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

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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 use of natural fibres has many advantages: high strength, low density, and biodegradable (De Bruijn, 2004 and Van de Velde *et. al.*, 2001). However, some disadvantages such as variable quality, poor fire resistance and incompatibility with hydrophobic polymer matrix limit their potential use in industrial application (Wambua *et. al.*, 2003). The incompatibility is due to the hydrophilicity of natural fibre, which is composed of cellulose that contains strongly polarised hydroxyl groups (Baley, 2002).

The mechanical behaviour of the composite depends to a great extent on the interfacial adhesion between the reinforcing fibre and the polymer matrix (Cantero *et. al.*, 2003). To improve this interfacial interaction, many chemical treatments can be used. The most popular is the maleic anhydride-polypropylene copolymer (MAPP) (Misha *et. al.*, 2000, Gauthier *et. al.*, 1998 and Arbelaiz *et. al.*, 2005).

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.

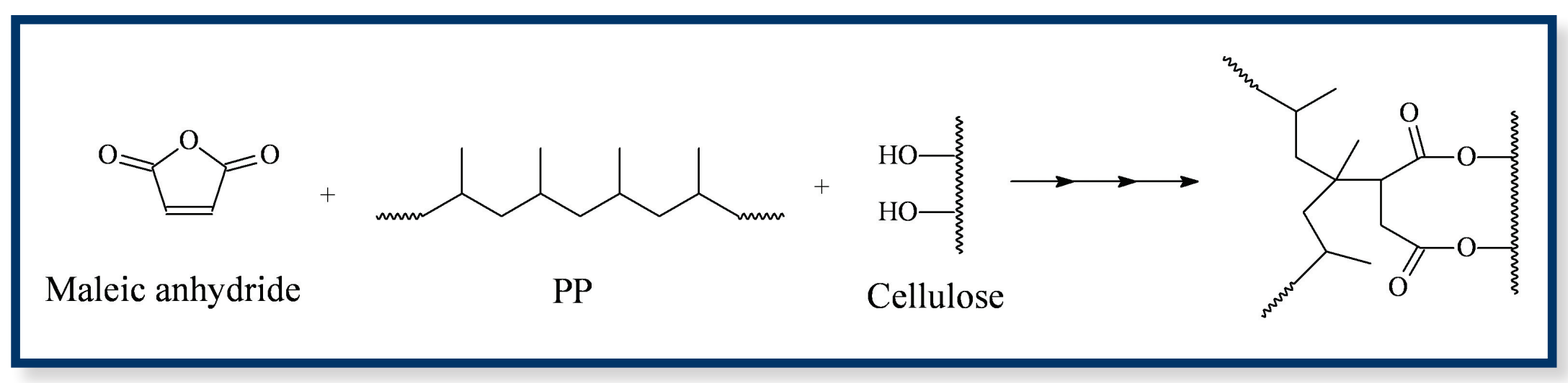


Figure 1: Schematic representation of the reaction, where maleic anhydride is used as a coupling agent between polypropylene and cellulosic fibre

