Enhancement of mechanical properties and interfacial adhesion by chemical modification of natural fibre reinforced polypropylene composites

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Abstract

Natural fibres are often used for reinforcing thermoplastics, like polypropylene, to manufacture composite materials exhibiting numerous advantages such as high mechanical properties, low density and biodegradability. The mechanical properties of a composite material depend on the nature of the fibres, the nature of the matrix and on the adhesion between fibre and the polymer matrix. The main problem with these natural fibres is their hydrophilic nature, which gives them poor compatibility with the polymer matrix. Therefore, the constituents need to be chemically modified to enhancing adhesion between fibre and polymer matrix. The aim of this work is to improve the interfacial adhesion between the polypropylene matrix and the natural fibre, to improve their mechanical properties. Various chemical treatments with acrylic acid, 4-pentanoic acid, 2,4-pentadienoic acid and 2-methyl-4-pentanoic acid were investigated. The natural fibre reinforced polypropylene composites were processed by compression moulding using a film stack method. The mechanical properties of these modified composites like tensile, flexural and impact strength were analysed and compared. It was found that all these properties are dependent on the amount and kind of chemical treatment. SEM studies revealed that in chemically treated composites the fibres were less inclined to pull out of the matrix which indicates a good interfacial adhesion.

1. Introduction

The use of natural fibre as reinforcements in thermoplastic polypropylene composites offers an environmentally friendly alternative to glass-fibre reinforced plastics in some technical applications.

The main advantages of using natural fibres in composites materials are: they have high strength per unit weight, are process-friendly, have lower specific weight (density), are biodegradable and have good thermal and acoustic insulation properties (de Bruijn, 2004 and van de Velde & Kiekens, 2001). However, some disadvantages such as variable quality (depending on unpredictable influences such as weather and moisture absorption), low maximum processing temperatures, poor fire resistance and incompatibility with hydrophobic polymer matrix can limit their potential use as reinforcements in polymer composites for industrial application (Wambua, Ivens & Verpoest, 2003). The incompatibility is due to the high hydrophilic property of natural fibre, which is composed of cellulose and ligno-cellulose, which contains strongly polarised hydroxyl groups (Baley, 2002).

Since the final mechanical behaviour of the composite material depends to a great extent on the interfacial adhesion between the reinforcing natural fibre and the surrounding polymer matrix (Cantero *et. al.*, 2003), it is necessary to evaluate the interfacial adhesion.

Various chemical treatments can improve the interfacial adhesion between the natural fibre and the polymer matrix (Bisanda & Anshell, 1991, Misha, Naik & Patil, 2000 and Bessabok *et. al.*, 2008). Grafting copolymers of polypropylene and maleic anhydride is known to be very effective in improving the interfacial adhesion. Much research has gone into the use of maleic anhydride-polypropylene copolymer (MAPP) (Misha, Naik & Patil, 2000, Gauthier *et. al.*, 1998 and Arbelaiz *et. al.*, 2005). The effectiveness of MAPP is due to better compatibility (Arbelaiz *et. al.*, 2005), and the ability of MAPP to decrease the amount of hydrogen bonding between the fibres (Kazayawoko *et. al.*, 1997), and rather form covalent bonding between hydroxyl groups of the cellulosic fibre and the anhydride groups of the maleic anhydride (Rana *et. al.*, 1998).

Figure 1 illustrates how MAPP binds the cellulosic fibre and polypropylene. It can be seen that a double bond is needed to bind to the polypropylene and a carboxylic acid is needed to bind to the cellulosic fibre. Thus in this work chemicals which contains the

