, Basell Polyolefins. Nominal MFI 25 g/600 s at 230°C.

Grafted polypropylene. Polybond 3200 (Pb), Crompton Corporation, maleic anhydride modified homopolymer polypropylene with maleic anhydride level 1% (w/w).

Nanoclay. Cloisite 20A, Southern Clay Products, USA, is a montmorillonite clay modified with dimethyl, dihydrogenated tallow quaternary ammonium chloride. This modified clay was chosen because of its nonpolar alkyl substituents.

Compounding

Polypropylene and additives were hand-mixed in a plastic container prior to compounding. A Betol

BTS30 twin screw extruder with a temperature profile over six heating zones between 179 and 190°C was used for compounding. The samples were passed through the compounder initially once and then twice to assess the effect of additional mixing on the dispersion of the clay within the polymer matrix. Polymer extrudates were pelletized after cooling in a water bath. The different formulations used are given in Table I. One set of samples, (5(a) and 5(b) in Table I), was prepared using a master batch comprising 5% clay and 6% graft which was then diluted with polypropylene to give samples containing 2.5% clay and 3% graft. All percentage concentrations are on a weight/weight basis.

Melt extrusion into filaments/tapes

Filaments were extruded from pellets using a laboratory-sized Labline Mk 1 single screw melt extruder. The electrically driven screw has a major diameter of 22 mm, $L/D = 20$ and three zones, a feed zone, a compression zone, and a metering zone which feeds into a cavity transfer mixer for enhanced mixing. The melting polymer is passed through a temperature profile of 180–230°C before being forced into the die head and extruded through a 40 hole spinneret. The filaments were passed over a set of four cool slow rollers and then a final two which were heated to 60°C prior to passing over the fast rolls for drawing. A draw ratio of 6 : 1 was selected to yield filaments of acceptable tensile properties, but on occasion it was necessary to reduce this to avoid filament breakage.

Tapes (40 mm width, 0.6 ± 0.2 mm thickness) were extruded using a tape die in place of the spinneret, primarily to provide samples more convenient for microscopic investigation while having experienced both compounding and extrusion cycles similar to that for filaments. Tapes were collected as they cooled with no draw ratio applied.

Fabric production

Because of the limited quantities of experimental filaments available, production of small samples of weft-knitted fabric only was possible in order to test each in fabric form. Filament bundles were knitted into fabric strips with a small hand, circular knitting machine, gauge E7 and area densities are recorded in Table II.

Film formation by compression moulding

Films (ca. 0.3 mm thickness) were also cast from compounded blends by compression moulding with

TABLE I
Sample Composition, MFI, DSC, and Rheology Results of Polymer Chips

Sample No.	Nanoclay, 20A (% w/w)	Graft, Pb (% w/w)	No. of extrusions	MFI (g/600 s)	Rheological properties at 240°C			DSC endothermic peak	
					Storage mod., G' (Pa)	Loss Mod., G'' (Pa)	Complex viscosity, η^* (Pa s)	Peak maxima (°C)	Heat of melting (mj/mg)
PP	—	—	—	25.9	1384	4342	1000	164	73.2
1(a)	0	0	1	36.0	—	—	—	163	79.1
1(b)	0	0	2	—	288	1298	230	166	61.2
2(a)	2.5	0	1	40.2	—	—	—	167	70.3
2(b)	2.5	0	2	35.4	315	3253	802	165	67.0
3(a)	2.5	1	1	28.8	—	—	—	166	85.0
3(b)	2.5	1	2	22.2	978	3752	808	165	70.0
4(a)	2.5	3	1	47.4	—	—	—	167	53.7
4(b)	2.5	3	2	49.8	—	—	—	162	75.2
5(a)	2.5	3	1	54.0	—	—	—	—	—
5(b)	2.5	3	2	—	—	—	—	—	—
6	—	1	2	—	615	3253	802	—	—

“—” denotes test not performed.

spacer plates, between aluminium foil-coated steel plates at a set plate temperature of 190°C.

Material characterization

Melt flow index (MFI) values were determined using a Davenport melt flow indexer, which gives an inverse measure of viscosity. For polypropylene measurements were taken at 230°C as per BS EN ISO 1133 : 200 to determine the effect of nanoclay on the viscosity of the polymer.

Differential scanning calorimetric (DSC) experiments were conducted using a Polymer Laboratories (PL-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 a sample weight of 1.0 mg for comparison. Thermogravimetric analysis was undertaken using a Polymer Laboratories TG 1000 instrument under flowing air (10 cm³/min) with a heating rate of 20°C/min. Approximately 6 mg samples were used in each case.

A Dynamic Analyzer Rheometer RDA II (Rheometrics) with parallel plate geometry and a plate diameter of 25 mm was used to characterize nanoclay dispersion in each compounded sample. Sample thickness was kept at 1 mm and to ensure the full coverage of viscoelastic region, linear rheological measurements were performed at a frequency range of 0.1 to 100%. Elastic moduli (G'), loss moduli (G'') and complex viscosities (η^*) were obtained at 240°C. The temperature control was accurate to within $\pm 1^\circ\text{C}$. Experiments were conducted under a nitrogen atmosphere in order to avoid oxidative degradation of the specimen.

X-ray diffraction (XRD) studies were carried out on both compounded polymer and selected filament samples using a Siemens D500 powder diffractometer (Cu-K α radiation) with a step size of 2θ , a step time of 1 s, and a diffracted angle range of 0–25° to characterize the dispersion of clay particles throughout the polymer matrix.

Optical microscopy was carried out using a Nikon Labophot 2 optical microscope with image capture by a JVC TK-C1381 color video camera.

