

## Effect of Chemical Treatments and HDPE-g-MA on the Physical and Mechanical Behaviour of HDPE/ Natural Fibre Composites

<sup>1</sup>Zhi Cao, <sup>2</sup>Marc Peyregne, <sup>1</sup>Michael Daly, <sup>1</sup>Tom Mullen, <sup>1</sup>Declan. M. Devine, <sup>1</sup>Luke M. Geever, <sup>1</sup>Clement. L. Higginbotham

<sup>1</sup>Materials Research Institute, Athlone Institute of Technology, Athlone, Ireland

<sup>2</sup>Mergon International, Castlepollard, Westmeath, Ireland University of South Brittany, Lorient, France

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**Abstract:** Many authors have reported on the use of natural fibres (raw or chemically modified) as reinforcing elements for high density polyethylene (HDPE). These materials have generated a lot of interest due to their low cost and high specific properties. In this work, HDPE and maleic anhydride (MA) compatibilised HDPE were compounded with chemically modified flax and hemp fibres using twin screw extrusion. The physical and mechanical properties of the composite were studied to investigate the effect of chemical modification of the reinforcement fibres. HDPE-g-MA was produced by grafting MA to HDPE's backbone in a twin screw extruder using a peroxide initiated reactive process. The two chemical treatments used in this study were sodium hydroxide (NaOH) and maleic anhydride (MA) treatments. A fixed fibre loading of 10 wt.% was used in all composites. Fourier Transform Infrared Spectroscopy (FTIR) was used to examine the effects of the chemical treatments on the fibres and it was found that non-cellulosic material had been removed. The mechanical properties of the composites exhibited a significant increase in tensile strength and flexural modulus, whereas a significant decrease was recorded in Impact strength when compared to the virgin HDPE. It was also observed that the addition of the compatibiliser HDPE-g-MA significantly increased the tensile strength when compared with composites containing no compatibiliser. The tensile strength of the NaOH treated fibres reinforced HDPE also showed a significant increase compared with untreated fibre reinforced HDPE composites. Melt flow index analysis indicated that the material remained melt processable following compounding with the natural fibres. Additionally, the composites did not show any significant increase in weight due to water absorption following submersion in water for seven days. Furthermore, cost analysis revealed that the use of composites is advantageous in comparison to virgin HDPE in terms of raw material costs. From this series of tests it has been shown that chemically treatment and HDPE-g-MA can be used to increase tensile strength and Young's modulus properties of HDPE/ natural fibres composites.

**Key words:** Natural fibre Composite; HDPE-g-MA; Mechanical properties; Physical properties

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### INTRODUCTION

Natural fibres reinforced polymer composites has become widely used in many industries (Souza *et al.*, 2011). Major car manufacturers in Germany now use natural fibre composites in a lot of their products. Door panels of E-Class Mercedes-Benz which are made from a mixture of flax and sisal fibres in an epoxy matrix have shown weight reduction of about 20% compared to metal door panels. Even though natural fibre matrix composite is not as strong as a glass fibre composite, for many applications, their properties exceed the minimum required to fulfill function (Jawaid and Abdul Khalil, 2011). Compared to conventional inorganic fillers such as glass fibre and carbon fibres, natural fibres provide many advantages: (1) production with low investment at low cost; (2) biodegradability; (3) renewable resources, production require little energy and low CO<sub>2</sub> emission; (4) thermal recycling is possible; (5) ease of handling, low tool wear and no skin irritation; (6) Low specific weight results in a higher specific strength and stiffness; (7) High electrical resistance; and (8) good thermal and acoustic insulating properties (Jawaid and Abdul Khalil, 2011).

Although natural fibres offer the resulting composites many advantages, the usually polar fibres have an inherently low compatibility with non-polar polymer matrices, especially polyolefins such as polypropylene (PP) and polyethylene (PE). This incompatibility causes problems in the composite processing and material properties (Xie *et al.*, 2010). Other disadvantages include: (1) lower strength especially impact strength; (2) variable quality, influenced by weather; (3) poor moisture resistant which causes swelling of the fibres; (4) restricted maximum processing temperature; (5) lower durability; (6) poor fire resistance; and (7) Price fluctuation by harvest results or agricultural politics. Nevertheless, the cost does remain lower than other alternative reinforcement fibres (Jawaid and Abdul Khalil, 2011).

Flax and hemp are basically long fibres extracted from the bast of the plants; they can be used as fillers in either long or short fibre form (La Mantia and Morreale, 2011). The main components of natural fibres are

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**Corresponding Author:** Zhi Cao, Materials Research Institute, Athlone Institute of Technology, Athlone, Ireland

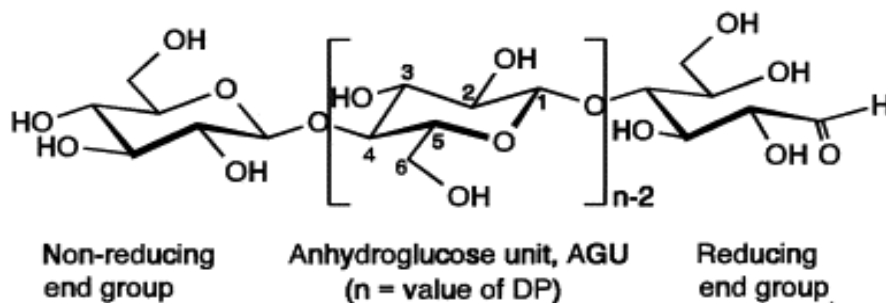
cellulose ( $\alpha$ -cellulose), hemicellulose, lignin, pectins, and waxes. The chemical composition and properties of flax and hemp fibres are shown in Table 1. The reinforcing efficiency of natural fibres is related to the nature and crystallinity of its cellulose (John and Thomas, 2008).