two functional groups (acrylic acid, 4-pentanoic acid, 2,4-pentadienoic acid and 2-methyl-4-pentanoic acid) will be used as coupling agents in the treatment of the polypropylene. The acrylic acid content will be varied to find the optimum conditions to be used, which gives the highest mechanical performance (flax nonwoven was used as reinforcement). Using the optimum acrylic acid content for the polypropylene modification, the fibre loading and kind of fibre (kenaf, flax, hemp, agave and sisal) will be varied. The mechanical properties including tensile, flexural and impact strength will be evaluated and compared. The tensile fracture surfaces of the chemically modified composites were further investigated by SEM to learn more about the fibre matrix interaction. The thermal behavior of the composites was also investigated.
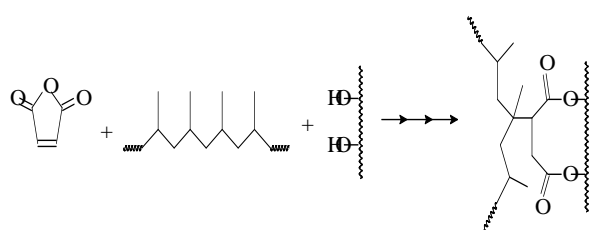

Figure 1 Schematic representation of the reaction, where maleic anhydride is used as a coupling agent between the polypropylene and the cellulosic fibre.

2. Experimental

2.1. Materials

Polypropylene sheets were supplied by Ampaglas (South Africa). Flax, hemp, sisal and agave fibres of South African origin, and kenaf fibres from Bangladesh were processed into nonwovens by needle-punching on the pilot plant line at CSIR in Port Elizabeth. The chemicals were purchased from Sigma-Aldrich and used as received.

2.2. Composite preparation

The composite preparation starts off with the modification of the polypropylene sheet. This is followed by the compression moulding using a film stacking method of layers of polypropylene sheets and flax nonwovens.

2.2.1. Modification

2.2.1.1. Acrylic acid grafted polypropylene

A solution of acrylic acid (n[*] % by weight of the PP) and dicumyl peroxide (0.1n % by weight of the PP) in 20 ml tetrachloroethylene was sprayed over polypropylene sheets. These sheets were stacked on each other between glass plates to prevent evaporation. Subsequently it was placed in an oven at a temperature of 125°C for 2h under weight to prevent the PP sheet from curling and accumulating the reaction mixture in one place.
[*]n = 1, 2 or 4.

2.2.1.2. Other polypropylene modifications

Modification with 4-pentanoic acid and 2-methyl-4-pentanoic acid is the same as the acrylic acid treatment. When modifying with 2,4-pentadienoic acid, it is dissolved in a mixture of toluene, aniline and methanol (1:1:1, 20 ml). The rest of the procedure is the same as that for acrylic acid.

2.2.2. Composite processing

Composites were processed by stacking sheets of modified polypropylene between sheets of nonwoven batting (the amount of sheets varied as the % fibre was desired). The material was then wrapped in a Teflon sheet, secured with tape and was further wrapped in aluminium foil. The composite was processed by pressing the material between two hot plates of a compression moulding press at 210°C for 30 min at 35 bar pressure on the material. Cooling of the sample was allowed at the same pressure by running cold water for 3 min to prevent void formation due to recrystallization of the polymer.

2.3. Mechanical Analysis

An Instron model 3300 testing machine was used to investigate the tensile and flexural properties of the composites. Samples were tested as per ISO 178-1975 (E) for flexural testing and ISO R527 for the tensile testing. The modulus, strain and strength were calculated from the stress-strain curves. The Instron Dynatup testing machine was used to investigate the charpy impact strength (unnotched) of the composites. The samples were tested as per ISO 179-1982 (E) for the impact testing.