Transmission electron microscopy was carried out using a Tecnai F30G2 FEG TEM running at HT 300 kV. Compounded polymers were cast into plaques, which were cut into thin films using an ultramicrotome.

Physical testing of filaments

Tensile testing was done on individual filaments using the Textech Statimat M Test with a gauge length of 100 mm, load cell 10 N, and test speed of

TABLE II
Physical Properties of Filaments and Derived Fabrics

Sample No.	Nanoclay, 20A (% <i>, w/w</i>)	Graft, Pb (% <i>, w/w</i>)	No. of extrusions	Linear density (tex)	Modulus (N/tex)	Tenacity (cN/tex)	Elongation-at-break (%)	Area density of fabrics (g/m ²)
PP								440
1(a)	0	0	1	5.4 ± 0.4	3.9 ± 0.5	32.6 ± 1.6	41 ± 20	410
1(b)	0	0	2	4.9 ± 0.3	4.1 ± 1.3	32.6 ± 2.5	101 ± 12	430
2(a)	2.5	0	1	4.1 ± 1.1	4.1 ± 1.7	31.6 ± 7.0	18 ± 6	390
2(b)	2.5	0	2	4.0 ± 0.8	5.6 ± 1.6	36.4 ± 8.0	20 ± 10	400
3(a)	2.5	1	1	3.4 ± 0.9	5.5 ± 0.7	33.1 ± .05	15 ± 5	410
3(b)	2.5	1	2	4.3 ± 0.9	3.7 ± 1.1	22.0 ± 6.0	15 ± 6	390
4(a)	2.5	3	1	4.8 ± 0.7	2.9 ± 1	19.7 ± 10.0	73 ± 70	490
4(b)	2.5	3	2	4.5 ± 0.1	3.4 ± 0.8	16.9 ± 7.0	96 ± 90	430
5(a)	2.5	3	1	4.9 ± 0.8	4.4 ± 0.9	28.4 ± 4.0	17 ± 2	410
5(b)	2.5	3	2	3.9 ± 0.4	5.2 ± 0.8	26.3 ± 8.2	14 ± 4	390

300 mm/min. Five different filaments from the same sample were tested and the results averaged.

Flammability testing of fabrics and cast films

Limiting oxygen index (LOI) values were determined on selected PP nanocomposite film samples with samples thicknesses of about 0.3–1.5 mm by 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 5660¹⁴ using an incident heat flux of 35 kW/m². Sample sizes for cast films and fabrics were 100 mm × 100 mm. For fabric samples, a set of wires were placed across the surface of the fabric to hold it flat in the sample holder¹⁵ and to prevent it curling while burning.

RESULTS AND DISCUSSION

Physical properties

Prior unpublished work gave an insight into the importance of the need for good dispersion of clay and other additives within the polymer matrix if further processing of compounded polymers into filaments is required. To produce a true nanocomposite, the clay platelets must be fully exfoliated within the polymer matrix or the polymer–clay system becomes a microcomposite. The Brabender mixer is ideal to assess morphology of small amounts of polymer but if further production into filaments is required then compounding in twin screw extruder is the only way to produce sufficient amounts of polymer. The samples described in Table I were compounded in the twin screw extruder with passage through once and then twice to assess the effect of additional mixing on the dispersion of the clay within the polymer matrix and also to observe the effect of varying amounts of the commercially available grafted poly-

propylene, Polybond 3200, on the levels of mixing and dispersion.

Melt flow index and rheology

It can be seen from Table I that the MFI of PP chips as they are received from the manufacturer have been included, whereas the control samples are derived from PP that has only passed through the twin screw extruder (samples 1(a) and (b)). The increase in MFI between the original PP chips and PP control passed through the twin screw extruder once is a measure of polymer degradation induced by the extra thermal cycle, where the residence time of the polymer in the extruder was ~ 12 min. The PP control (sample 1a) has MFI = 36, which rises to 40.2 g/600 s with the addition of 2.5% Cloisite 20A (sample 2a) corresponding to a decrease in the melt viscosity. The addition of the 1% grafted PP (sample 3a), causes a decrease in MFI with respect to sample 2a, which then increases on addition of 3% grafted PP (sample 4a). The results for the polymer that has gone through the twin screw extruder twice show that, for samples 2b and 3b, there is a reduction in MFI suggesting an increase in viscosity. This could be indicative of a nanocomposite structure and although there is no claim at this stage that fully exfoliated nanocomposites have been produced it does show that the extra mixing improves the dispersion of the nanoclay. The effect of addition of grafted PP is significant as seen from the values containing 3% grafted PP compared to those containing 1% grafted PP.

Rheological data determined for various PP films at 240°C is also given in Table I and complex viscosity versus frequency data is shown in Figure 1 for selected samples. The complex viscosity value at low frequency (0.1 rads/s) of PP films produced from PP chips have reduced significantly from 1000 Pas to 230 Pas for twice extruded PP control samples (sample 1b). This is in agreement with respective MFI values, which reflect the changes in reduction

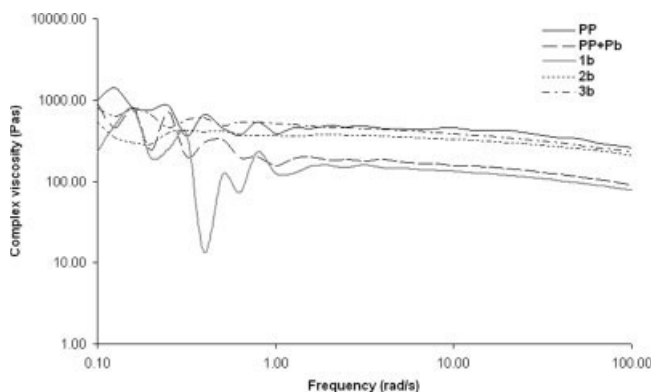


Figure 1 Complex viscosity of compounded polymers with and without clay.

