The Effect of Maleic Anhydride Grafting Efficiency on the Flexural Properties of Polyethylene Composites

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ABSTRACT: Many authors have reported on the property enhancements possible by compounding high density polyethylene (HDPE) with fillers to produce composites. It is accepted that polyethylene combined with materials such as nanoclay or wood flour will not yield favorable properties unless a compatibilizing material is used to form a link. In this work, compatibilized HDPE was produced by grafting maleic anhydride (MA) to its backbone in a twin screw extruder using a peroxide initiated reactive process. Fourier transform infrared spectroscopy (FTIR) was used to examine the effects of varying peroxide and MA levels on the grafting percentage and it was found that a high percentage could be achieved. The gel content of each HDPE-*g*-MA batch was determined and twin bore rheometry analysis was carried out to examine the effects of crosslinking and MA grafting on the melt viscosity. These HDPE-*g*-MA compatibilizers were subsequently compounded with nanoclay and wood flour to produce composites. The composite materials were tested using a three point bending apparatus to determine the flexural modulus and strength and were shown to have favorable mechanical properties when compared with composites containing no compatibilizer. X-ray diffraction (XRD) was used to examine the effects of grafted MA content on the intercalation and exfoliation levels of nanoclay composites. The results from XRD scans showed that increased intercalation in polymer nanoclay composites was achieved by increasing the grafted MA content. This was confirmed using a scanning electron microscope, where images produced showed increased levels of dispersion and reductions in nanoclay agglomerates. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4799–4808, 2012

Key words: compatibilization; composites; compounding; extrusion; functionalization of polymers

INTRODUCTION

The production of new polymer materials with enhanced performance and reduced costs has been investigated heavily in recent years with much of this work focusing on the modification of existing polymers. Of these processes, the modification of polyethylene with polar monomers by reactive extrusion has received much attention in the literature.[1] Single screw extruders were first used in studies of polymer chain breaking and grafting of monomers to polyolefins[2]; however, most current efforts concentrate on the use of twin screw extruders.[3] This reactive extrusion process consists of a free-radical initiator, a monomer and polyethylene combined together as they are conveyed along a heated extruder barrel.[3] The monomers which are typically chosen for this process are maleic anhydride (MA), glycidyl methacrylate, and acrylic acid[4,5] while a wide range of peroxides can be chosen as the free-radical initiator. This process has been investigated previously[4,6,7] and it is widely accepted that at the high temperatures used during extrusion, free-radicals generated by the initiator first abstract hydrogen from the polyethylene backbone to form macroradicals, after which these macroradicals undergo grafting with the monomer or crosslinking with themselves.[8] Many of the variables, which can increase grafting yield such as initiator concentration melt temperature and pressure can also promote side reactions[9]; therefore, the grafting yield cannot be increased by simply increasing the initiator concentration and producing more radical sites without an increase in unwanted side reactions.[10–12]

Functionalized polyethylenes are prepared to increase the compatibility between polyolefins and polyamides, polyesters and various fillers.[13,14] Wood flour and nanoclays are two fillers that can be used to improve the properties of high density polyethylene

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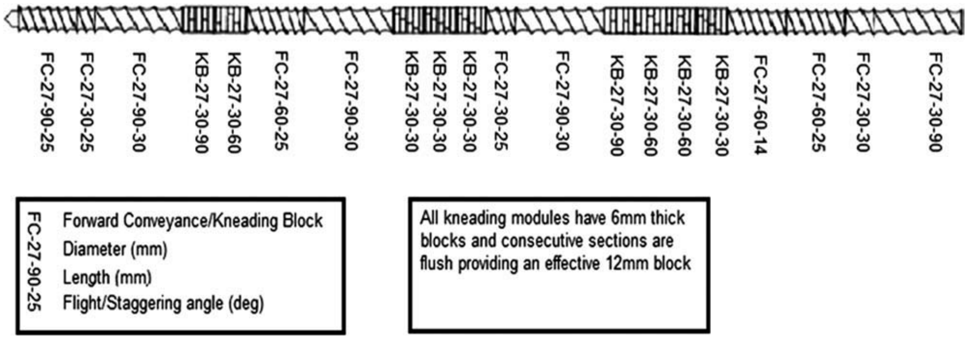

Figure 1 Screw geometry for Leistritz 27 mm labscale twin screw extruder.

(HDPE). It is widely accepted both nanocomposites and wood polymer composites prepared with HDPE perform better with the incorporation of a compatibilizing material.[15–18] Adhikary et al. reported a 5.6, 4.9, and 0.88 GPa increase in tensile strength, flexural strength, and flexural modulus, respectively, when 3 wt % compatibilizer was added to a wood polymer composite in comparison with a similar composite with no compatibilizer. Compatibilized nanocomposites of PE and organoclay, have previously demonstrated reductions in the peak of the heat release rate of 30–40%,[19,20] attributed to increased dispersion of nanoclay platelets throughout the polymer matrix. To achieve the improvements possible in polymer nanoclay composites, the silicate layers need to be intercalated and/or exfoliated and sufficient interaction between polymer and clay is necessary for this to occur. Since, polyethylene does not include any polar groups in its backbone, it is not thought that homogeneous dispersion of clay layers in PE would be realized without the use of compatibilizer.[21] In this study, the effect of grafted MA content on the interfacial reactions between polyethylene and wood flour, and also on the interaction between polyethylene and nanoclay is examined. The possibility of producing a grafted HDPE, which is optimized to suit the particular grade of HDPE being used for nanoclay or wood flour composites means that even greater improvements in the mechanical properties of these composites may be achievable.