**Table 1:** Chemical composition and properties of lignocellulosicfibres.

Fibre	Flax	Hemp
Chemical composition		
Cellulose	64.1%	74.4%
Hemi-cellulose	16.7%	17.9%
Lignin	2.0%	3.7%
Extract	1.5-3.3%	0.9-1.7%
Water soluble	3.9%	-
Mechanical properties		
Density (g/cm <sup>3</sup> )	1.4	1.48
Tensile strength (MPa.)	800-1500	550-900
Young's modulus (GPa.)	60-80	70
Elongation at break (%)	1.2-1.6	1.6
Physical properties		
Length of fibre (mm)	10-65	5-55
Diameter of fibre ( $\mu$ m)	5-38	10-51

Source: (Jawaid and Abdul Khalil, 2011)

Cellulose is a natural polymer consisting of anhydroglucose repeating unit (Fig 1), each containing 3 hydroxyl groups. It is resistant to strong alkali and oxidizing agents, but is easily hydrolyzed by acid to water-soluble sugars (John and Thomas, 2008). However, these fibres are covered with pectin and waxy materials that prevent the hydroxyl groups from reacting with polymer matrices. This can lead to the formation of ineffective interfaces between the fibres and matrices, resulting in debonding and voids in resulting composites (Sawpan *et al.*, 2011b). Traditional dew retting, tank retting and chemical methods are used to separate natural fibre bundles, remove non-cellulosic material and add functional groups to enable better bonding in polymer composites (Li *et al.*, 2009). In addition, treatment can alter the crystalline structure of the cellulose as well as fibre tensile properties (Sawpan *et al.*, 2011 a).



**Fig. 1:** Molecular structure of cellulose including numbering of C-atoms (Heinze and Liebert, 2001)

Several methods such as graft copolymerization of monomers onto the fibre surface, use of maleic anhydride copolymers, alkyl succinic anhydride and stearic acid, have been used to modify the surface of natural fibre (Herrera-Franco and Valadez-González, 2004). Furthermore, it is also known that bonding between the fibres and the polymers can be improved using polar adhesion promoters such as maleic anhydride grafted polyethylene (La Mantia and Morreale, 2011). The anhydride groups of the copolymers can react to the hydroxyl groups on the cellulose of natural fibres, forming ester bonds. The other end of the copolymer entangles with the HDPE backbone because of their similar polarities (Gao *et al.*, 2012). Adhikary *et al* reported that the addition of 3 wt. % compatibiliser to a natural fibre composite increased the tensile strength by 5.6 GPa, the flexural strength by 4.9 GPa, and the flexural modulus by 0.88 GPa in comparison with a similar composites with no compatibiliser (Adhikary *et al.*, 2008). Gunning *et al* studied the effects of processing parameters on grafting maleic anhydride to HDPE's backbone during twin screw extrusion in the presence of dicumyl peroxide (DCP). They reported that FTIR confirmed grafting of MA had occurred using a reactive extrusion process. In this study, the effect of two different chemicals (NaOH, MA) and compatibiliser (HDPE-g-MA) on the physical and mechanical behaviour of flax and hemp fibre reinforced HDPE composites was examined. The goal of the current study was to develop and fabricate cost effective high density polyethylene parts for industrial applications. Tensile, flexural and impact testing were performed to determine the mechanical properties of fibre reinforced HDPE composites. MFI was used to ensure material remained melt processable. Density comparison

was used to investigate the weight changes of the composites. Water uptake analysis was employed to examine the effect of water on the composite and cost analysis was used to compare the economic benefit of the composite.

#### **Materials And Experimental Procedures:**

##### **Materials:**

HDPE (Marlex® HHM 5502BN) was supplied by Chevron Phillips Chemicals International N.U. Belgium. Hemp fibre was procured from Hemp flax Ltd (Holland). Flax fibre was supplied by Hempire Building Materials Ltd (Ireland). Fibres were cut into approximately 7cm strands prior to surface treatment and extrusion. Sodium hydroxide (NaOH), dicumyl peroxide (DCP) and maleic anhydride (MA) (95% purity) were purchased from Sigma Aldrich (Ireland) and used as received.

##### **Fibre Surface Treatments:**

Untreated and chemically treated flax and hemp fibres were used for fabricating the composites. Flax and hemp fibres were subjected to different surface treatments using sodium hydroxide and maleic anhydride.

In alkali treatment, the chopped fibres were soaked in a solution containing 10 wt. % NaOH for 18 hrs. Subsequently the fibres were washed with water until all the NaOH was eliminated and dried in oven at 70 °C for 24 hrs.

In maleic anhydride treatment, the NaOH treated fibres were soaked in a solution of MA in acetone (5 wt. %) in a round-bottom flask for 18 hrs. The treated fibres (MA) were washed thoroughly with water to remove residual chemicals and dried in oven at 70 °C for 24 hrs.

##### **Melt processing:**

High density polyethylene grafted maleic anhydride (HDPE-g-MA) production.

2 wt. % of MA and 0.006 wt. % of DCP were mixed and ground to a fine-powder using a pestle and mortar. This powder was hand mixed with a 97.994 wt. % powdered HDPE. The mixture was transferred to a feeder fitted with screws of suitable geometry and dimensions for feeding powdered materials. These materials were fed into the APV twin screw extruder and the temperature profile for the grafting process was increased from 170°C at the hopper to 200°C at the die, with a screw speed of 100rpm and a polymer feed rate of 5kg/hr. 700 g of the resultant compound was collected for compounding with fillers.