in molecular weight as a result of substantial chain degradation during extrusion. However, the complex viscosity of PP increases significantly (802 Pas) on addition of maleic anhydride (sample 6) because of the formation of interchain anhydride crosslinks. Addition of 2.5% w/w of nanoclay to PP (sample 2b) also slightly increases complex viscosity (545 Pas, see Fig. 1) of the formulation in the low frequency region. This increase in the complex viscosity of sample 2b is not comparable to the large increase in viscosity values observed in PP-clay nanocomposites by Solomon et al,¹⁶ however. Moreover, the complex viscosity curves for samples 2b and 3b in Figure 1 do not show noticeable shear thinning effects thus indicating little or no intercalation of polymer chains with clay platelets.¹⁷ Sample 3b has comparable complex viscosity value (808 Pas) with sample 6 (containing Polybond and extruded twice) at 0.1 rads/s, but the complex viscosity values over entire range of frequency tested for sample 3b are higher than for sample 6. However, while these slight increases in complex viscosity are due to addition of nanoclay, they are not sufficient to indicate significant nanodispersion. Furthermore, the storage (G') and loss (G'') moduli at 10 rads for various PP films in Table I show that $G'' \gg G'$, suggesting that the viscoelastic behavior of all the PP films is dominated by viscous liquid behaviour. G' and G'' when plotted (not shown here) as functions of frequency, do not show a characteristic cross-over frequency where $G' \gg G''$. This suggests that the viscoelastic properties of all the PP samples tested in this study are dominated by viscous liquid behavior with no evidence of pseudo-solid-like behavior in the samples containing nanoclay. This, in addition to the shear-thinning criteria proposed by Waganer and Reisinger,¹⁷ reinforces the fact that the nanoclay is not fully nanodispersed in the PP matrices in samples prepared here. This view is corroborated by the recent work of Százdi et al.⁴

Structural characterization by XRD and optical and transmission electron microscopies

Compounded polymers and tapes

The XRD curves in Figure 2 indicate the presence of clay, shown by diffraction peaks at $2\theta \cong 4^\circ$ in single-extruded samples of compounded polymer composites containing 2.5% Cloisite 20A clay. These show no evidence of peak shifts, even for the samples containing the grafted PP, Polybond as would be expected if intercalation was significant. Furthermore, there is no evidence of diminution in peak intensity as would be expected if exfoliation was present. This evidence taken with the complex viscosity curves, shows that there is no evidence of significant nanocomposite structure formation present in any of the samples.

Observation of the optical micrographs of tapes in Figure 3 shows the differences in dispersion of the clay with addition of the grafted polypropylene, Polybond 3200 when compared with the image containing clay and no graft. Figure 3(a) shows the typical spherulitic structure expected in slowly cooled polypropylene polymer. The presence of clay particles is clearly seen in Figure 3(b) for sample 2b plus a more coarse spherulitic structure probably promoted by particle surfaces. The addition of compatibiliser [see Fig. 3(c), sample 3b] suggests a reduction in size of both clay particle sizes and spherulite diameters and these effects are compatibilizer concentration-dependent as shown in Figure 3(d). This higher dispersing effect at the 3% level of grafted PP does not seem to be entirely backed up by the rheological data, however.

The transmission electron micrographs of different twice-compounded samples in Figure 4 show the effect of graft and processing on clay dispersion. Figure 4(a) for the control polypropylene passed through the twin screw extruder twice (sample 1b) indicates absence of any clear structure apart from a granular character and possibly related to spherulitic

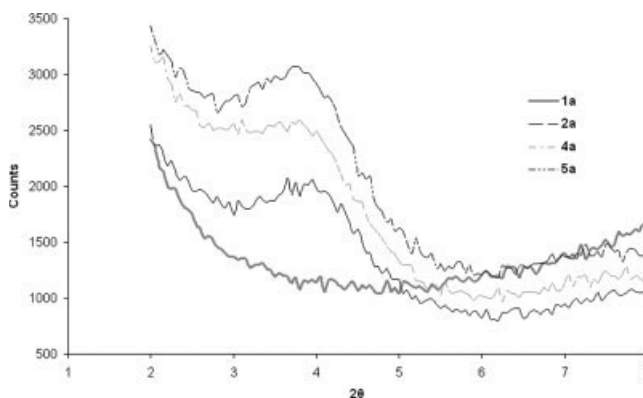


Figure 2 XRD curves showing the clay peak of compounded polymers.