3. Results and Discussion

3.1. Chemical modification of polypropylene with acrylic acid

The modification of polypropylene is a quick and easy reaction. Grafting of acrylic acid onto polypropylene is initiated by peroxide radicals. The peroxide grafting of the acrylic acid occurs at the tertiary carbons of the polymer chain or at the terminal unsaturated part of the chain. The proposed mechanism for the acrylic acid grafting onto polypropylene and binding to the cellulose is given in Scheme 1. Peroxides undergo homolytic cleavage at the oxygen-oxygen bond to form radicals when heated. The radicals extract hydrogen atoms, preferably from the tertiary carbon of the polymer chain, leading to the creation of the new reactive sites, which are expected to be reactive with other monomers or, as in this case, with acrylic acid. A drawback of this process is that, as the polymer is grafted with acrylic acid, the molecular weight is lowered due to chain degradation via the ß-scission reaction which results in reduction in viscosity.
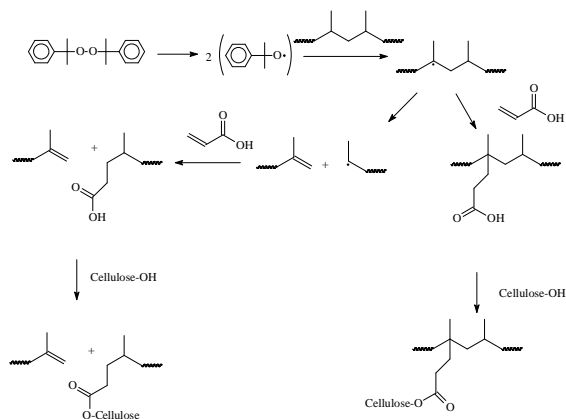
Scheme 1 Proposed mechanism of interaction between acrylic acid and polypropylene.

To verify the grafting of acrylic acid onto the polypropylene, infra-red spectra were recorded and compared as shown in Figure 2. In the spectra of the modified polypropylene, peaks appeared at 3000-3600 cm^{-1} (with mean at $\pm$ 3300 cm^{-1}) which is the area where OH groups from carboxylic acids are, and 1600-1800 cm^{-1} , the area where carbonyl peaks of carboxylic acids are, thus an indication of the presence of carboxylic acid. From the schemes proposed by other researchers (Park et. al., 2006 and Lu & Chung, 2000), it is shown that the double bond of the acrylic acid binds to the polypropylene. We may assume that the acrylic acid formed a covalent bond to the polypropylene and did not merely adsorb onto the surface of the polypropylene, seeing as the area 1400-1600 cm^{-1} (this is the area

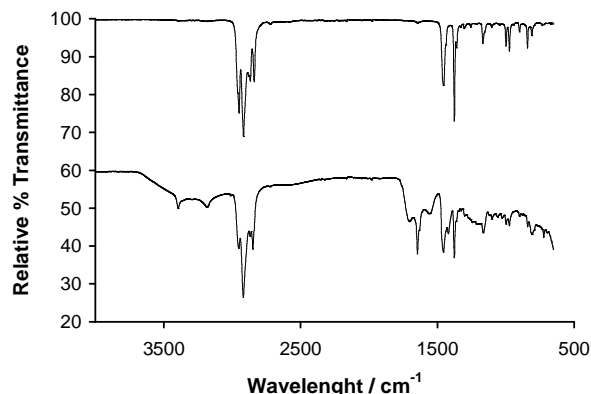were the C=C appears) has not changed much, which would have been an indication of adsorbed double bonds.

Figure 2 Infra-red spectra of unmodified polypropylene (top) and acrylic acid modified polypropylene (bottom).

3.2. Mechanical properties (acrylic acid grafted polypropylene composites, flax reinforced)

The data for the mechanical properties are given in Table 1 and Figures 3-5. Both tensile strength and modulus increases, with the increasing acrylic acid content up to 2% where a maximum is achieved, and then decreases with the further increase in acrylic acid content. The same is observed for the flexural modulus, the flexural strength showed a different result. Addition of 1% acrylic acid as coupling agent causes a decrease in flexural strength, but as the amount of the acrylic acid increase, there is an increase in flexural strength. A possible explanation for this behaviour may be attributed to some experimental variations as well as insufficient amount of acrylic acid available to graft on all available anchoring bonds on the PP, which may have led to only partial modification. However, as the amount of acrylic acid increased, the benefit of the coupling between the polymer matrix and the fibre comes into play and the stress is transferred from the matrix to the fibre more effectively. Thus the optimum chemical treatment for this composite content and procedure is 2% acrylic acid weight with respect to the polypropylene mass.

The improvement in tensile strength and tensile and flexural modulus is due to the increased interfacial interaction between the fibres and the polypropylene. This causes enhanced stress

transfer from the matrix to the fibre through the acrylic acid linkage. The drop in modulus and tensile strength at the higher concentration could possibly contribute to damage caused to fibre, instead of causing coupling. Another possible explanation could come from the increased use of peroxide during the 4% acrylic acid modification, which causes an increase in ß-scission as shown in Scheme 1. The decrease in molecular weight of the polypropylene could cause the composite strength to decrease.