##### **Extrusion Compounding:**

All the composite processing was carried out on a micro 27 lab scale twin screw extruder (Leistritz) with a 27 mm screw diameter and a 38/1 length to diameter ratio, using the screw geometry outlined by (Gunning *et al.*, 2012). In compounding process, the temperature profile was increased from 160°C at the hopper to 200°C at the die with screw speed of 120rpm utilised. Fibre polymer composites were produced by compounding 90 wt. % of HDPE fed into the barrel at a rate of 6 kg/h using a K-Tron feeder, with 10 wt. % of the fibre which was hand fed into the barrel at a rate of 10 g/min. (600 g/hr.). Fibre polymer compatible composites were produced by hand mixing 3 wt. % of the MA-g-HDPE with 87 wt. % of HDPE: This mixture was placed into the K-Tron feeder and compounded with the natural fibres as before. Tables 2 outline the composition of high density polyethylene/ natural fibre composites.

##### **Injection moulding:**

Injection moulding was carried out on an Arburg™ All-rounder 221 K which has a maximum clamping force of 350 kN and a screw diameter of 25 mm. The theoretical stroke volume for this machine is 49 cm<sup>3</sup>. All natural fibre composite materials were dried for 8 hours at 70 °C prior to injection moulding to remove any moisture retained from the extrusion process. The temperature profile for injection moulding increased from 160°C at the hopper to 200°C at the nozzle with injection speed of 100 mm/sec. The holding pressure used was 600 bars with a holding time of 6.5 sec. The cooling time used was 10 sec with a back pressure of 50 bars.

**Table 2:** Composition of high density polyethylene/ natural fibre composites

a. Flax polymer composites

Batch name	HDPE (wt. %)	HDPE-g-MA (wt. %)	Flax (wt. %)	Flax (NaOH)(wt. %)	Flax (NaOH, MA) (wt. %)
PE	100	0	0	0	0
PE-F	90	0	10	0	0
PE-F1	90	0	0	10	0
PE-F2	90	0	0	0	10
PEMA-F	87	3	10	0	0
PEMA-F1	87	3	0	10	0
PEMA-F2	87	3	0	0	10

## b. Hemp polymer composites

Batch name	HDPE (wt. %)	HDPE-g-MA (wt. %)	Hemp (wt. %)	Hemp(NaOH) (wt. %)	Hemp(NaOH, MA) (wt. %)
PE	100	0	0	0	0
PE-H	90	0	10	0	0
PE-H1	90	0	0	10	0
PE-H2	90	0	0	0	10
PEMA-H	87	3	10	0	0
PEMA-H1	87	3	0	10	0
PEMA-H2	87	3	0	0	10

**Characterisation:**

Fourier transform Infrared spectroscopy (FTIR)

The FTIR analysis was performed using a Perkin Elmer Spectrum One FTIR spectrometer. All data was recorded at room temperature, in the spectral range of 650 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. FTIR have been also used to characterise and compare the chemically modified fibres against untreated fibres.

**Melt flow index:**

Melt flow index was assessed in accordance with ASTM standard D1238 and the measured value was expressed in g/10mins. The melt flow rate inducer was preheated to 190 °C. The material was loaded into the cylinder from the top and a specified weight of 2.16kg was placed on the piston. Six specimens per batch were tested and the average melt flow rate was calculated.

**Mechanical Properties:**

Tensile tests were carried out using a Lloyd LRX tensometer according to ASTM standard D 638-10. Composites specimens were mounted and strained at a rate of 2 mm/min until failure occurred. Six specimens per batch were tested and the average strength was calculated.

Flexural analysis, a Lloyd LRX tensometer was used in compression mode at a rate of 2 mm/min with a span of 80 mm in accordance with ASTM standard D790-10. Six specimens per batch were tested and the average flexural modulus was calculated.

Impact testing was carried out using a Resil 25 Digital Impact Tester, manufactured by Ceast, fitted with a 4 kJ hammer according to ASTM standard D256. A notch of 1 mm was made on each virgin HDPE sample and 0.5 mm was made on each composites sample to ensure failure. Six specimens per batch were tested and the average fracture energy was calculated. Notched izod impact strength was calculated using Equation 1.

**Equation 1:**

$$\text{Impact strength (KJ/ m}^2\text{)} = (W / h \times b_N) \times 10^3$$

Where:

W is the corrected energy in J, absorbed by breaking the test specimen; h is the thickness, in mm, of the test specimen; b<sub>N</sub> is the remaining width, in mm, at the notch base of the test specimen.

**Water Uptake Analysis:**

Water uptake was measured according to ISO 62:2008. HDPE fibre composite samples were dried at 60 °C for 24 hours and their weight was recorded. These dry samples were immersed in water at 20 °C for 24 hours then wiped with clean paper and their weight was recorded again. The additional weight gain was calculated as the percentage water uptake.

**Cost analysis:**

The raw material cost of the composites was calculated using Equation 2. Price for HDPE and natural fibres were taken at the cost per kg. The extra labour and energy costs were not take into account. For cost analysis purposes the cost of HDPE was assumed to be € 1.3/ kg, add in all other components.

**Equation 2:**

$$\text{Price per kg} = \% F \times F_c + \% P \times P_c + S_c + C$$

Where:

% F= percentage fibre used; F<sub>c</sub> = cost of fibre per kg; % P= percentage polymer used; P<sub>c</sub> = cost of the polymer per kg; S<sub>c</sub>= cost for surface treatment; C= cost of HDPE-g-MA.