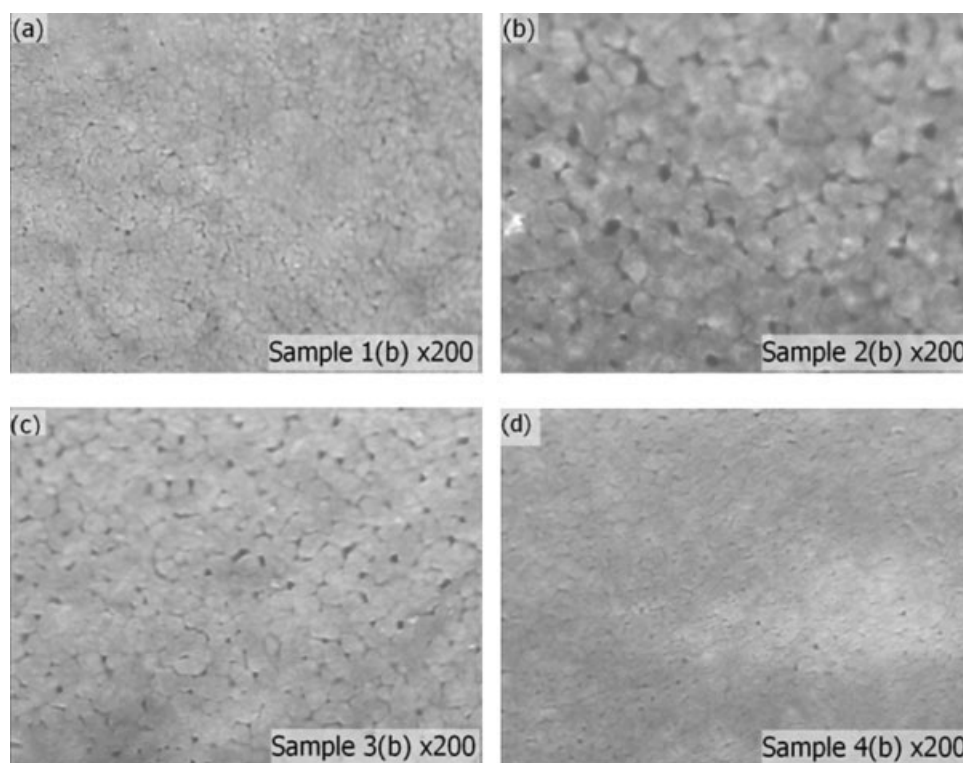


Figure 3 Optical micrographs of tape samples showing effect of Polybond on clay dispersion.

structures at the polycrystalline level. Addition of 1% compatibilizer with 2.5% clay in sample 3b has caused microdispersion of the clay particles [Fig. 4(b)]. However, by increasing level of compatibilizer to 3%, the dispersion at the microlevel has improved as observed by absence of clay layer aggregates in Figure 4(c). For sample where compatibilizer and clay have been previously masterbatched prior to dilution and blending (sample 5b), the dispersion is improved and heterogeneity reduced with respect to sample 4b. Although structures observed here are not obviously intercalated or exfoliated microcomposites, dispersion is at nanolevel, i.e., particle size $\ll 1 \mu\text{m}$. In samples 3b, 4b, and 5b, the clay particle widths appear to be $< 0.1 \mu\text{m}$ with lengths up to $0.5 \mu\text{m}$.

Careful observation of enlarged sections of the more highly resolved TEM micrographs in Figures 4(c) and 4(d), there is some indication that platelets are indeed starting to delaminate and separate thereby indicating that exfoliation is taking place. Furthermore, the overall absence of microdispersed particles in these same figures is evidence that delamination of micro- into nano-aggregates of clay is occurring.

In principle, nanodispersion means:

1. distribution of particles such that particle dimensions are $\ll 1 \mu\text{m}$,
2. intercalation of individual nanodispersed particles, and

3. ultimate exfoliated lamellae.

However, in most publications, the terms nanodispersion and nanocomposite are taken to mean conditions fulfilling (2) and (3) above, it is evident that condition (1) is feasible and is clearly observed here with less distinct evidence of exfoliation.

Filaments

In terms of observing the effect of additives on finer physical levels of structure, Figure 5(a) presents the complete XRD curves for selected fibers, including the control polypropylene (sample 1b) to show the effect of adding clay (sample 2b), clay and compatibilizer (samples 4a and 4b), masterbatching (samples 5a and 5b), and two compounding passes (samples 4b and 5b). Here, the presence of polypropylene crystalline diffraction is observed with the relatively less intense clay-related diffraction for $2\theta < 5^\circ$. Expansion of this latter area is shown in Figure 5(b) in which, the agreement with XRD curves in Figure 2 for the compounded precursor polymers, clay diffraction peaks are seen at $2\theta \cong 4^\circ$. Even for sample 5b, which has the most intense shear history coupled with higher compatibilizer content, there appears to be no clear evidence of either intercalation or exfoliation although the tensile results discussed later may suggest otherwise.