EXPERIMENTAL

Materials

MA (95% purity), stearamide, Aldrich 329,541 dicumyl peroxide (DCP) and Luperox A75 benzoyl peroxide (BP) were obtained from Sigma-Aldrich in powder form and were used as received. The chosen peroxides have 10 h half-lives at 117.1 and 72.9°C, respectively. Struktol TPW 104 lubricant was procured from Velox GmBh in flake form and was used as received. Grades HMA 016 (MFI 20, density 0.956 g/cm^3), 018 (MFI 30, density 0.954g/cm^3), and 025 (MFI 8, density 0.964 g/cm^3) HDPE were supplied by ExxonMobil and SI508 HDPE (MFI 8, density 0.950 g/cm^3) was supplied by Total Petrochemicals. Medium density polyethylene was provided by GEM Plastics. LLDPE 6101 (MFI 20, density 0.924g/cm^3) was supplied by ExxonMobil and was powdered prior to use. Fusabond M603 (MFI 25) was supplied by DuPont. The nanoclay used in this work was Nanomer I44.P, organically modified with dimethyl dialkyl (C14-18) ammonium, supplied by Nanocor. Wood flour (Fibertron 40) with a mesh size of 40 was supplied by WTL International.

Melt processing

Extrusion

The extrusion of all materials in this work was carried out on a micro 27 labscale twin screw extruder (Leistritz) with a 27 mm screw diameter and a 38/1 length to diameter ratio. The screw geometry used is shown in Figure 1. Tables I and II outline the composition of all grafted blends and their composites. Processing conditions for the grafting process and composite processing are outlined in Table III.

Reactive extrusion processing. In this study, MA, a choice of initiators (BP or DCP) and a lubricant were mixed and ground to a fine-powder using a pestle and mortar. This powder was hand mixed into a powdered LLDPE where appropriate and the mixture was transferred to a K-Tron feeder fitted with screws of suitable geometry and dimensions. A second K-Tron feeder was filled with the appropriate grade of HDPE/MDPE and the feed rates (kg/h) of each was set to give the correct ratio of additives to polymer. These materials were fed into the twin screw extruder and 1 kg of the resultant compound was collected for compounding with fillers and a further 500 g was collected for characterization.

Composite extrusion. Wood polymer composites were produced by hand mixing 3 wt % of the appropriate

TABLE I
Composition of HDPE-*g*-MA Blends

	HDPE (%)	HDPE Grade	MFI	LLDPE (%)	MA (%)	DCP (%)	BP (%)	Lubricant (%)	Lubricant Type	Throughput (kg/h)
Batch 1	98.745	HMA O16	20	0	1	0.005	–	–	–	10
Batch 2	98.747	HMA O18	30	0	1	0.003	–	0.25	Stearamide	5
Batch 3	97.494	MDPE	4	0	2	0.006	–	0.5	Struktol	10
Batch 4	92.994	HMA O25	8	5	2	0.006	–	–	–	5
Batch 5	93.99	SI508	8	5	1	–	0.005	–	–	10
Batch 6	93.39	SI508	8	5	1.6	–	0.01	–	–	10

compatibilizer with 37 wt % of SI508 HDPE: this mixture was placed in a K-Tron feeder. Another K-Tron feeder was filled with 60 wt % wood flour and the correct feed ratios were set. These materials were compounded and the resultant composite material was granulated and collected for compression molding. HDPE/I44.P nanoclay composites were prepared using a masterbatch/letdown system. The previously prepared compatibilizers were compounded with nanoclay at a ratio of 50 : 50 to produce a masterbatch containing equal parts of nanoclay and compatibilizer. This masterbatch was then mixed at a ratio of 20 : 80 with SI508 HDPE to produce a let-down material containing 10 wt % nanoclay and 10 wt % compatibilizer.

Blow molding

The let-down material containing 10 wt % nanoclay was hand mixed with HDPE at a 50 : 50 ratio and the resultant mixture was blow molded to produce nanocomposite bottles containing 5 wt % nanoclay. Blow molding was carried out using a Battenfeld Fischer VK1- 1.02 extrusion blow molding machine to produce 1 L bottles with an average wall thickness of 1 mm. Processing conditions for the blow molding are listed in Table III.

Compression molding

Wood polymer composite material collected from the composite extrusion process was molded using a Bucher Guyer 55-167 compression molder to produce plaques of 150× 150 mm^2. Compression molding conditions are outlined in Table III.

Characterization of Hdpe-*g*-MA

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) testing was conducted using a Perkin–Elmer System 2000 FTIR microscope. FTIR was carried out using the transmission mode of the FTIR with a 100 scan per sample cycle and a resolution of 8 cm^{-1}. The sample was scanned from 650 to 4000 cm^{-1}. Samples for FTIR were first refluxed in xylene at 145°C for 4 h. After this time acetone was added and the precipitate filtered and washed with acetone. The resultant material was then dried at 50°C overnight. This process was carried out to remove any unbound MA. This residue was then melt pressed into films suitable for FTIR analysis.