**Statistical Analysis:**

A statistical comparison of the density, melt flow index, water absorption, tensile strength, flexural modulus and impact strength was performed. Following assessment of normality of distribution and homogeneity of variance, treatments were compared using a one way ANOVA with a Turkey's Honesty Significant Difference Post hoc test to determine differences between individual batches. Differences were considered significant when  $p \leq 0.05$ . To perform this analysis, the IBM SPSS statistics version 19 software was used.

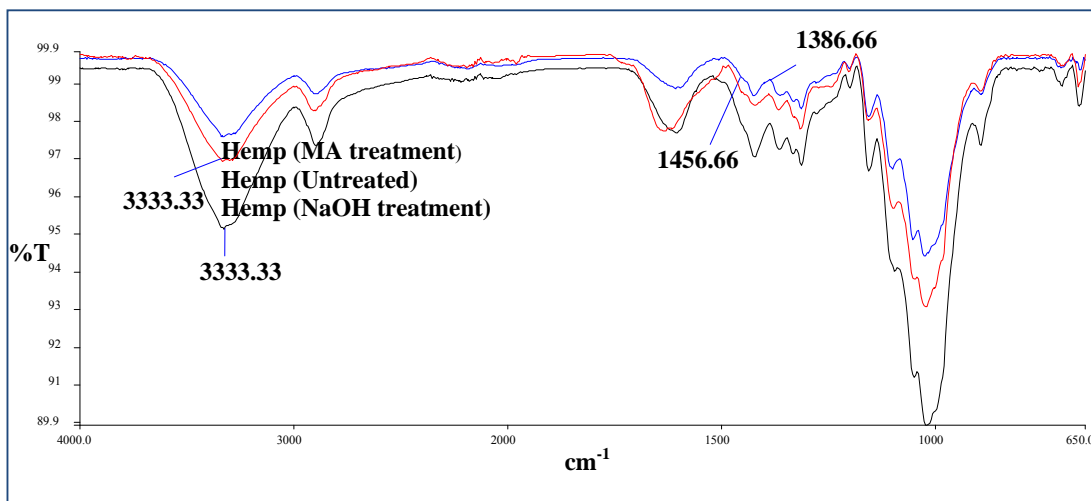
**RESULTS AND DISCUSSION**

**Fourier transform Infrared spectroscopy (FTIR)**

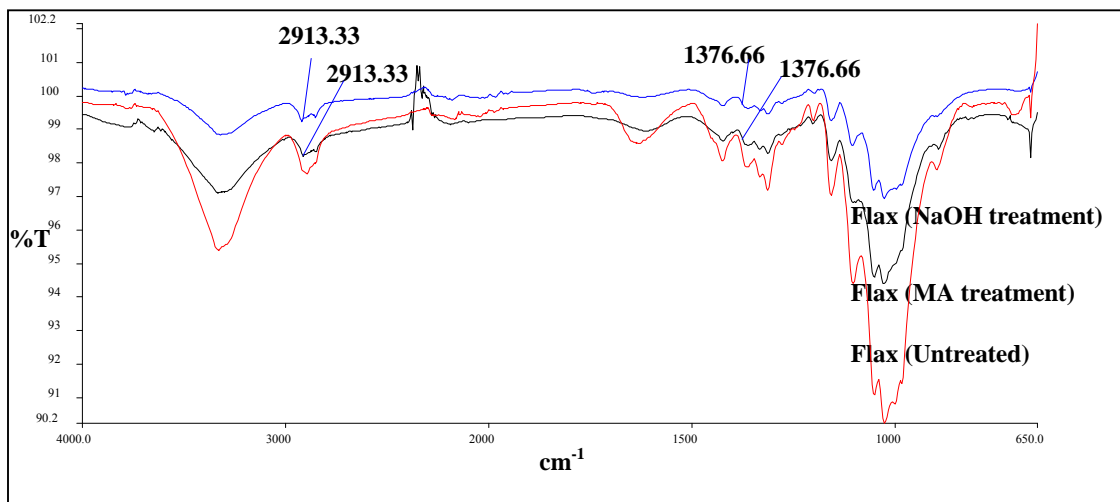
FTIR is widely used in the characterisation of the chemically modified natural fibres (Sawpan *et al.*, 2011b, Gunning *et al.*, 2012, Saha *et al.*, 2010).

From the FTIR spectra of the untreated, NaOH treated and MA treated hemp fibres (Figure 3). It was found that the spectrum of NaOH treated hemp fibres was similar to that of the untreated hemp fibres. However, the peak at  $3333 \text{ cm}^{-1}$  seen in untreated fibres increased after NaOH treatment. In the case of MA treated hemp fibres, the reduction of the peak heights at  $1456 \text{ cm}^{-1}$  and  $1386 \text{ cm}^{-1}$  assigned to  $-\text{CH}_3$  asymmetric and C-H symmetric deformations.

The FTIR spectra of the untreated, NaOH treated and MA treated flax fibres are shown in Figure 4. The strong peak  $2913 \text{ cm}^{-1}$  represents C-H stretching vibration of methyl and methylene groups in hemicellulose, becomes less intense after alkali and MA treatment. There was also a decrease in the intensity of the peaks at  $1376 \text{ cm}^{-1}$ , which represents C-H bands deformations of lignin.