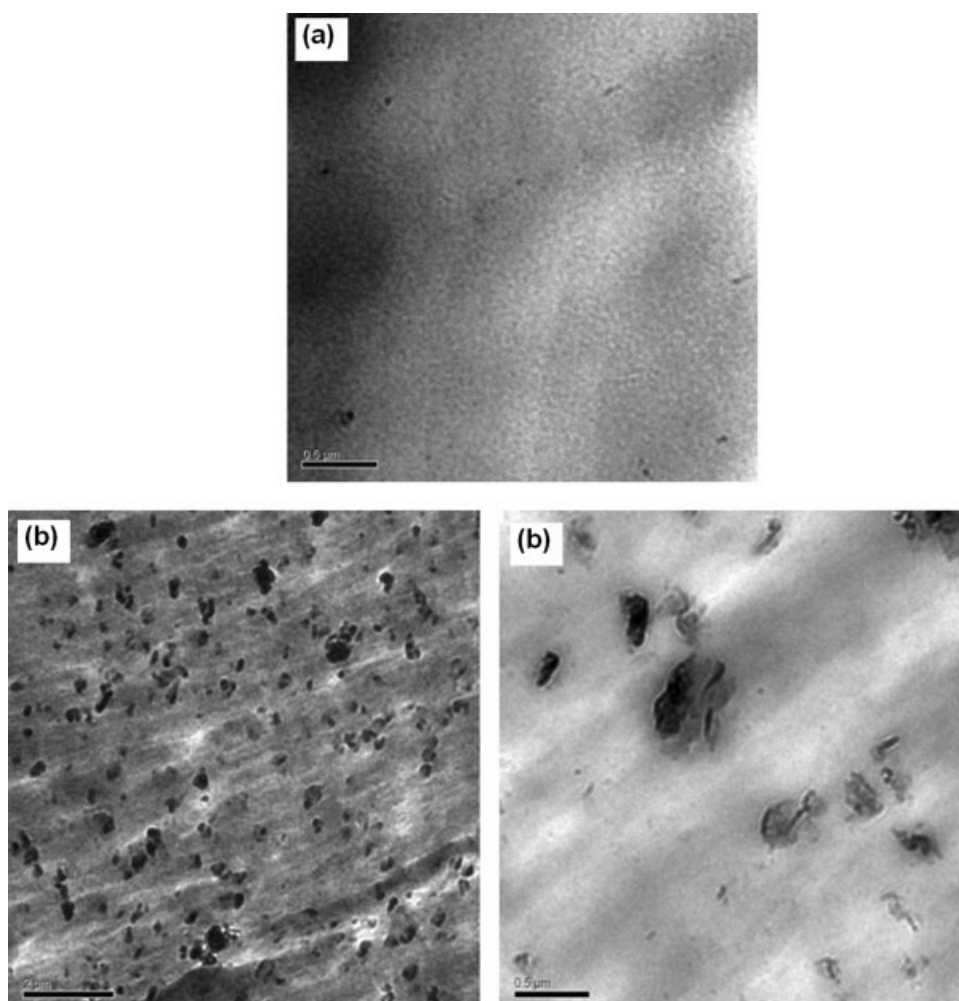


Figure 4 TEM of (a) Sample 1b, twice-compounded polypropylene free of additives showing evidence of spherulitic structure; (b) Sample 3b, twice-compounded polypropylene with 1% compatibilizer and 2.5% Cloisite 20A clay; (c) Sample 4b, twice-compounded polypropylene containing 3% compatibilizer and 2.5% Cloisite 20A clay with enlarged section of higher resolution micrograph; (d) Sample 5b, twice-compounded polypropylene containing 3% compatibilizer and 2.5% Cloisite 20A clay (sample 5(b)) with enlarged sections of the higher resolution micrograph.

Extrusion and physical testing of filaments

Generally, the compounded polymers extruded into filaments well with a screw speed of 10 rpm and first rollers set at 4 m min^{-1} . Samples 4a, 4b, 5a, and 5b suffered some filament breakage during winding up and drawing. It was necessary to reduce the draw ratio from the default of 6 : 1 to 5 : 1 for filaments 4a and 4b. Samples 5a and 5b showed less filament breakage and so draw ratios of 6 : 1 continued to be used. To observe the effect of the compatibilizer on the processing conditions, some PP was compounded with just compatibilizer (sample 6). Without the clay present, the compounded polymer proved impossible to melt extrude into filaments. Furthermore, as the levels of compatibilizer increase from 1 to 3% in the clay-containing samples, the processability of the polymer generally reduced. Thus, the optimum level of the compatibilizer would

appear to be very low at about 1% level and clay needed in the compounded mix to make filament extrusion feasible.

As discussed earlier, the nominal draw ratio was 6 : 1, although reduced slightly in some cases to accommodate the effects of different additives/compounding histories. In all cases, therefore, draw ratio values were close to the maximum achievable and so it is entirely in order, from a fiber technological position, to compare the physical properties. The variation in elongations-at-break is a consequence of the different abilities of each filament internal structure to orientate during the application of a tensile stress. The drawing occurs at a much higher elongation rate than tensile testing and so residual levels of orientation may only be realized during the latter more gently/slower and not former more rapid conditions.