The addition of acrylic acid to the matrix has a negative effect on the charpy impact strength. As the amount of acrylic acid increased, the composites showed a reduction in impact strength. This result is consistent with the findings reported, namely that good interaction between fibre and matrix leads to poor impact strength (Sain, 2005). This might suggest that the acrylic acid causes good interfacial interaction.
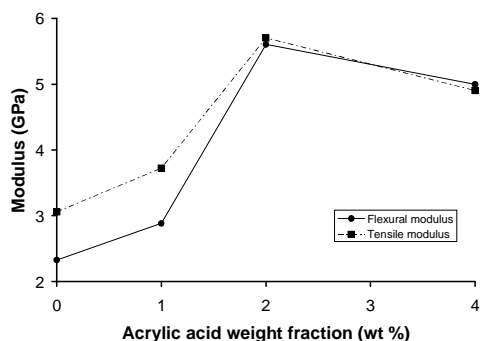

Figure 4 Effect of acrylic acid content on the tensile and flexural strength of the flax nonwoven reinforced polypropylene composite with 35% flax by weight.
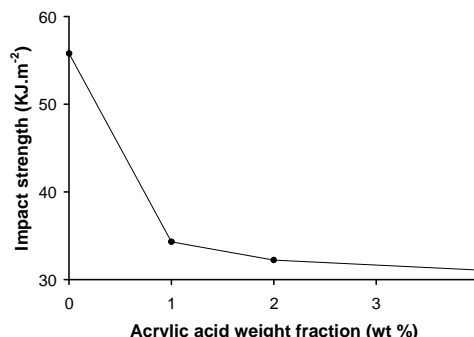
Figure 5 Effect of acrylic acid content on the flexural strength of the flax nonwoven reinforced polypropylene composite with 35% flax by weight.

Table 1 Mechanical data for flax nonwoven reinforced polypropylene composites, where the polypropylene was treated with different chemicals.

Modification	Tensile		Flexural		Impact
	Tensile strength (MPa)	E-modulus (GPa)	Flexural strength (Mpa)	Flexural Modulus (GPa)	Charpy impact strength (kJ/m^2)
Standard	47.7 (±3.5)	3.0 (±0.5)	51.7 (±3.3)	2.3 (±0.3)	55.8 (±6.4)
Acrylic acid 1%	56.9 (±4.5)	3.7 (±0.2)	39.5 (±8.3)	2.8 (±0.4)	34.3 (±10.3)
Acrylic acid 2%	77.5 (±5.3)	5.7 (±0.3)	54.3 (±6.2)	5.6 (±0.7)	32.2 (±4.3)
Acrylic acid 4%	68.7 (±7.9)	4.9 (±0.1)	64.7 (±8.2)	4.9 (±0.4)	31.0 (±2.5)
4-Pentanoic acid 2%	62.6 (±5.1)	4.1 (±0.3)	44.9 (±1.8)	3.4 (±0.2)	27.1 (±12.1)
2-Methyl-4-pentanoic acid 2%	62.0 (±4.5)	4.0 (±0.2)	33.0 (±4.3)	2.9 (±0.4)	26.4 (±5.1)
2,4-Pentadienoic acid 2%	70.4 (±3.8)	6.5 (±0.2)	38.7 (±3.4)	2.9 (±0.7)	53.4 (±3.6)

3.4. Acrylic acid 'like' chemical modification

The proposed chemical interaction between the fibre, coupling agent and polypropylene is shown in Scheme 2. The double bond (of the coupling agent) acts as the anchoring point for the polypropylene and the carboxylic acid (of the coupling agent) ultimately forms the ester linkage to the cellulose.