**Fig. 3:** FTIR spectra of hemp fibres (untreated, NaOH treated and MA treated).



**Fig. 4:** FTIR spectra of flax fibres (untreated, NaOH treated and MA treated).

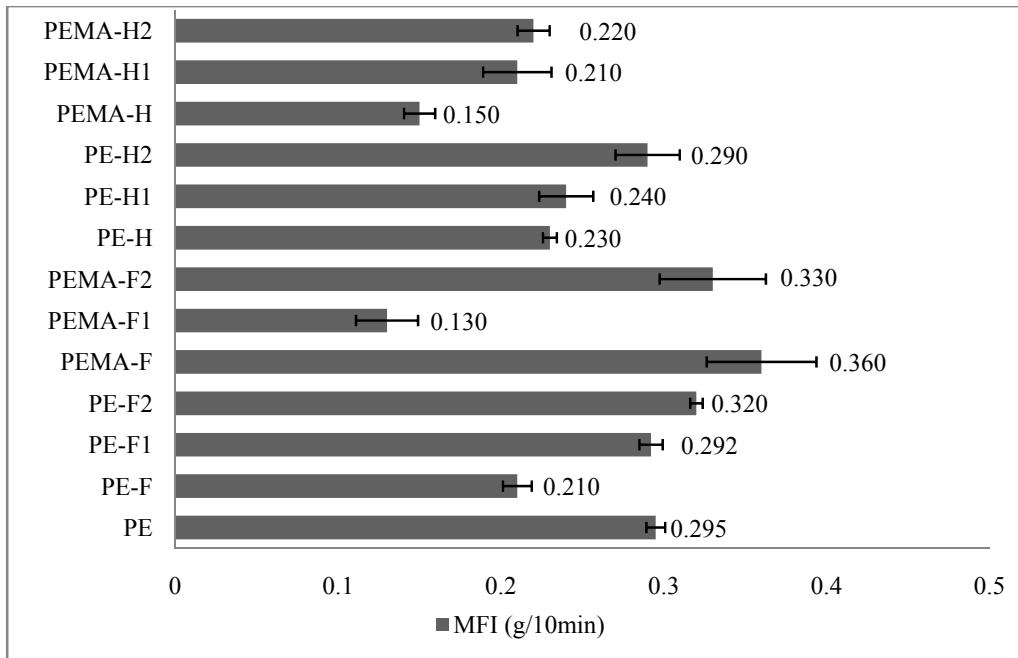
FTIR analysis was performed to determine if these treatments were effective at removing undesirable waxes from the surface of the fibres. In this analysis the peak appearing at 3200- 3600  $\text{cm}^{-1}$  (Figure 3) was attributed to -OH stretching for untreated hemp fibre (Sawpan *et al.*, 2011a, Sawpan *et al.*, 2011b). As a result of NaOH treatment the hemp fibre exhibited an increase in the intensity of this peak which indicates that the fibre has become less hydrophilic and more reactive to react with the HDPE matrix (Kabir *et al.*, 2012). In the case of MA treated hemp fibres, the reduction of the peak heights at 1456  $\text{cm}^{-1}$  and 1386  $\text{cm}^{-1}$  assigned to  $-\text{CH}_3$  asymmetric and C-H symmetric deformations of lignin indicates the removal of the lignin. A better packing of cellulose chains can be made by removal of cementing substances like lignin and hemicellulose (Annie Paul *et al.*, 2008). Similar observation has also been made by other researchers (Saha *et al.*, 2010, Sawpan *et al.*, 2011a, Roy *et al.*, 2012). The FTIR spectra of the NaOH treated and MA treated flax fibres (figure 4) indicate a reduction of the C-H stretching vibration of methyl and methylene groups in hemicellulose at 2913  $\text{cm}^{-1}$ . This decrease was due to the removal of hemicellulose molecules (Roy *et al.*, 2012, Saha *et al.*, 2010). There decrease in the intensity of the peaks at 1376  $\text{cm}^{-1}$ , which represents C-H bands deformations of lignin is further evidence that lignin was removed from the surface of fibre by the designated chemical treatments (Roy *et al.*, 2012). Observation made from FTIR results after all treatments indicate that none of the chemical treatment was successful in completely removing non-cellulose compounds including lignin and hemicellulose from hemp and flax fibre bundles.

**Melt Flow Index:**

Melt flow index analysis was used to ensure that the material remained melt processable following compounding with the natural fibres.

For HDPE flax composites, the MFI varied from 0.13 to 0.36 g/10min. While in the HDPE hemp composites, the MFI varied from 0.15 to 0.29 g/10min (Figure 5). Based on the MFI measurements of composites, it was found that MA treated flax fibre composites (PE-F2, PEMA-F2) are significantly higher in melt flow rate compared to raw fibre composite PE-F ( $p < 0.05$ ). NaOH treated hemp fibres composites (PE-H1) had a significantly higher MFI compared to the one without treated fibres (PEMA-H) ( $p < 0.05$ ).

Results also show that the addition of the compatibiliser HDPE-g-MA (PEMA, PEMAH, PEMAH1, and PEMAF1) significantly lowers the melt flow rate compared to virgin HDPE ( $p \leq 0.05$ ). Aside from these, no further significant difference were detected.



**Fig. 5:** Melt flow index of different batches at 200°C with 2.16kg weight.

The results from MFI analysis indicate that the partial removal of lignin and hemicellulose from the fibres did allow a better interaction between fibre-matrix. In addition, when the composite was subjected to compression during MFI testing, the fibres were compressed and this further increases the MFI. When HDPE-g-MA was added to the polymer composite, it was found that there was a significant reduction in the MFI of

the material. Since MFI is an indirect measurement of viscosity, it follows that incorporating HDPE-g-MA into the HDPE increases the viscosity of the fluid suspension compared to virgin HDPE. MFI values had a substantial effect on moulding operations. With lower flowability such as compatibilised HDPE fibre composites, heat would be applied unevenly to the composite due to its poor flow properties. Thus melting would be inconsistent and would result in high porosity and, consequently, low composite properties (Pedroso and Rosa, 2005). Nevertheless, as batches PE-F, PE-F2, PEMA-F, PEMA-F2, PE-H, PE-H1, PE-H2, and PEMA-H2 did not show significant differences to virgin HDPE in terms of MFI they could be used as a direct replacement for HDPE.