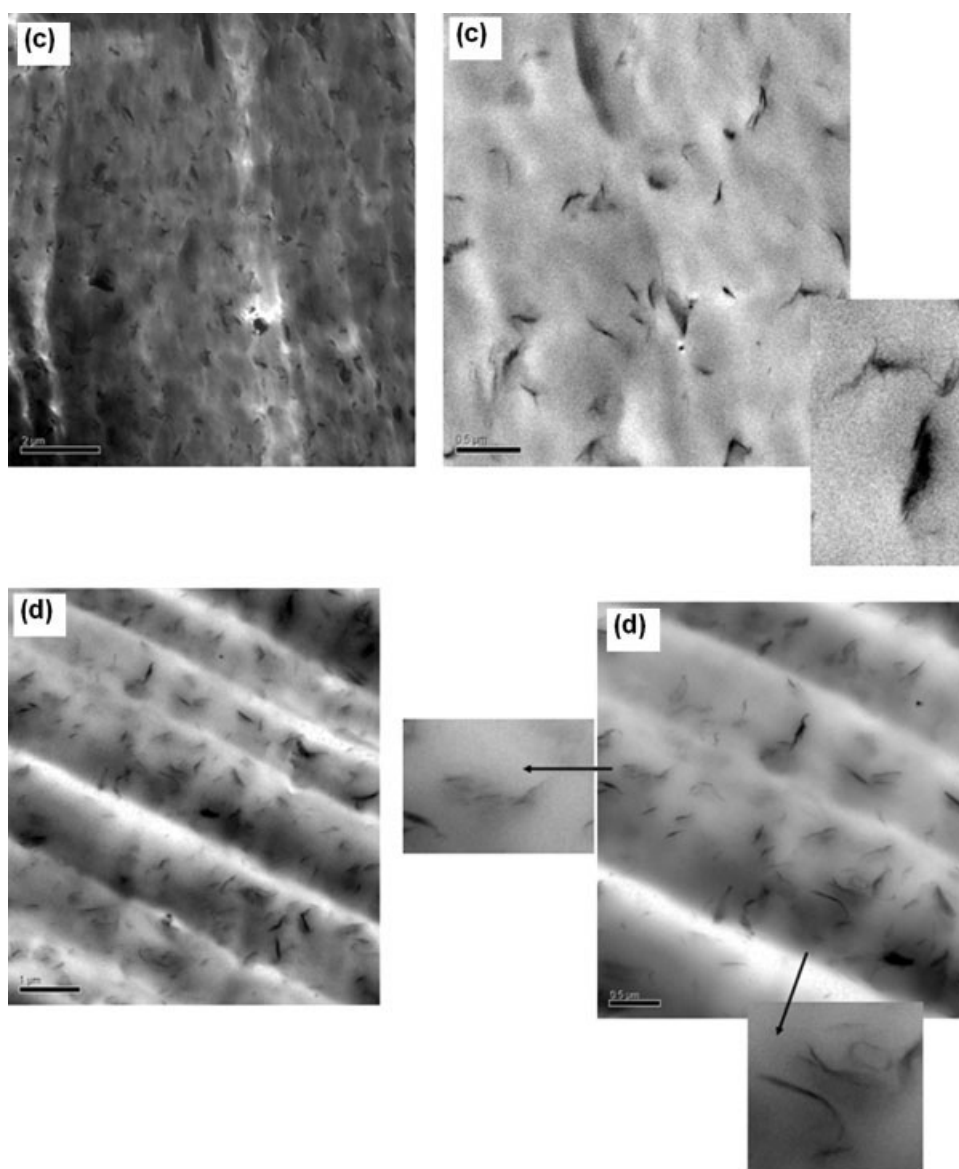


Figure 4 (Continued from the previous page)

Examination of results of physical testing of the filaments in Table II reveals that there is considerable variation in the filament properties within each sample. The magnitude of this error is suggested by the unexpected slight decreases in linear density recorded with addition of clay at constant processing conditions (compare samples 1, 2, and 3). Furthermore, it would have been expected that the linear density of samples 4a and 4b would have been higher than for samples 5a and 5b, which have the same components present but have lower draw ratios.

From the literature,¹² inclusion of nanodispersed clays in fibers tends to increase their moduli more than respective tenacities and so any real increases in moduli in this work could be indicative of nanocomposite formation. Within error, the increasing the

number of compounding cycles when no additives are present yields no change in modulus (samples 1a and 2a); however, when 2.5% clay is added, the effect of compounding twice is significant in that the modulus of sample 2b is significantly higher than samples 1a and 2a, which are effectively the same. The addition of compatibilizer at 1% for singly compounded polymer (sample 3a) appears to show an increase in modulus relative to sample 2a, but the effect of a second compounding cycle causes a significant modulus reduction in sample 3b. This suggests that as the compatibilizer has greater time to crosslink during compounding, so the modulus increase promoted by the clay presence is offset by crosslink formation. Higher levels of compatibilizer (3%, samples 4a and 4b) promote higher levels of crosslinking with significant decreases in filament

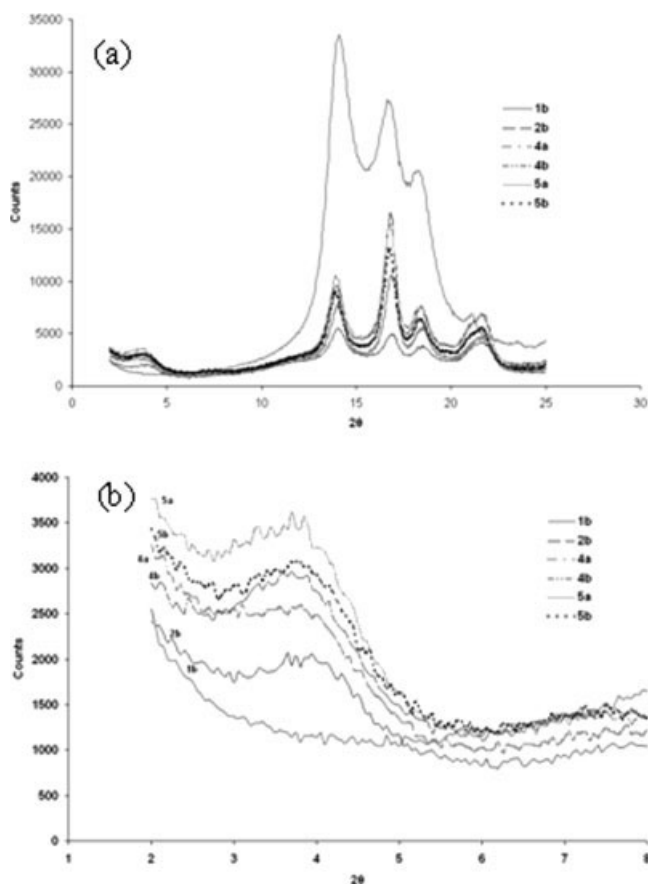


Figure 5 XRD curves for selected filaments.

modulus. However, if both compatibilizer and clay are previously masterbatched prior to dilution and blending (samples 5a and 5b), modulus values are comparable with those for compatibilizer-free, twice-compounded sample 2b. These increases suggest higher levels of homogenation and dispersion of the clay present with possible nanocomposite formation.

Tenacity values appear to be far less sensitive than for initial modulus with samples 1a, 1b, 2a, and 2b essentially being the same within error. That sample 3b has a much lower tenacity suggests that crosslinking is the cause and this is corroborated by the further reduction observed for sample 4b. However, samples 5a and 5b have higher tenacities than 4a and 4b inferring once again that masterbatching has improved dispersion of all additives within the filaments.