Figure 3 Effect of acrylic acid content on the tensile and flexural modulus of the flax nonwoven reinforced polypropylene composite with 35% flax by weight.
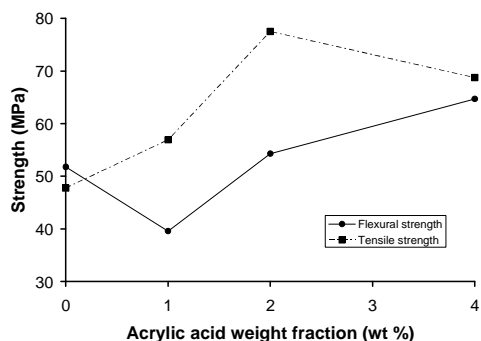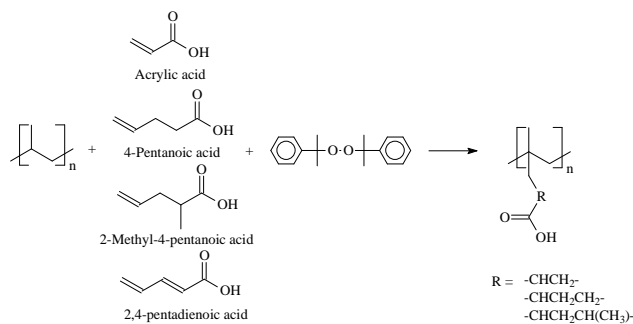

4

Scheme 2 Schematic representation of the chemical interaction between the fibre, coupling agent and the polypropylene.

An acrylic acid content of 2% weight with respect to polypropylene weight gave the best results (see Table 1). Therefore the 2% coupling agent by the weight of polypropylene was used in the subsequent experiments where acrylic acid was replaced with 4-pentanoic acid, 2,4-pentadienoic acid and 2-methyl-4-pentanoic acid.

Figures 6-8 show the effect of different matrix modifiers on the tensile, flexural and impact properties respectively, for the flax reinforced composites studied. The data is summarized in Table 1.
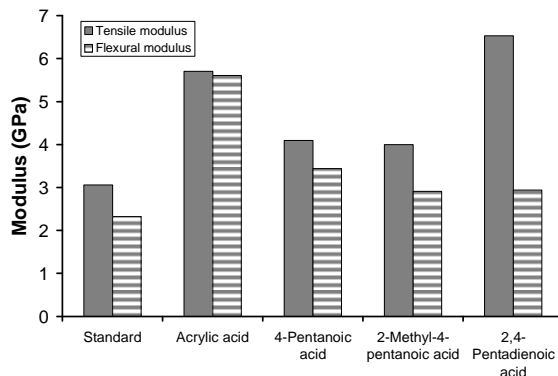

Figure 6 Tensile and flexural modulus of different chemical treatments in flax reinforced polypropylene composites.
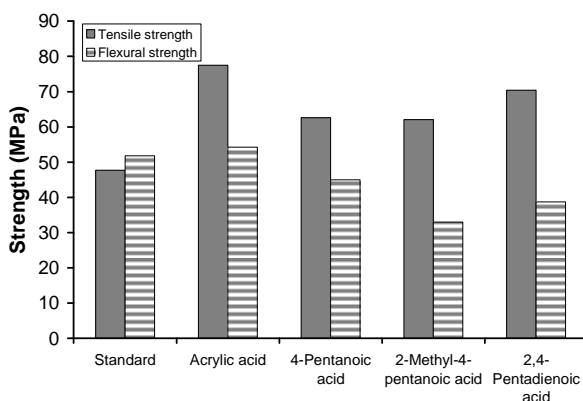

Figure 7 Effect of different chemical modifications on tensile and flexural modulus of flax reinforced polypropylene composites.

All chemically modified composites revealed an improvement in tensile and flexural modulus in comparison to the unmodified composite. The 2,4-pentadienoic acid modified composite showed the highest (6.5 GPa) tensile modulus while the 2-methyl-4-pentanoic acid modified gave the lowest (4.0 GPa). The acrylic acid gave the highest flexural modulus (5.6 GPa) with 2-methyl-4-pentanoic acid again showing the lowest modulus (2.9 GPa). When the chemical structure of the coupling agent is changed by the addition of two extra carbon atoms between the carboxylic acid and the double bond, there is a perceptible decrease in tensile modulus (acrylic acid to 4-pentanoic acid). 4-Pentanoic acid and 2-methyl-4-pentanoic acid gave similar tensile modulus of about 4 GPa. This means that the

5

addition of a methyl group in a coupling agent does not really influence the tensile modulus. However, when an extra double bond is included in the chemical structure of 2,4-pentadienoic acid as coupling agent, it leads to an increase in tensile modulus. This means that the extra double bond provides an extra affinity for bonding to the polypropylene matrix, and thus more effective transfer of tensile stress from the polymer matrix to the fibre reinforcement occurs.