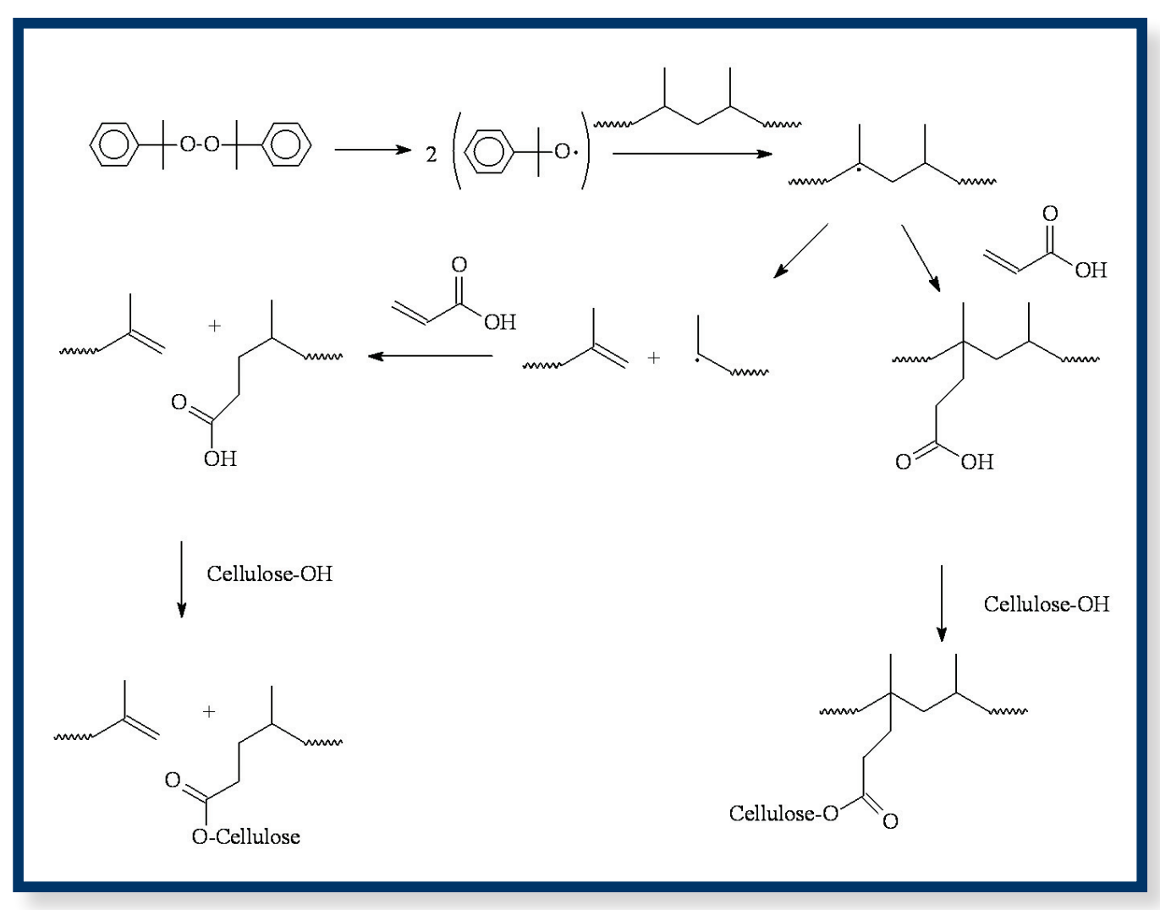
EXPERIMENTAL

Polypropylene sheets are grafted by either acrylic acid, 4-pentanoic acid, 2,4-pentadienoic acid or 2-methyl-4-pentanoic acid. Composites are processed by compression moulding using a film stacking method of layers of polypropylene sheets and flax nonwovens.

RESULTS AND DISCUSSION

Grafting of acrylic acid onto polypropylene is initiated by peroxide radicals. The proposed mechanism for the acrylic acid grafting onto polypropylene and binding to the cellulose is given in **Scheme 1**.

Verification of the grafting of acrylic acid onto the polypropylene comes from infra-red spectra as shown in **Figure 2**.



Scheme 1: Proposed mechanism of interaction between acrylic acid and polypropylene