**Mechanical Properties:**

Good interfacial adhesion between the matrix and fibres is critical factor for the resulting composites to achieve improved mechanical properties (Xie *et al.*, 2010, Arrakhiz *et al.*, 2012). Chemical treatment of the fibre surface was used in this study to improve interfacial adhesion in the composite. From the mechanical testing of the composites, the tensile strength and flexural modulus results clearly show the reinforcement properties of the natural fibres.

**Tensile Test Results:**

The tensile strength of the HDPE fibre composites is shown in Table 3. A general increase in the tensile properties of the composites was observed when compared with virgin HDPE.

For HDPE-flax composites, tensile strength varied from 31.33 MPa to 36.08 MPa. Results showed that all the HDPE-flax composites had a significantly higher tensile strength than virgin HDPE ( $p \leq 0.033$ ). For HDPE-hemp composites, tensile strength varied from 30.93 MPa to 37.33 MPa. All of HDPE-hemp composites had a significantly higher tensile strength than virgin HDPE ( $p \leq 0$ ), except the non-treated hemp fibre PE-H ( $p=0.35$ ).

The addition of the compatibiliser HDPE-g-MA (PEMA-F, PEMA-H) significantly increases the tensile strength when compared with composites containing no compatibiliser (PE-F, PE-H) ( $p \leq 0.001$ ).

The NaOH treated fibres (PE-F1, PE-H1) had a significantly higher tensile strength than the non-treated fibre (PE-F, PE-H) ( $p \leq 0.001$ ).

The addition of compatibiliser into the NaOH treated fibres (PEMA-H1) yielded a significantly higher tensile strength than the one without compatibiliser (PE-H1) ( $p \leq 0$ ).

Furthermore, treatment of fibres with NaOH solution followed by MA solution (PE-F2, PE-H2) had a significantly lower tensile strength than the one without MA treatment (PE-F1, PE-H1). Similarly, the addition of compatibiliser to MA treated fibres (PEMA-F2, PEMA-H2) had a significantly lower tensile strength than the one without (PEMA-F1, PEMA-H1).

**Table 3:** Tensile strength of HDPE composites made with the various chemically treated fibres.

Batch	Stress at Max (Mpa)	% Increase in Tensile strength
	Mean ± SD	
PE	30.02 ± 0.25	0
PE-F	31.33 ± 0.17 *	4.36
PE-F1	35.51 ± 1.05 *, **, ****	18.29
PE-F2	31.30 ± 0.19 *	4.26
PEMA-F	34.65 ± 0.42 *, ***	15.42
PEMA-F1	36.08 ± 0.62 *, ****	20.19
PEMA-F2	33.46 ± 0.47 *	11.46

(A) Percentage increase of tensile strength of HDPE composite made with the various chemically treated flax fibres.

Batch	Stress at Max (Mpa)	% Increase in Tensile strength
	Mean ± SD	
PE	30.02 ± 0.25	0
PE-H	30.93 ± 0.34	3.03
PE-H1	35.40 ± 0.76 *, **, ****	17.92
PE-H2	33.21 ± 0.17 *	10.63
PEMA-H	35.09 ± 0.91 *, ***	16.89
PEMA-H1	37.33 ± 1.04 *, **, ****	24.35
PEMA-H2	36.06 ± 0.45 *	20.12

(B) Percentage increase of tensile strength of HDPE composite made with the various chemically treated hemp fibres.

\*Denotes a significant difference with virgin HDPE; \*\*Denotes a significant difference with none treated fibre composites; \*\*\*Denotes a significant difference with composites without compatibiliser; \*\*\*\*Denotes a significant difference with MA treated fibre composites.

The tensile strength of the composites shows a general increase when compared with virgin HDPE. The NaOH treated fibres yielded the most promising results. In the case of a combined treatment with NaOH and MA, the average tensile strength of the fibres decreased compared to that of alkali only treated fibres. The

increase in tensile strengths of NaOH treated fibre composites originate from the removal of non-cellulosic components found at the surface of individual fibres as indicated in FTIR analysis. Removal of this material reduces the fibres' density and rigidity in the interfibrillar region making the fibrils more capable of rearranging themselves during stretching (Bledzki and Gassan, 1999, Kalia *et al.*, 2009). Conversely the treatment of the fibres with MA had a detrimental effect on the tensile properties of the composites. This is most likely due to the weakening of interfibrillar spaces of the cellulose in the presence of acetone. Weakening of interfibrillar interaction in MA treated fibres always had adverse effect on the stress transfer between fibrils, thereby, on the overall stress development in fibres under tensile deformation (Mwaikambo and Ansell, 2006, Sawpan *et al.*, 2011b). The addition of the compatibiliser HDPE-g-MA significantly increases the tensile strength of the composites when compared with composites containing no compatibiliser. This indicates that the presence of HDPE-g-MA has increased the interfacial attraction between the HDPE and natural fibre (Gunning *et al.*, 2012). This increased interaction between the polymer and filler results in a large increase in tensile strength value.

#### Flexural Properties:

A three point bending test was used to examine the flexural properties of the polyethylene composite materials. The percentage improvement in flexural modulus calculated from the data collected during three point bending tests on the composite samples is shown in Table 4.