The flexural moduli of 4-pentanoic acid, 2,4-pentadienoic acid and 2-methyl-4-pentanoic acid were about 3 GPa, however slightly higher in the case of 4-pentanoic acid. It can thus be concluded that the increase in chain length (of two carbon atoms, from acrylic acid to pentanoic acid) between the carboxylic acid and the double bond functional groups in the coupling agent causes a lowering in flexural modulus. The same was observed in the case of tensile modulus. However, it can also be observed that additional changes to the coupling agent like the addition of a methyl group or extra double bond does not really influence the flexural modulus.
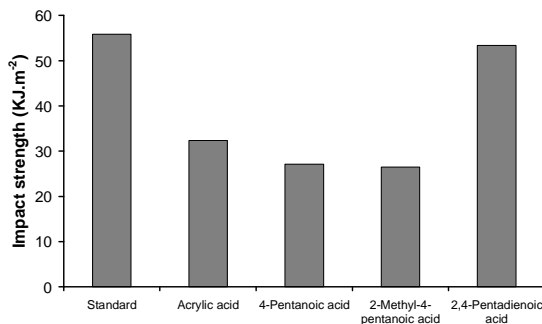

Figure 8 Effect of different chemical modifications on impact strength of flax nonwoven reinforced polypropylene composites.

The impact strength of all the chemically modified composites showed a decrease in comparison to the unmodified composite as shown in Figure 8. The composite modified with 2,4-pentadienoic acid showed the highest impact strength (53.4 kJ.m^2), which is comparable to that obtained in glass reinforced composites (54 kJ.m^2) (Jang & Lee, 2000).

Figure 9 shows the SEM photomicrographs of the tensile fracture surface of the unmodified, the 2% acrylic acid treated and 2,4-pentadienoic acid treated composites at 90 x magnification. The

unmodified composite displayed poor interfacial adhesion as evident from many clean fibre surfaces and empty holes resulting from fibre pull-out, as shown in Figure 15(a). It is also consistent with the mechanical properties of the unmodified composite (Table 1), which showed poorer tensile and flexural properties and better impact strength than the modified composites. Better fibre matrix adhesion is seen in the case of composite modified with acrylic acid and 2,4-pentadienoic acid (Figure 15b, 15c), which is indicated by the fibres being well encapsulated by the polypropylene matrix. Thus the fibres did not pull out of the polymer matrix but the composites yielded mainly due to matrix failure, implying that the interfacial adhesion between the fibre and the matrix is good. This observation is substantiated by the mechanical properties obtained as shown in Table 1, where the chemically modified composites showed better tensile and flexural properties than the unmodified composite. Fibre fracture is common for high interfacial bonding, while a weak interfacial bonding is associated with fibre pull-out (Wambua, Ivens & Verpoest, 2003). From the good tensile and flexural properties and the visual observation of SEM photomicrographs, we can assume that good interfacial bonding is imparted by some of the chemical modifications of PP studied.
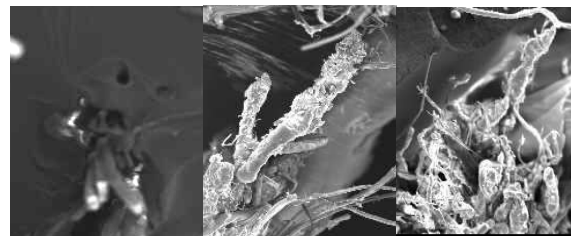

Figure 9 Tensile fracture surface of unmodified (left), acrylic acid treated (middle) and 2,4-pentadienoic acid treated (right) flax reinforced polypropylene composites.