Breaking elongations show considerable differences as well as higher errors typical of experimentally-produced filaments. Of note is the general reduction in values when clay is added, and the higher values when clay and 3% compatibilizer are present (samples 4a and 4b), although the masterbatched equivalents (samples 5a and 5b) show the opposite. If full crosslinking by the compatibilizer only occurs during masterbatching along with improved clay dispersion, then filaments would be

expected to show much lower extensibilities, which in fact they do.

Thermal and flammability properties of fabrics and films

Differential scanning calorimetry of films

Table I lists the fusion minima temperature or the melting temperatures and heat of melting peaks. It can be seen that additions of clay and graft have minimal effects on the melting point of the polypropylene.

TGA results listed in Table III show that the temperature at the onset of decomposition is higher in the PP sample than in the samples 2a, 3a, and 4a. This is because these samples have gone through two extra thermal cycles, which cause degradation of the polymer. Sample containing only clay (sample 2a) has an onset temperature of 236°C, which is slightly lowered by the addition of the maleated polypropylene graft. However, the rate of decomposition of the sample containing clay (sample 2a) is much slower than PP, as indicated by higher D_{20} , D_{50} , and D_{80} values (representing temperatures at which 20, 50, and 80% mass loss occurs) for the former. With compatibilizer, these temperatures are higher and increase with increasing compatibilizer level (samples 3a and 4a). The compatibilizer itself does not add to the thermal stability of the polymer, but since it helps in better dispersion of the clay, the effect will be positive. Char residue left at the end of the experiment (obtained by deducting total mass loss value from 100) indicates residual silica content of the formulation.

Flammability of knitted fabrics

Cone calorimetry. Previously reported work has shown that when sample masses are below the 5 g level typically observed when fabric samples are being studied, errors in cone results are rarely lower than $\pm 10\%$.¹⁵ As a consequence in the data shown in Tables IV and V there are significant variations in each set of replicate samples. From the results in Table IV for fabric samples, it can be seen that there is no significant effect on time-to-ignition (TTI) with addition of nanoclay although a slight increase is

TABLE III
TGA-Derived Decomposition Temperatures and Mass Losses

Sample	D_0 (°C)	D_{20} (°C)	D_{50} (°C)	D_{80} (°C)	Total mass loss (%)
PP	245	298	325	345	99.7
2a	236	311	359	386	97.2
3a	231	316	367	393	97.3
4a	233	326	376	399	97.1

D_0 , onset decomposition; D_{20} , 20% mass loss; D_{50} , 50% mass loss; D_{80} , 80% mass loss.

TABLE IV
Cone Results of Fabrics at 35 kW/m² Incident Heat Flux

Sample No.	Nanoclay, 20A (% w/w)	Graft, Pb (% w/w)	No. of extrusions	Mass (g)	TTI (s)	PHRR (kW/m ²)	THR (MJ/m ²)	Mass residue (%)	Smoke (m ² /m ²)
PP				4.4 ± 0.2	22 ± 4	499 ± 100	15.3 ± 2.0	18.0 ± 2.0	336 ± 70
1(a)	0	0	1	4.1 ± 0.2	20 ± 4	475 ± 100	16.5 ± 2.0	13.7 ± 1.0	405 ± 25
1(b)	0	0	2	4.3 ± 0.1	25 ± 1	525 ± 40	16.8 ± 2.1	14.5 ± 5.1	405 ± 20
2(a)	2.5	0	1	3.9 ± 0.3	18 ± 2	477 ± 90	16.0 ± 1.1	4.8 ± 1.1	349 ± 6
2(b)	2.5	0	2	4.0 ± 0.1	25 ± 2	477 ± 105	17.8 ± 1.0	9.6 ± 4.0	473 ± 30
3(a)	2.5	1	1	4.1 ± 0.1	18 ± 2	492 ± 90	17.8 ± 0.4	7.7 ± 3.1	450 ± 20
3(b) ^a	2.5	1	2	3.9	18	531	17.3	5.1	400
4(a)	2.5	3	1	4.9 ± 0.1	24 ± 3	600 ± 16	21.4 ± 0.2	3.1 ± 4.0	460 ± 35
4(b)	2.5	3	2	4.3 ± 0.2	31 ± 6	420 ± 90	18.1 ± 1.6	5.0 ± 2.5	497 ± 12
5(a)	2.5	3	1	4.1 ± 0.8	22 ± 6	417 ± 65	19.1 ± 0.5	4.6 ± 2.0	532 ± 30
5(b) ^a	2.5	3	2	3.9	34	394	17.4	4.2	369

^a Because of limited sample size, only 1 specimen tested.

recorded for samples 4 and 5 containing 3% grafted PP. The peak heat release rate (PHRR) shows an increase in samples with 1% grafted PP (samples 3a and b) plus a further increase when the grafted PP levels are increased to 3% (samples 4a and b), but PHRR values decrease in samples 5a and 5b, indicating better dispersion when clay and compatibilizing grafted-PP are added as part of a masterbatch. However, given our recent analysis of the effect of sample thickness on peak heat release rates, any reductions in PHRR with nanoclays observed in thick samples may not be evident in the thin fabrics used in these experiments.^{12,18}

Since most of the work in literature is on plaques, which are physically and thermally thick, we also have studied the cone calorimetry of cast films similar in thickness to the fabrics tested above. As seen for the fabric samples, some of these results indicate too much variation and therefore are not reproducible. Mass loss and ultimate residual reading in particular are associated with errors $> \pm 50\%$ and this is most likely due to error again associated with low sample masses used. Observation of the samples as they burned showed considerable bubbling and flowing of the polymer during burning which caused anomalies in the balance recording weight loss. These phenomena should be less in thermally thick samples and were not noticed to the same

extent in knitted fabric samples which, because of their construction, held together better while burning. Images were taken of the films after burning and those shown in Figure 6, suggest that the addition of clay does promote char formation.