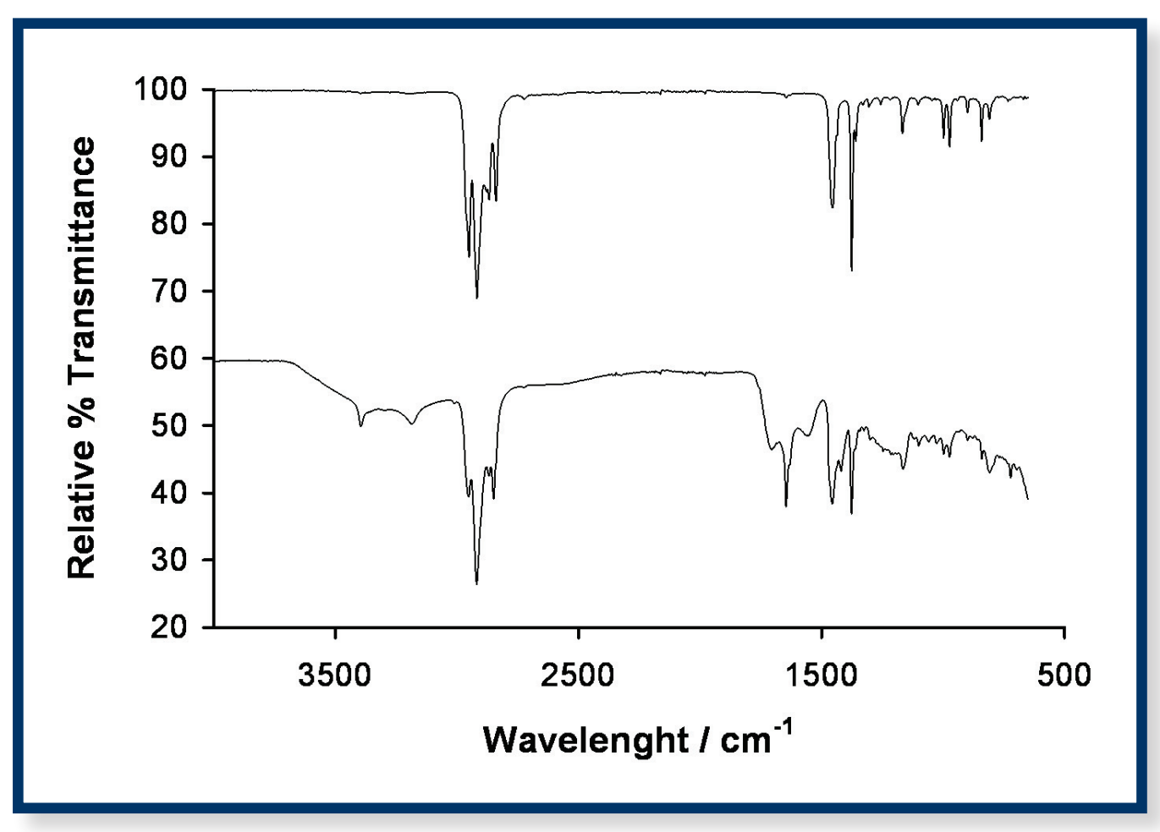


Figure 2: Infrared spectra of unmodified polypropylene (top) and acrylic acid modified polypropylene (bottom)

The data for the mechanical properties are given in **Table 1** and **Figure 3.** A maximum modulus is achieved at a 2% treatment.

The improvement in mechanical properties is attrbuted 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 be contributed to damage caused to the fibre or by increased ß-scission of the polypropylene.