Gel content

A 500 mL round bottom flask, was weighed and this weight was recorded. Two hundred milliliter of xylene

TABLE II
Composition of Wood Polymer and Polymer Nanoclay Composites

	SI508 (wt %)	Fibretron 40 (wt %)	Compatibilizer (wt %)	I44.P Nanoclay (wt %)
WPC 1	37	60	Batch 1 (3%)	–
WPC 2	37	60	Batch 2 (3%)	–
WPC 3	37	60	Batch 3 (3%)	–
WPC 4	37	60	Batch 4 (3%)	–
WPC 5	37	60	Batch 5 (3%)	–
WPC 6	37	60	Batch 6 (3%)	–
WPC 7	37	60	Fusabond (3%)	–
WPC 8	40	60	–	–
HDPE/I44.P 1	90	–	Batch 1 (5%)	5
HDPE/I44.P 2	90	–	Batch 2 (5%)	5
HDPE/I44.P 3	90	–	Batch 3 (5%)	5
HDPE/I44.P 4	90	–	Batch 4 (5%)	5
HDPE/I44.P 5	90	–	Batch 5 (5%)	5
HDPE/I44.P 6	90	–	Batch 6 (5%)	5
HDPE/I44.P 7	90	–	Fusabond (5)	5
HDPE/I44.P 8	95	–	–	5

TABLE III
Processing Conditions

Process	Temp (°C)									Screw speed (RPM)	Throughput (kg/h)
	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Zone 8	Die		
Reactive extrusion	170	175	180	190	200	210	210	200	200	200	See Table 1
Nanoclay composite extrusion	170	175	180	185	190	195	200	200	200	200	10
Wood polymer composite extrusion	160	160	160	160	170	170	175	200	200	120	5
	Zone 1	Zone 2	Zone 3	Zone 4	Head 1	Head 2	Head 3	Head 4	Die		
Blow molding	170	170	170	170	170	170	170	170	170	30	–
	Mould temp (°C)		Pressure (ton)		Time (min)						
Compression molding	180		30		5						

and 2 g of HDPE-*g*-MA material were added to the flask. This was refluxed at 145°C for 6 h. After refluxing, the contents of the flask were filtered to remove the xylene and the flask was again weighed. As HDPE dissolves in xylene but crosslinked HDPE does not, the additional weight of the flask after the xylene was removed, recorded, and measured as undissolved material or crosslinked polyethylene. The procedure followed was a slightly modified from the work previously performed by Ghaemy and Roohina.[13]

Twin bore rheometry

Twin bore shear viscosity testing was carried out on granules of HDPE-*g*-MA using a Rosand RH7 twin bore capillary rheometer at a 190°C from 100–1000 s^{-1}.

Characterization of composites

Three point bending test

Three point bending tests were carried out on a Llyod LRX Tensometer at a rate of 2 mm/min in accordance with ASTM standard D790-10. Samples of wood polymer composites were cut from plaques produced from compression molding while polymer nanoclay composites were tested by cutting samples of 1 mm thickness from blow molded bottles.

X-ray diffraction

X-ray diffraction (XRD) was performed on a Phillips PW1720 power X-ray diffractometer. Scans were carried out on samples of HDPE/nanoclay composites cut from the wall of blow molded bottles. All measurements were run from 2° to 10° (2-Theta) at a step size of 0.02° and 2.5 s/step.

Scanning electron microscopy

SEM was also used to more closely observe the dispersion of clay in the nanocomposites. Cryofractured samples from the walls of nanocomposite bottles were sputter-coated with gold and measured using a Mira SEM.

RESULTS AND DISCUSSION

Hdpe-*g*-MA processing and characterization

Twin screw extrusion is the method of choice for reactive extrusion processing.[3] This process is often used to produce new polymers by the chemical modification of existing polymers. The extruder provides the environment for melting, mixing, and reaction of the polymer and additives. HDPE-*g*-MA blends in this study were characterized using FTIR, Gel content studies and twin bore rheometry.

Characterization of Hdpe-g-MA batches 1–6

Fourier transform infrared spectroscopy. FTIR is used widely in the characterization of grafted polyethylenes.[13,21–23] In this work FTIR was used to show the presence of grafted MA and the spectra produced were subsequently used to quantify the grafted percentage. HDPE-*g*-MA exhibits an absorption peak at 1786–1784 cm^{-1} for the symmetric stretching of carbonyl C=O.[22] The presence of an absorption band at 919 cm^{-1} confirms the presence of grafted MA. This peak corresponds to the stretching of a cyclic five membered anhydride.[24,25] The content of grafted MA was determined from the area ratio of the absorption peak at 1790–1784 cm^{-1} (MA) and 730 cm^{-1}, a typical CH_2 rocking band. Figure 2 shows the IR spectrum for Batch 4 only. Batches 1–4 all contained peaks in the region of 1786–1784 cm^{-1}, with Batch 4 exhibiting a strong carbonyl peak at 1786 cm^{-1}, as well as a cyclic five membered anhydride peak at 919 cm^{-1} representing a single MA monomer grafted to the polyethylene backbone. Batches 5 and 6 exhibited none of the characteristic peaks of MA indicating that no grafting had taken