For HDPE-flax composites, flexural modulus varied from 0.825 GPa to 1.030 GPa. For HDPE-hemp composites, flexural modulus varied from 0.832 GPa to 0.985 GPa. Results showed that all the flax and hemp composites had a significantly higher flexural modulus than virgin HDPE ( $p \leq 0.01$ ).

The addition of the compatibiliser into the NaOH treated fibres (PEMA-F1) had a significant higher flexural modulus than the one without (PE-F1) ( $p \leq 0.03$ ). Similarly, treatment of fibres with NaOH solution followed by MA solution (PE-F2) had a significantly higher flexural modulus than the one without MA treatment (PE-F1) ( $p \leq 0.05$ ).

**Table 4:** Flexural modulus of HDPE composites made with the various chemically treated fibres.

Batch	Flexural modulus	% Improvement
	Mean $\pm$ SD	
PE	774.83 $\pm$ 12.45	0
PE-F	883.60 $\pm$ 33.41 *	14.04
PE-F1	871.33 $\pm$ 33.72 *, ****	12.45
PE-F2	966.33 $\pm$ 43.06 *	24.72
PEMA-F	864.00 $\pm$ 26.44 *	11.51
PEMA-F1	921.17 $\pm$ 48.21 *, ***	18.89
PEMA-F2	935.67 $\pm$ 27.54 *	20.76

(A). Flexural modulus of HDPE composite made with the various chemically treated flax fibres

Batch	Flexural modulus	% Improvement
	Mean $\pm$ SD	
PE	774.83 $\pm$ 12.45	0
PE-H	899.50 $\pm$ 50.98 *	16.09
PE-H1	959.60 $\pm$ 17.09 *	23.85
PE-H2	973.00 $\pm$ 9.97 *	25.58
PEMA-H	895.50 $\pm$ 60.19 *	15.57
PEMA-H1	959.00 $\pm$ 12.96 *	23.77
PEMA-H2	964.25 $\pm$ 15.52 *	24.45

(B). Flexural modulus of HDPE composite made with the various chemically treated hemp fibres.

\*Denotes a significant difference with virgin HDPE; \*\*\*\* Denotes a significant difference with MA treated fibre composites.

The results clearly show the reinforcing effect of the natural fibres on the polymer matrix in flexion. Also, it shows that the surface treatments of the fibres had a significant effect on the flexural modulus. It is apparent that the fibres induce a large improvement in the stiffness of the polymer composite matrix. The addition of the compatibiliser into the NaOH treated fibres also had positive effect on flexural modulus. Treatment of fibres with NaOH solution followed by compounding with MA compatibilized HDPE had a significantly higher flexural modulus than the one without MA treatment. This indicates that the presence of MA and chemical treated flax fibre generally increases the interaction between the HDPE and flax fibre resulting in a better dispersion of the fibres and better adhesion between the fibres and the polymer (Dányádi *et al.*, 2007).

#### Impact Properties:

For HDPE-flax composites, impact strength varied from 14.20 MPa to 25.84 MPa (Table 5). Results showed that all the HDPE-flax composites had a significantly lower impact strength than virgin HDPE ( $p \leq 0.05$ ), except Batch PEMA-F, the addition of the compatibiliser HDPE-g-MA to non-treated flex fibre composite ( $p=0.064$ ). For HDPE-hemp composites, impact strength varied from 11.96 MPa to 25.12 MPa. All of HDPE-hemp composites had significantly lower impact strength than virgin HDPE ( $p \leq 0.002$ ).



**Table 5:** Impact strength of HDPE composites made with the various chemically treated fibres.

Batch	Impact strength	% Improvement
	Mean ± SD	
PE	29.52± 3.26	0
PE-F	16.89± 1.98 *	- 42.78
PE-F1	16.37± 1.37 *	- 44.55
PE-F2	16.41± 1.77 *	- 44.42
PEMA-F	19.17± 2.94	- 35.08
PEMA-F1	17.20± 1.40 *	- 41.73
PEMA-F2	16.12± 2.75 *	- 45.40

(A). Impact strength of HDPE composite made with the various chemically treated flax fibres.

Batch	Impact strength	% Improvement
	Mean ± SD	
PE	29.52± 3.26	
PE-H	16.10± 1.62 *	- 45.47
PE-H1	15.28± 3.29 *	- 48.25
PE-H2	17.35± 2.72 *	- 41.25
PEMA-H	15.43± 1.79 *	- 47.75
PEMA-H1	14.26± 2.18 *	- 51.69
PEMA-H2	16.66± 2.94 *	- 43.56

(B). Impact strength of HDPE composite made with the various chemically treated hemp fibres.

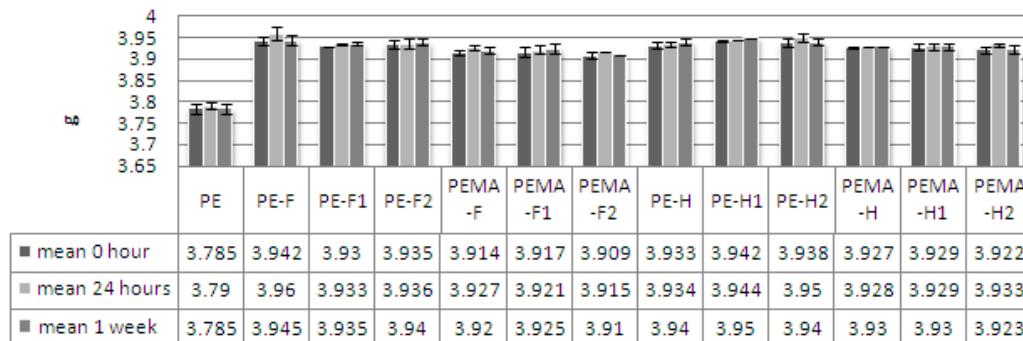
\*Denotes a significant difference with: virgin HDPE.