3.4. Use of different fibres as reinforcement of acrylic acid grafted polypropylene composites

Figures 10-12 show the respective mechanical properties of different fibres used to reinforce an acrylic acid modified polypropylene composite. The data is summarized in Table 3.
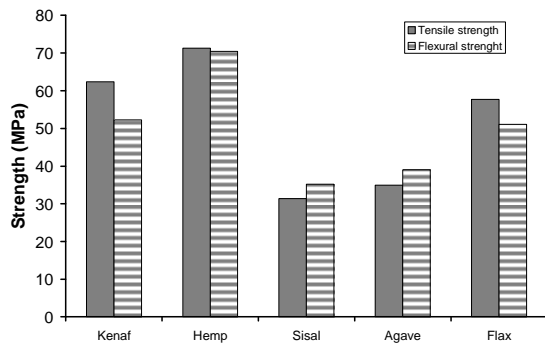
Figure 10 Effect of different fibres on the tensile and flexural strength of the acrylic acid modified polypropylene composite.

The hemp fibre composite showed the highest tensile strength (71 MPa) while sisal fibre composite showed the lowest (31 MPa). Agave fibre composite also showed poor tensile strength (37 MPa), while flax and kenaf fibre composites exhibited similarly good tensile strength (± 60 MPa).

Looking at the flexural strength, the hemp fibre composite gave the highest flexural strength (70 MPa), with flax and kenaf fibre composites giving similar flexural strength of about 52 MPa. Sisal fibre composites again gave the lowest strength (35 MPa) and agave not much stronger at 39 MPa. Other researchers have also found that hemp fibre composites gave the highest tensile and flexural strength (Wambua, Ivens & Verpoest, 2003).

The tensile and flexural modulus of the agave fibre composite was very low (1.4 and 1.0 GPa) compared to hemp reinforced composites which gave excellent tensile and flexural modulus (5.4 and 4.7 GPa). Sisal fibre composites also gave poor tensile and flexural modulus (2.4 and 1.6 GPa). Flax and kenaf fibre composites again gave similar good tensile and flexural modulus above 3 GPa.
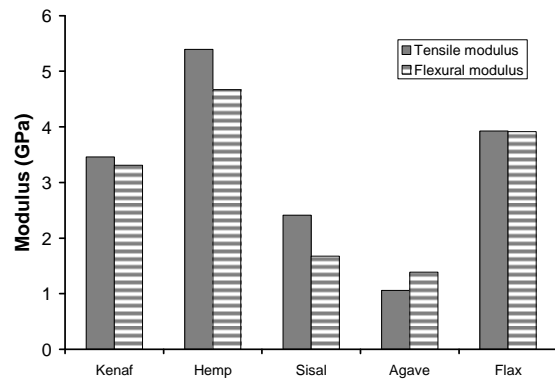

Figure 11 Effect of different fibres on the tensile and flexural modulus of the 5% acrylic acid modified polypropylene composite (±28% fibre loading).

The composites made from hemp, kenaf and sisal all displayed low impact strength < 20 kJ.m^{-2} (see Figure 12). Only agave and flax showed impact strength greater than 30 kJ.m^{-2}, which is still considered to be poor.
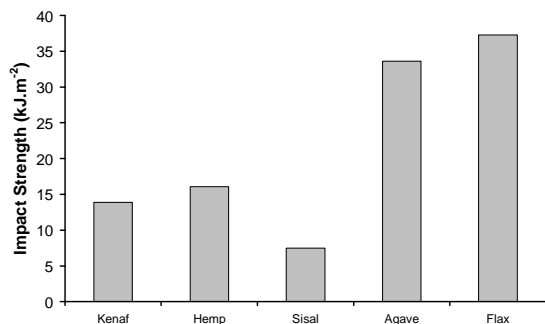

Figure 12 Effect of different fibres on the impact strength of the 5% acrylic acid modified polypropylene composite.

Due to good tensile and flexural properties and poor impact strength we can assume that the chemical modification in hemp and kenaf caused good interfacial bonding, but this can only be confirmed by scanning electron microscopy (SEM).