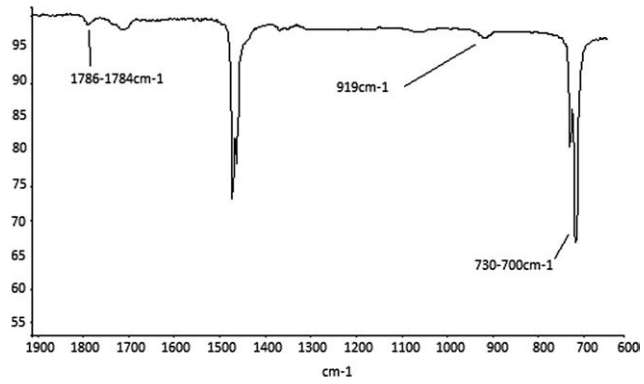

Figure 2 FTIR spectrum of HDPE-*g*-MA (Batch 4).

place. This may be due to the peroxide chosen in producing these batches. Batches 1–4 all contained DCP as the initiator and show signs of MA grafting while Batches 5 and 6 contained BP as the initiator. The lack of grafting in these batches may be a result of the short half-life of BP.[26] It is widely accepted that grafting will not take place after the initiator has been exhausted.[3] At the temperatures used during the reactive extrusion process, BP would have decomposed rapidly and is likely to have been fully reacted before the MA has had time to disperse throughout the polymer melt. Grafting yields calculated show that Batch 4 also has the highest degree of grafting. This level of grafting in Batch 4 is attributed to the lower throughput (5 kg/h), giving an increased residence time, and the higher levels of DCP and MA present. The grafting yield calculated can be seen in Figure 3. The presence of electron donors appears to have had a negative effect on the grafting yield of Batches 2 and 3. The presence of these lubricants may have reduced the level of macroradicals for MA to graft with and thus reduced grafting yield. The effect of these electron donors has been discussed by Moad and Gaylord and Xanthos and it has been observed by both that they are effective in reducing unwanted side reactions such as crosslinking and homopolymerization of MA but may also be responsible for a reduction in grafting yield.[3,27]

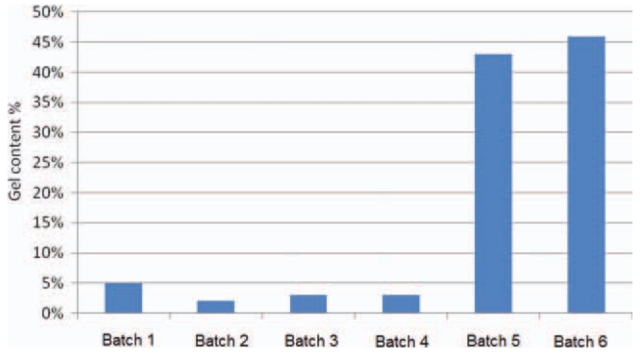

Figure 4 Insoluble gel content of Batches 1–6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Gel content analysis. The determination of gel content within a grafted polymer is important in evaluating the level of side reactions, which have occurred as polyethylenes are prone to crosslinking during processing. The presence of initiators and monomers only serves to increase their susceptibility to crosslinking. It has been observed in other studies that the formation of macroradicals on the polymer backbone can lead to crosslinking between polymer chains if these macroradicals do not become sites for monomer grafting.[3,4,13] It can be seen from the results in Figure 4 that polymer morphology has a large part to play in the grafting process. Batches 5 and 6 exhibit very high levels of insoluble material and both of these batches are comprised of primarily SI508 HDPE. Pinheiro and Chinellato proposed that crosslinking could be measured by an increase in molecular weight and that different methods of polymerization could lead to increased susceptibility to crosslinking.[28] Moss and Zweifel studied the degradation of HDPE under multiple extrusions in a single screw extruder and observed that Phillips type HDPE showed an increase in molecular weight, whereas a reduction was observed for Ziegler Natta HDPE.[29] Dontula and Campbell found the same effect when HDPE was processed in a twin screw extruder, following differences in viscosity of the extruded material at different temperature profiles

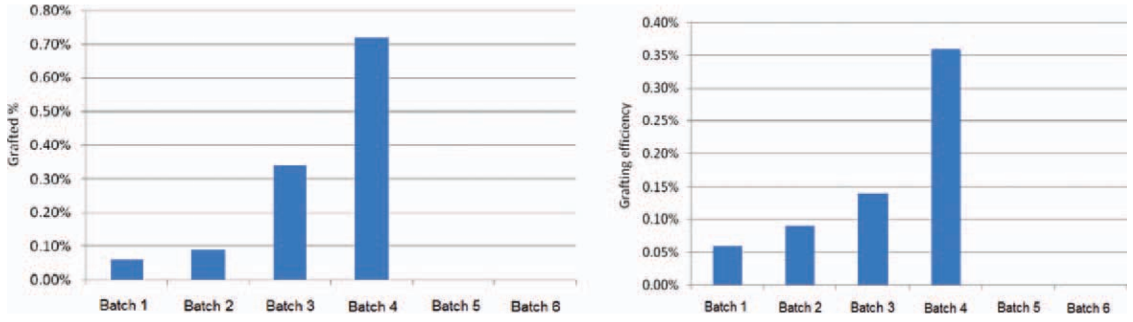

Figure 3 MA grafting percentage and grafting efficiency of Batches 1–6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