In terms of impact strength there was a general decrease in the impact properties of the composites was observed when compared with virgin HDPE. This may be due to the combined effect of the matrix embrittlement under impact load and the fibres restriction to matrix yielding. Other factors such as the fibre content and interlaminar, interfacial bond strength can also influence the impact strength of short fibre reinforced composites (Ruksakulpiwat *et al.*, 2009, Kalia *et al.*, 2009). This phenomenon is also reported by other researchers (Wambua *et al.*, 2003, Ruksakulpiwat *et al.*, 2009, Afrifah *et al.*, 2010). Afrifah *et al.* reported that the addition of natural fibres to plastic reduces the ductile behaviour of the matrix and makes the composites more brittle. It is well known that the impact properties of the polymeric material are directly related to the overall toughness of the material(Kalia *et al.*, 2009). Toughness means the ability of the polymer to absorb applied energy.

**Water Uptake:**

The major concern in relation to the use of natural fibres reinforced composite materials is their extreme sensitivity to water, which reduces their mechanical performances in a damp atmosphere. In the current the results from the water absorption analysis as a function of the immersion time for HDPE-based composites reinforced with 10 wt. % natural fibres is shown in Figure 7

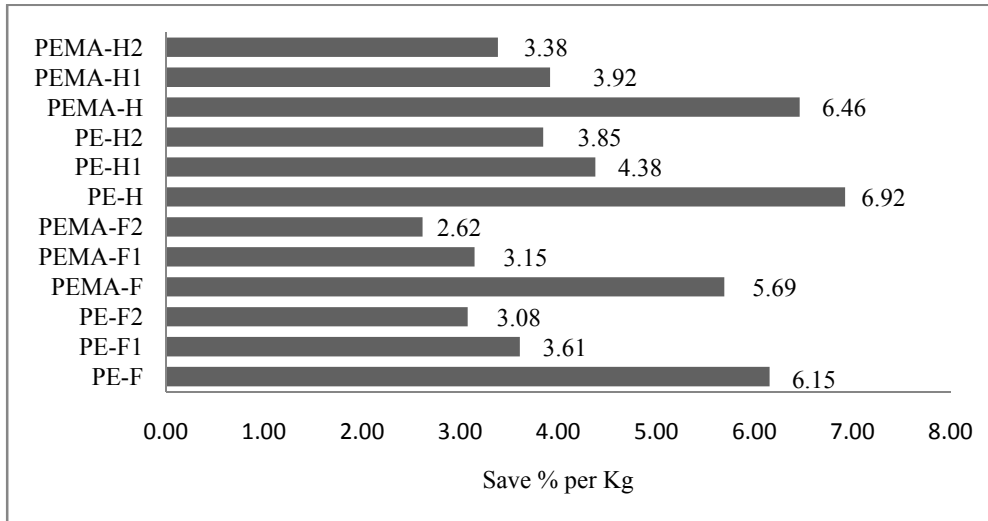
For all composites, water absorption analysis indicated that the weight of composites was not significantly affected following immersion in water for 1 or 7 days at room temperature ( $0.05 \leq p \leq 1$ ). This indicates that the addition of the 10% Flax and Hemp fibre had a marginal effect on water uptake. It seems therefore that the covalent bonding between the fibres and the matrix could play an important role in reducing the water absorption by the composite (Abdelmouleh *et al.*, 2007).



**Fig. 7:** Weights of HDPE composites materials after immersion in water for 0 hour, 24 hours and 7 days at room temperature.

**Cost Analysis:**

The incorporation of natural fibres into HDPE reduces its cost by more than 6%. When the cost of fibre treatments is considered, these cost of the composites reduce to between 3 and 4.4% however when HDPE is first compatibilised with MA 3.1 to 6.5%. In all cases Hemp fibre composites yielded greater cost savings than the equivalent flax fibre composite (Figure 8).



**Fig. 8:** Cost comparison of composite materials compared with virgin HDPE.

As the raw materials used in the production of HDPE-g-MA are relatively expensive, the use of these compatibilisers in the production of HDPE natural fibre composites does affect the final price. As shown in Figure 8, the percentage saving per kg decreases upon addition of HDPE-g-MA. The price differences are however still substantial when compared with virgin HDPE. As hemp and flax also offer the greatest reinforcement they may make the end product more economical as smaller parts could fulfil the required function. The limitation of the cost calculation is the extra labour and energy costs were not taken into account. However these vary considerably between producers and users therefore the extra costs were ignored.

**Conclusions:**

This study investigated the effects of chemical treatments and HDPE-g-MA on the physical and mechanical behaviour of HDPE/ natural fibre composites. The results of this study indicate that

1. The use of chemical treatments and HDPE-g-MA significantly increased the tensile strength and flexural modulus of HDPE/ natural fibre composites. Conversely, there was a significant decrease of impact strength found for all composites in comparison to the virgin HDPE.
2. The addition of the HDPE-g-MA and chemical treated fibre significantly increased themelt flow index. However no significant different were detected on water uptake between untreated composites and treated composites indicating that these materials could be used as a direct replacement for HDPE in applications where impact strength is no a critical factor.
3. The use of HDPE-g-MA and chemical treatments does affect the final price. Nevertheless, as natural fibre reinforcement does offer increased tensile properties, this may make the end product more economical as lower wall thickness parts can be used to fulfill the same function.

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