Limiting oxygen index. Because of the instability of knitted fabrics and the limited quantities available from each compounded polymer sample, only extruded tapes were submitted to limiting oxygen testing. Values for tape samples from twice-compounded composites are presented in Table VI. Within error, all samples yield identical values indicating that the presence of clay has no effect on the flammability of polypropylene. These results are compatible with those observed in other polymer-clay combinations,¹² which suggest that presence of dispersed clays alone do not impart flame retardancy although it may reduce burning rates as observed in cone calorimetry.

CONCLUSIONS

The chosen nanoclay in spite of its nonpolar functionality has proved difficult to disperse in the extremely nonpolar PP. Dispersion can be improved by compounding polymer-clay samples and by adding maleic anhydride-grafted polypropylene. While

TABLE V
Cone Results of Cast Films at 35 kW/m² Incident Heat Flux

Sample No.	Nanoclay 20A (% w/w)	Graft, Pb (% w/w)	No. of extrusions	Mass (g)	TTI (s)	PHRR (kW/m ²)	THR (MJ/m ²)	Mass residue (%)	Smoke (m ² /m ²)
1(a)	0	0	1	3.3 ± 0.3	45 ± 5	220 ± 80	6.2 ± 2.0	15.8 ± 5.0	186 ± 30
1(a)	0	0	2	3.5 ± 0.2	23 ± 3	364 ± 40	11.3 ± 1.1	22.7 ± 3.0	211 ± 25
2(a)	2.5	0	1	3.5 ± 0.3	33 ± 3	494 ± 100	12.9 ± 1.0	6.7 ± 3.0	263 ± 40
2(b)	2.5	0	2	3.6 ± 0.2	35 ± 3	366 ± 100	10.6 ± 1.1	1.3 ± 2.0	280 ± 40
3(a)	2.5	1	1	3.2 ± 0.1	30 ± 5	346 ± 80	9.0 ± 3.2	2.4 ± 2.1	237 ± 30
3(b)	2.5	1	2	3.5 ± 0.4	29 ± 2	485 ± 50	13.2 ± 2.0	7.6 ± 3.0	239 ± 30
4(a)	2.5	3	1	3.5 ± 0.2	29 ± 6	578 ± 30	12.5 ± 1.1	11.8 ± 2.0	231 ± 30
4(b)	2.5	3	2	3.0 ± 0.2	29 ± 4	579 ± 20	10.7 ± 1.2	2.5 ± 0.5	254 ± 25

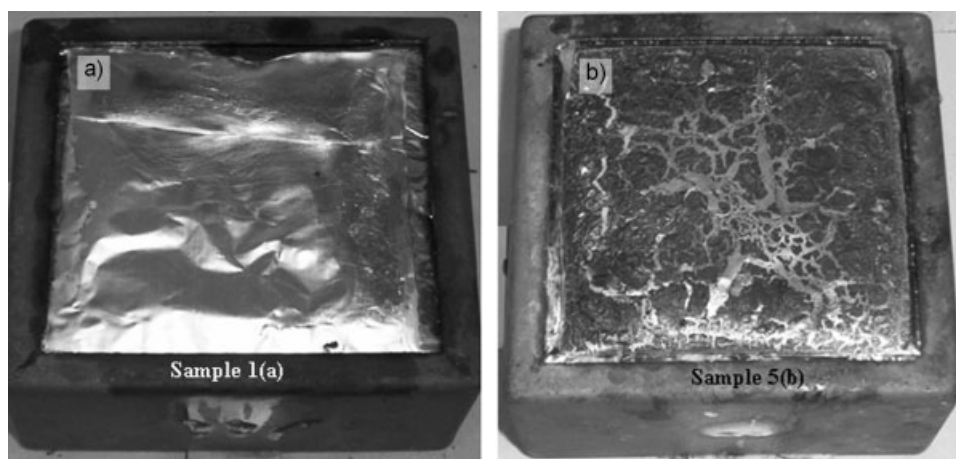


Figure 6 Images of films taken after burning in the cone calorimeter to show evidence of char formation in samples containing clay.

this latter effect is concentration dependent, in order to keep the rheological properties necessary for extrusion into fiber, lower levels are preferred. Whether or not the dispersion of the clay particles has occurred at the nanolevel is not clear since while optical microscopic evidence shows an improvement in dispersion at the microlevel, XRD does not provide evidence of intercalation or exfoliation. TEM results show that the general dispersion is at the nanolevel in samples containing both clay and compatibilizer with some evidence of exfoliation. LOI values are not changed following addition of clay, however, the presence of a clay changes the burning behavior and evidence of char residue formation has been presented during cone calorimetry.

In conclusion, our study shows that while true nanocomposite structures could not be attained, nanodispersion was achieved and both micro- and nano-dispersed polymers were processable and could be extruded into filaments, which were sufficiently strong to be knitted into fabrics. This work has, therefore, shed light on factors critical in optimizing the filament extrusion performance of a polymer like polypropylene which has a high incompatibility with functionalized clays. In the second publication of this series, studies of the compatibility between different organically modified nanoclays and compatibilizers (as grafts) will be reported with an overall aim of producing nanocomposite, fiber-forming structures.

TABLE VI
LOI Results for Extruded Tapes

Sample No.	LOI (%)
1(b)	19.8–20.0
2(b)	19.6–19.8
3(b)	19.8–20.0
4(b)	19.9–20.0
5(b)	19.9–20.0

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