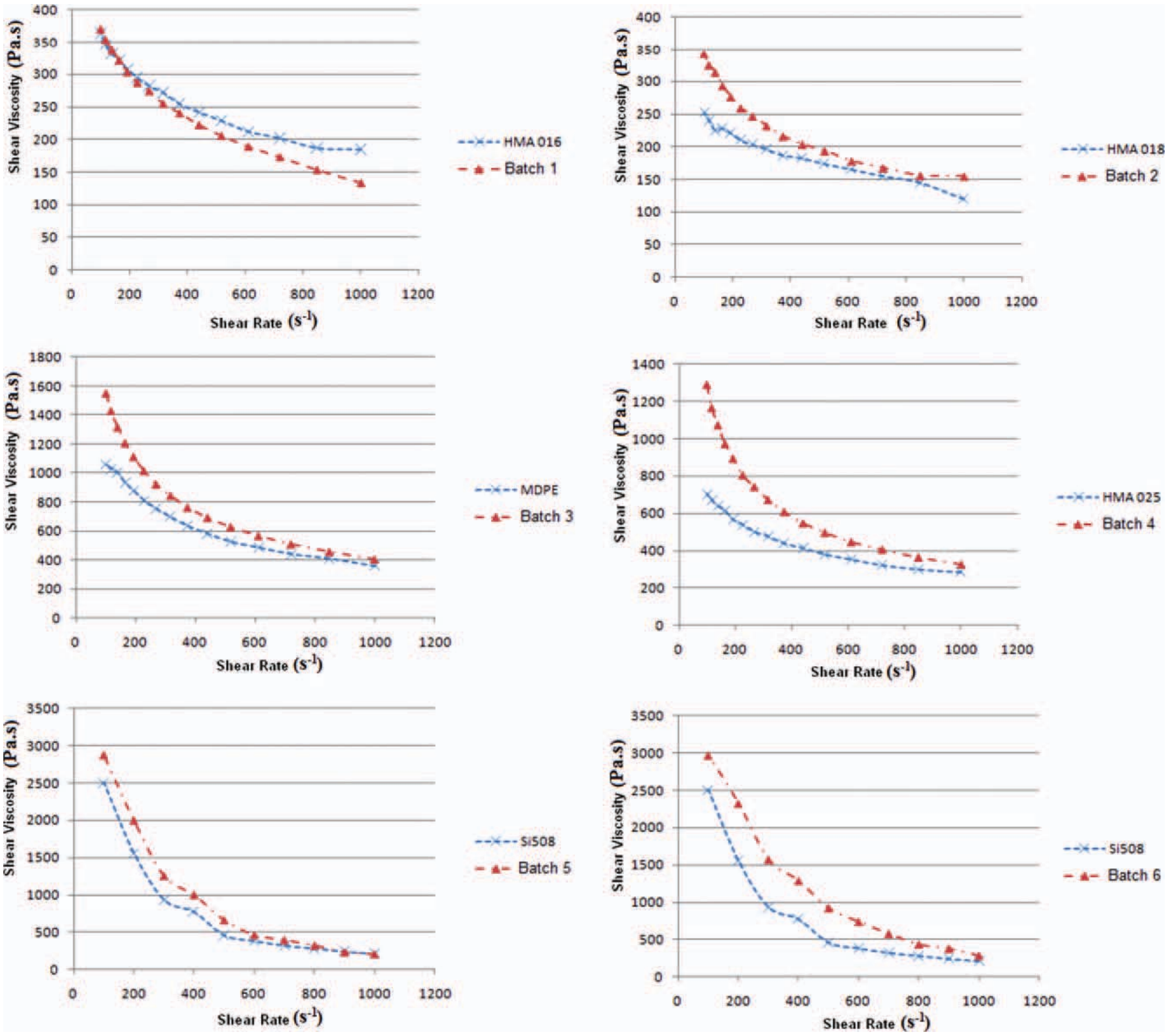

Figure 5 Shear viscocity versus shear rate for Batches 1–6 compared with base polyethylenes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and feeding rates.[30] SI508 is produced by a slurry loop system and is therefore a Phillips HDPE whereas the HDPE grades supplied by Total Petrochemicals (Batches 1-4) are all Ziegler Natta polyethylenes. The effect of peroxide percentage on the gel content is also evident. Batch 6 contains twice as much BP as Batch 5 and as a result exhibits a percentage increase in crosslinked material. This is consistent with the findings of Gaylord and Mehta and Ghaemy and Roohina (2003).[4,13] The type of peroxide used may also have had an effect of the % crosslinking observed. Batches 1–4, which contain DCP, show reduced crosslinking when compared with 5 and 6 which contain BP. This increase in gel content attributed to BP can be explained by the generation of radicals at an early stage of extrusion and thus termination reaction by recombination of the radical species can take place. Finally, the presence of lubricants during extrusion would seem to have aided in the reduction of side reactions. Batches 2 and 3 contain different types of lubricants, which are said to donate electrons and nullify any ungrafted macroradical sites and thus reduce the level of side reactions possible.[1] The percentage gel contents for Batch 2 and 3 would seem consistent with this and the results of other studies.[13,31]

Twin bore rheometry. Twin bore rheometry was used to ascertain if the grafting of MA or the side reactions outlined in sections "Fourier transform infrared spectroscopy" and "Gel content analysis" affected the shear viscosity of polyethylene. It can be seen in Figure 5 that crosslinking and grafting have a noticeable effect on the melt viscosity of the samples. Batches 2–4 show increases in viscosity consistent with their

TABLE IV
Processing Observations for Batches 1–6

	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6
Extruder torque (%)	25	26	29	34	32	37
Melt temperature (°C)	185	184	189	192	184	182

grafted content. The melt viscosity of a polymer is dependent on the rate at which chains can move relative to each other. Large monomers such as MA, when grafted to the polymer backbone can restrict chain motion and rotation and as such increase the melt viscosity. The movement of polymer chains, which are crosslinked requires the rupture of covalent bonds to flow. As a result a large increase in shear viscosity is also evident for the crosslinked polyethylene samples.