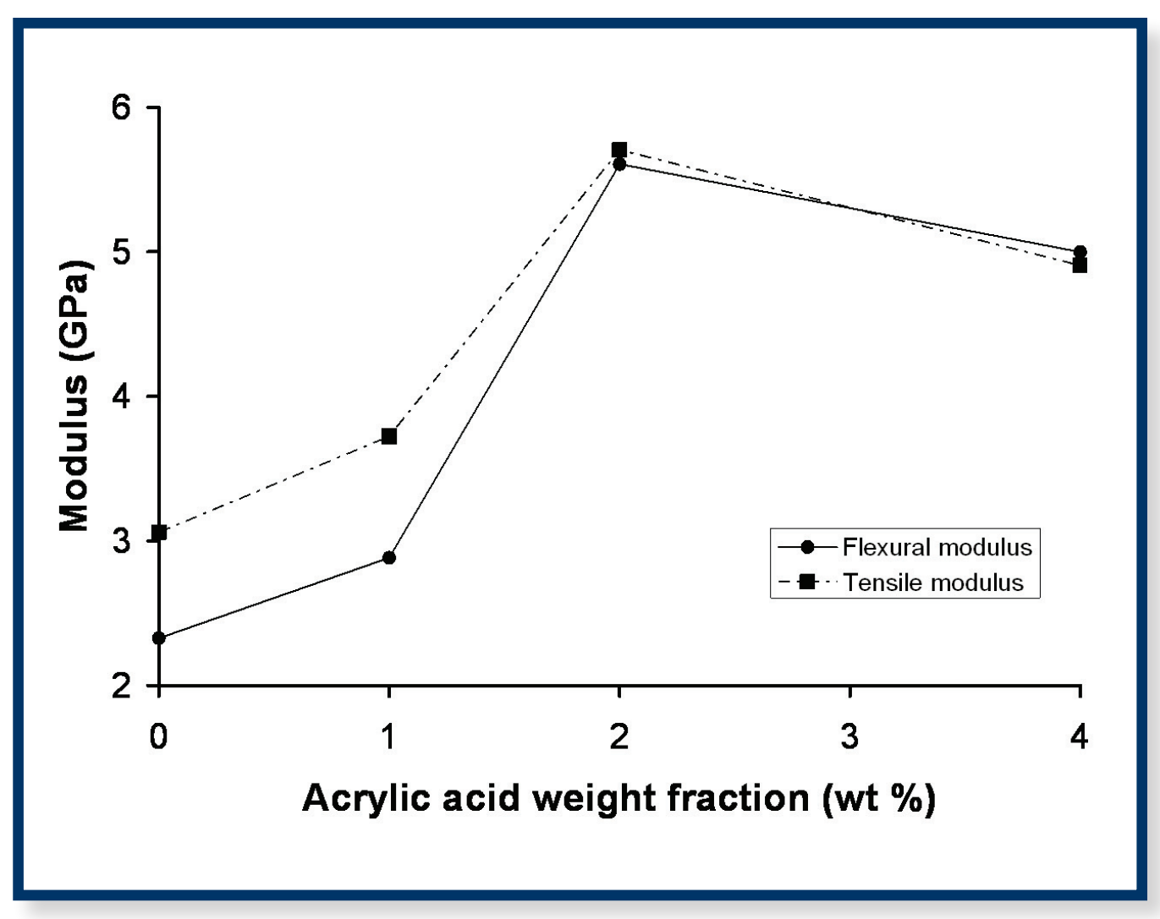


Figure 3: Effect of acrylic acid content on the tensile and flexural modulus of the flax-reinforced polypropylene composite

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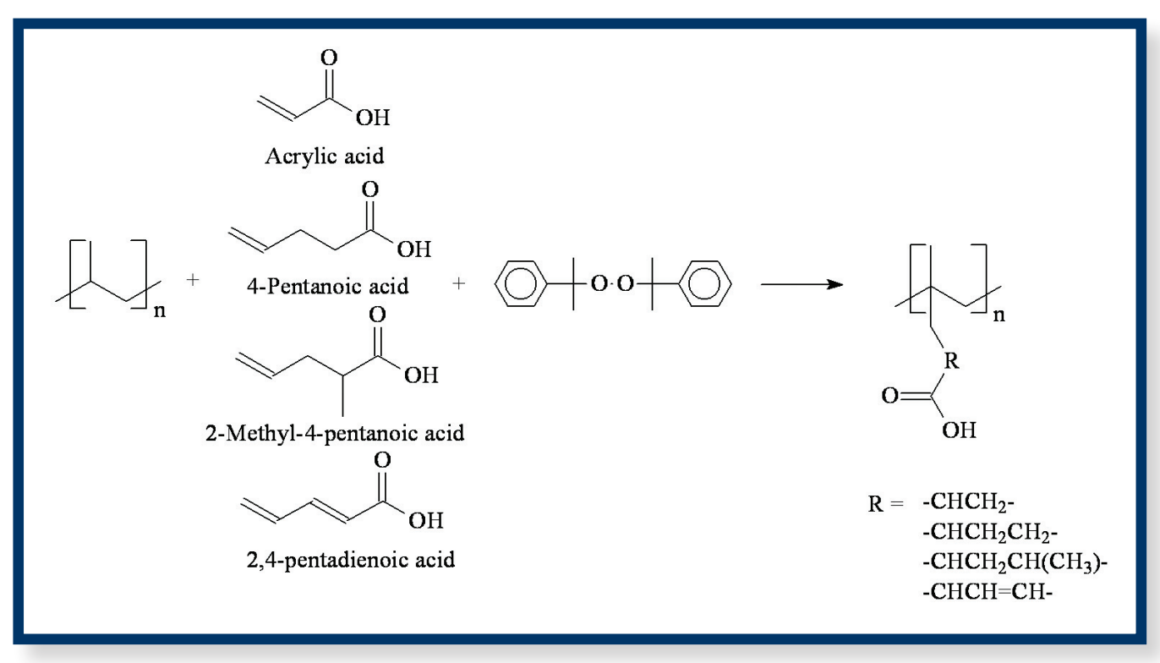
Table 1: Mechanical data for flax-reinforced polypropylene composites, where the polypropylene was treated with different chemicals

Modification	Tensile		Flexural		Impact
	Tensile strength (MPa)	E-modulus (GPa)	Flexural strength (Mpa)	Flexural modulus (GPa)	Charpy impact strength (kJ/m2)
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)

The proposed chemical interaction between the fibre, coupling agent and polypropylene is shown in **Scheme 2**.