The SEM analysis of the fracture surfaces of the chemically modified composites after tensile testing has allowed us to evaluate the effect of the acrylic acid treatment of different fibres. The morphological observations of all the different fibres revealed good interfacial interaction, as deduced from the textured fibres. If the hydrophilic fibres had smooth surfaces,

7

it would show poor chemical compatibility with the hydrophobic polypropylene and lots of empty holes in the matrix. As can be deduced from Figures 13 and 14, the fibre reinforced composite shows good interfacial interaction, as deduced by the textured surface of the fibres, some encapsulated fibres and very few pull out "empty holes".
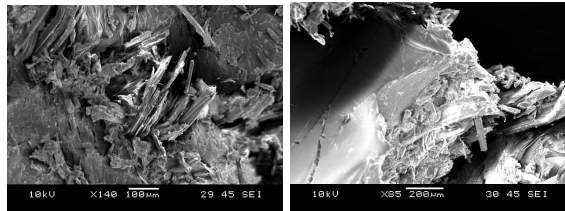

Figure 13 Tensile fracture surface of sisal (left) and flax (right) reinforced polypropylene composite.
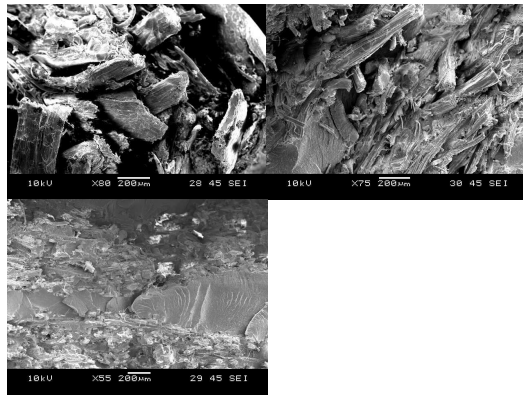

Figure 14 Tensile fracture surface of agave (top left), hemp (top right) and kenaf (bottom) reinforced polypropylene composite.

Table 2 Mechanical data for different fibres used in a 5% acrylic acid modified nonwoven reinforced polypropylene composites.

Fibre	Tensile		Flexural		Impact
	Tensile strength (MPa)	E-modulus (GPa)	Flexural strength (Mpa)	Flexural Modulus (GPa)	Charpy impact strength (kJ/m^2)
Kenaf	62.42 (±5.0)	3.46 (±0.3)	52.28 (±6.2)	3.31 (±0.6)	13.9 (±3.2)
Hemp	71.31 (±2.0)	5.39 (±0.1)	70.43 (±6.8)	4.67 (±0.1)	16.1 (±2.2)
Sisal	31.42 (±2.0)	2.41 (±0.2)	35.19 (±3.9)	1.67 (±0.2)	7.48 (±51.4)
Agave	34.92 (±2.4)	1.06 (±0.3)	39.02 (±3.3)	1.39 (±0.1)	33.6 (±11.8)
Flax	57.71 (±5.9)	3.92 (±0.1)	51.05 (±8.0)	3.92 (±0.3)	37.3 (±2.5)

4. Conclusion

The influence of the chemical modification of polypropylene with acrylic acid (in different concentrations), 4-pentanoic acid, 2-methyl-4-pentanoic acid and 2,4-pentadienoic acid on mechanical properties of flax nonwoven reinforced polypropylene has been investigated. The use of acrylic acid, 4-pentanoic acid, 2-methyl-4-pentanoic acid and 2,4-pentadienoic acid as coupling agent improved tensile and flexural properties of the composites by enhancing the adhesion between the flax and the polypropylene.

The optimum amount of acrylic acid is 2% which gave the best tensile and flexural properties. The 1% acrylic acid modification gave the best impact strength (of the acrylic acid content study), which was still poor compared to the unmodified composite.

Treatment with 2,4-pentadienoic acid gave the best tensile modulus, but the acrylic acid gave the best flexural modulus. For tensile and flexural strength the acrylic acid gave the best results, but for the impact strength the 2,4-pentadienoic acid gave the best results.

Of the different fibres used to reinforce acrylic acid modified polypropylene composite, hemp gave the highest mechanical properties, while agave and sisal registered the lowest mechanical properties.

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