Reactive extrusion processing observations. Extruder torque is a measure of the resistance that the motor experiences as a consequence of the melt viscosity inside the barrel.[32] Although, values obtained for the extruder torque in this work cannot be used as a measure of change in viscosity because of the differences in throughput for each batch, they are worthy of observation in light of the results already reviewed. The level of grafted content or crosslinking could have a significant effect on the ability of these compatibilizing materials to be processed. Table IV shows the data for extruder torque and melt temperature observed during the reactive extrusion process. It is also evident that the grafting process has a significant effect on the process ability of the resultant material. Extruder torque values are consistent with the melt viscosity results shown in Figure 5. The effect of grafted content on the viscosity of the material can be seen to alter the torque necessary to turn the extruder screws. The melt temperature values seen in Table IV are recorded between the final extruder zone and the die. These values offer an interesting insight into the grafting process. Batches 3 and 4, which contained the highest degree of grafting, also exhibited the highest melt temperatures. This increase in temperature indicates that the grafting reaction taking place within the barrel is exothermic, causing the melt temperature to rise. The lower temperatures recorded for Batches 1 and 2 may be due to the lower level of grafting which occurred. Batches 5 and 6, which showed no evidence of grafted content, also exhibited lower melt temperatures. This may be due to the lack of any grafting reaction taking place as the decomposition of BP is likely to have occurred in the initial melting zones of the extruder.

Composite processing and characterization

It has been widely reported that the mechanical properties of polyethylene can be significantly enhanced by the addition of fillers such as wood flour and nanoclay.[21,33–34] The aim of this study was to ascertain the effect of MA content on the interfacial interactions between polyethylene and wood flour, and also the interaction between polyethylene and nanoclay.

Characterization of wood flour and nanoclay/polymer composites

Three point bending. A three point bending test was used to examine the flexural properties of the polyethylene composite materials (Table V). A general increase in the mechanical properties of the composites containing HDPE-*g*-MA was observed when compared with WPC 8 and HDPE/I44.P 8, which contain no compatibilizer. This shows that the presence of MA has increased the interfacial attraction between the polymer and filler. In the case of nanoclays, silicate layers must be separated to be of any use as nanofillers. Natural clays are generally hydrophilic and polymers are generally hydrophobic and this leads to problems when trying to disperse the silicates throughout the polymer.[35] The presence of MA generally leads to the formation of nanocomposites, and hydrogen bonding between the MA and the Si—O group's results in greater dispersion of the nanoclay platelets.[35] Where no compatibilization is present in polyolefin composites, there is little chance of intercalation of the nanoclay platelets.[36] As with natural clays, natural fibers are hydrophilic, resulting in little compatibility with hydrophobic polyethylene. Wood polymer composites with no compatibilizers can contain large agglomerates of wood fiber because of a lack of polymer fiber interaction. The strength of these wood polymer composites is dependent on the ability of the polymer to transfer the stress from the polymer matrix to the load bearing fibers.[37] Poor adhesion and dispersion limits the ability of the polymer to transfer this stress. The presence of MA generally increases the interaction between polymers and wood flour resulting in a better dispersion of the fibers and better adhesion between the fibers and the polymer.[38] This increased interaction between the polymer and wood flour results in large increases in both modulus and strength values. In the case of WPC 3, containing 3 wt % of Batch 3, an increase of ~ 55% in flexural strength was recorded when compared with WPC 8 that contains no compatibilizer. WPC 4 which contains 3 wt % of Batch 4 as a compatibilizer

TABLE V
Flexural Modulus and Strength Results for Wood Flour and Nanoclay Polyethylene Composites Compared with Virgin HDPE

	HDPE	WPC 1	WPC 2	WPC 3	WPC 4	WPC 5	WPC 6	WPC 7	WPC 8
Flexural modulus (Gpa)	1.52	2.52	3.15	3.54	3.38	2.03	2.19	2.76	2.28
Improvement (%)	0	65.7	108.55	132.89	122.36	33.55	44.07	81.57	50
Flexural strength (Mpa)	16	20.62	24.76	29.7	33.89	22.42	23.12	28.22	21.5
Improvement (%)	0	28	54.75	86.63	111.81	40.13	44.57	76.38	34.38
	HDPE	**HDPE/I44.P 1**	**HDPE/I44.P 2**	**HDPE/I44.P 3**	**HDPE/I44.P 4**	**HDPE/I44.P 5**	**HDPE/I44.P 6**	**HDPE/I44.P 7**	**HDPE/I44.P 8**
Flexural modulus (Gpa)	0.61	0.81	0.98	0.87	0.93	0.71	0.78	0.84	0.69
Improvement (%)	0	32.8	60.65	42.62	52.45	16.39	27.86	37.7	13.11
Flexural strength (Mpa)	14.76	17.36	19.47	18.06	19.3	16.57	17.21	18.93	11.58
Improvement (%)	0	17.6	31.9	22.36	30.76	12.26	16.6	28.26	−21.6