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

Figures 4 and **5** show the effect of different matrix modifiers on the tensile, flexural and impact properties, respectively for the flax-reinforced composites studied. The data are summarised in **Table 1**.

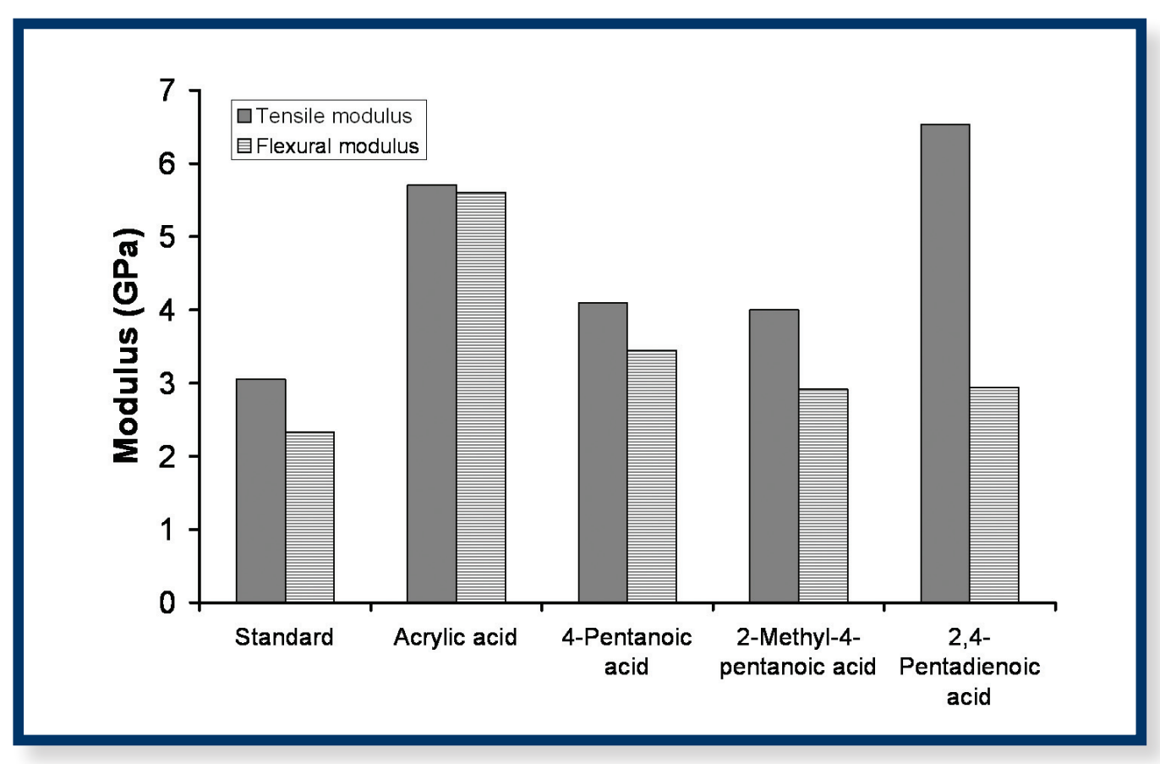


Figure 4: Tensile and flexural modulus of different chemical treatments in flax-reinforced polypropylene composites

All chemically-modified composites revealed an improvement in tensile and flexural modulus in comparison to the unmodified composite.