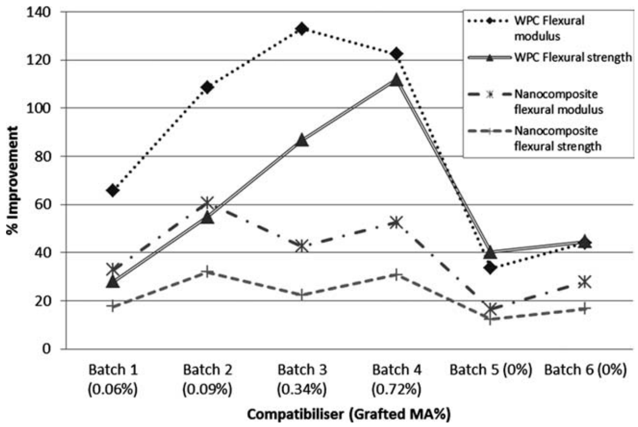

Figure 6 Effect of MA grafted content on the flexural properties of wood polymer and polymer nanoclay composites.

exhibited a 57% increase in flexural modulus when compared with WPC 8. It can be observed in Figure 6 that the level of grafted MA has a significant effect on the mechanical performance of these composites, as values for flexural modulus and strength increased with grafted MA. WPC 4 and HDPE/I44.P 4, both of which were produced using Batch 4, which had the highest grafted percentage of all the compatibilizers produced in this study, exhibited the greatest increase in flexural strength. Grafted polyethylenes produced in this work also compare favorably with a commercially available compatibilizer (Fusabond). WPC 7 and HDPE/I44.P 7 containing 3 and 5 wt % of Fusabond, a commercially available HDPE-*g*-MA, exhibited lower flexural modulus and strength values than composites containing the compatibilizers produced in this study (Batches 3 and 4).

X-ray diffraction. XRD was used to identify the intercalated structure of the polymer/nanoclay composite samples. Note that the dispersion of wood flour in WPCs was not examined using this technique because the cell walls of most natural fibers mainly consist of cellulose, hemicellulose, and lignin.

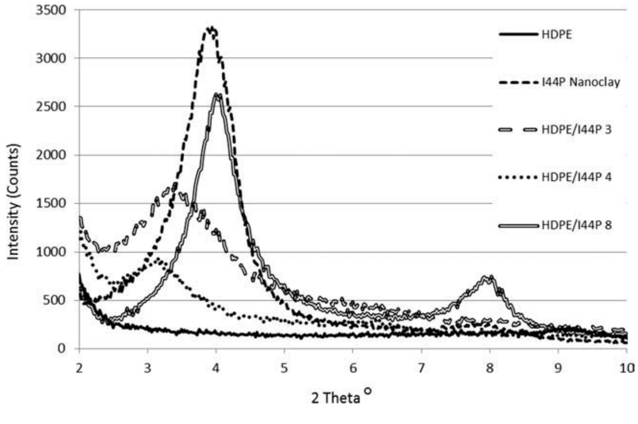

Figure 7 XRD scans for HDPE, I.44P nanoclay, HDPE/I.44P 3, HDPE/I.44P 4, and HDPE/I.44P 8

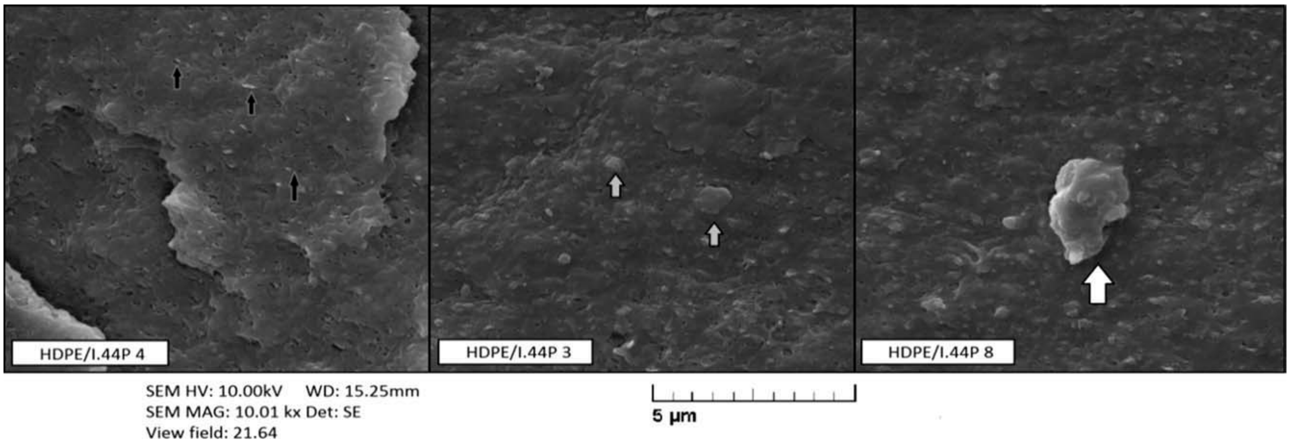

Figure 8 SEM micrographs of HDPE/I.44P 3, HDPE/I.44P 4, and HDPE/I.44P 8.

Cellulose has mostly amorphous and some crystalline regions, although hemicellulose and lignin are completely amorphous meaning that XRD cannot easily detect any crystalline regions. In nanocomposites, the repetitive multilayer structure is well preserved, allowing the interlayer spacing to be determined. The intercalation of the polymer chains increases the interlayer spacing, in comparison with the spacing of the organoclay used, leading to a shift of the diffraction peak towards lower 2θ angle values.[39] The XRD scans shown in Figure 7 confirm that the presence of MA has increased the levels of intercalation achieved, though full exfoliation has not occurred. The spectrum for HDPE/I44.P 8 is typical of an immiscible system; there is no shift in the 2θ angle meaning that neither intercalation nor exfoliation has occurred. There is little affinity between the polymer and silicates because of the absence of MA and as such a phase separated material is formed. In general, such composites do not exhibit remarkably enhanced mechanical properties compared to those of the virgin material.[39] When compared with the XRD pattern for I44.P nanoclay a reduction in the diffraction peak intensity and a shift in the 2θ angle is evident for HDPE/I44.P 4. This confirms that the presence of MA has increased the affinity between the polymer chains and the silicate layers. The HDPE/I44.P 4 represents an intercalated structure because the diffraction peak attributed to nanoclay is still evident, and therefore it cannot be considered to be fully exfoliated. The effect of MA content on the levels of intercalation achieved can be seen when comparing the spectra of HDPE/I44.P 3 and HDPE/I44.P 4. The higher level of grafted MA present in Batch 4 when compared with Batch 3 has resulted in a greater level of intercalation due to the increased interaction between MA and the nanoclay silicate layers. These findings are consistent with the mechanical properties detailed in section "Three point bending".

Scanning electron microscopy. SEM images of nanocomposite samples are shown in Figure 8. It can be observed in these images that there is a significant increase in the size of clay agglomerations when compatibilizers containing low-levels of grafted MA are incorporated. The images shown in Figure 8 correlate to the previously discussed XRD data. HDPE/I.44P 4 shows evidence of well dispersed silicate layers; the black arrows indicate thin silicate structures. Larger agglomerations of silicate platelets can be observed in HDPE/I.44P 3, these are represented by the gray arrows and the clay structures are visibly larger than those observed in HDPE/I.44P 4. HDPE/I.44P 8, which exhibited the highest diffraction peak, was shown by SEM to contain large silicate agglomerations, as highlighted by the large white arrow. This is typical of an immiscible system and the size of the silicate agglomeration could lead to this being considered a microcomposite rather than a nanocomposite. Similar SEM images were shown by Villanueva et al. when compatibilizers were added to HDPE nanoclay blends.[40]

CONCLUSIONS

The work described in this research article outlines the use of MA as a compatibilizer between polyethylene and two fillers, namely nanoclay and wood flour. MA was grafted to the polyethylene backbone using a reactive extrusion process. It was confirmed by FTIR that grafting of MA had occurred in four of the six batches produced. BP was eliminated as a possible initiator for this process because of its short half-life at the temperatures used in the reactive extrusion process. DCP was found to be more thermally stable at these temperatures. Crosslinking is the main side effect of the grafting process and the degree of crosslinking was evaluated using gel content analysis. It was found that gel content could be controlled by choosing the optimum ratio of initiator to monomer, thus ensuring that macroradicals created by the initiator became sites for grafting rather than possible crosslinking sites. Lubricants incorporated during the process were also shown to reduce crosslinking although they had a negative effect on the level of grafting achieved. The results obtained from FTIR and gel content analysis are in keeping with the findings from twin bore rheometry analysis. Batches containing higher levels of grafted MA exhibited an increase in shear viscosity and this trend correlated to their grafted content. Crosslinking was also shown to increase the shear viscosity and these results were in agreement with the observations recorded during extrusion as increases in extruder torque were comparable with the trends in shear viscosity observed during the rheological analysis. These HDPE-*g*-MA compatibilizers were then compounded with nanoclay and wood flour to produce composites. When compounded with these fillers an increase in mechanical properties was observed. The performance of all composites was dependent on the percentage MA grafted. This has been attributed to the increased interaction between the polymer and filler leading to better interfacial attractions and higher levels of dispersion. The results obtained from wood polymer composites in particular were promising. The mechanical properties of nanoclay composites suggest that intercalation of the clay platelets has occurred in composites containing Batches 3 and 4; while there have been increases in flexural modulus and flexural strength they are not to the degree that would be expected when full exfoliation and delamination of the nanoclay layers occurs. Further work to examine the effect of screw geometry and increased MA on the exfoliation of nanoclay platelets is currently underway. The work described herein indicates that MA can be grafted onto polyethylene in a reactive extrusion environment. It highlights the importance of initiator choice and shows that the ratio of monomer to initiator has a great effect on the grafting yield. The results from mechanical testing of wood flour and nanoclay composites show that a composite material can be produced, which has superior mechanical properties to that of virgin HDPE. There are possibilities to use this technology to produce lightweight materials to reduce production costs, reduce energy use, and cut emissions.

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