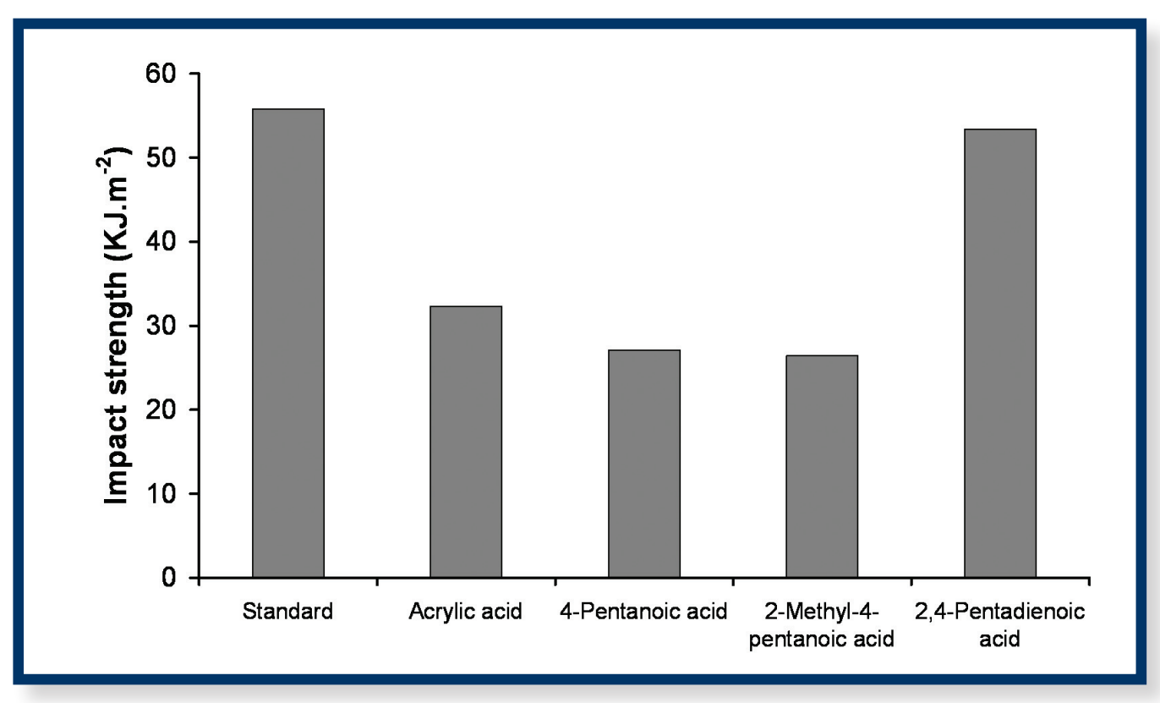


Figure 5: Effect of different chemical modifications on impact strength of flax-reinforced polypropylene composites

The impact strength of all the chemically-modified composites showed a decrease in comparison to the unmodified composite as shown in **Figure 5**. 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).

The SEM photomicrographs of the tensile fracture surface of some selected composites are shown in **Figure 6**. Good interfacial bonding is imparted by some of the chemical modifications of PP studied.

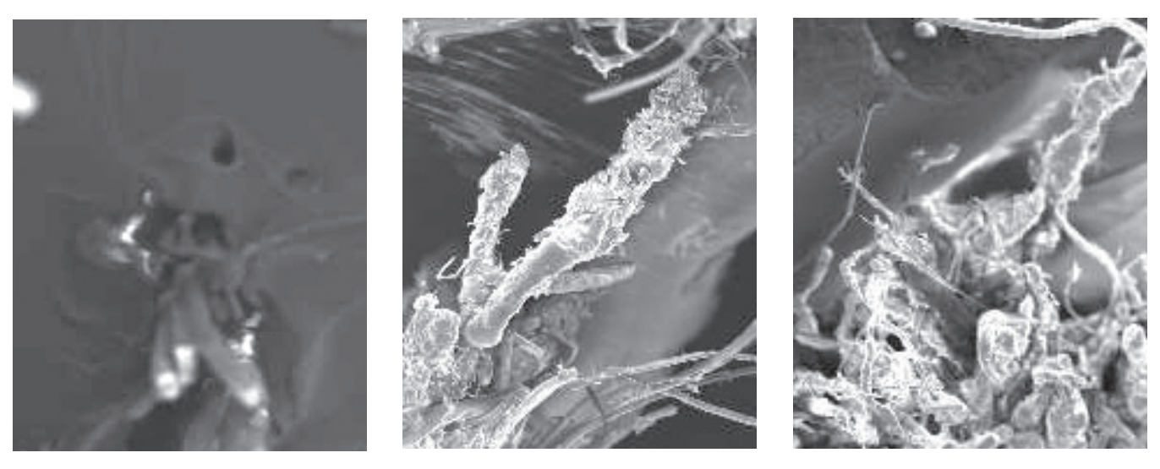


Figure 6: Tensile fracture surface of unmodified (left), acrylic acid (middle) and 2,4-pentadienoic acid treated (right) flax-reinforced polypropylene composites

Figure 7 shows the mechanical properties respectively of different fibres used to reinforce an acrylic acid modified polypropylene composite and the data are summarised in **Table 2**.

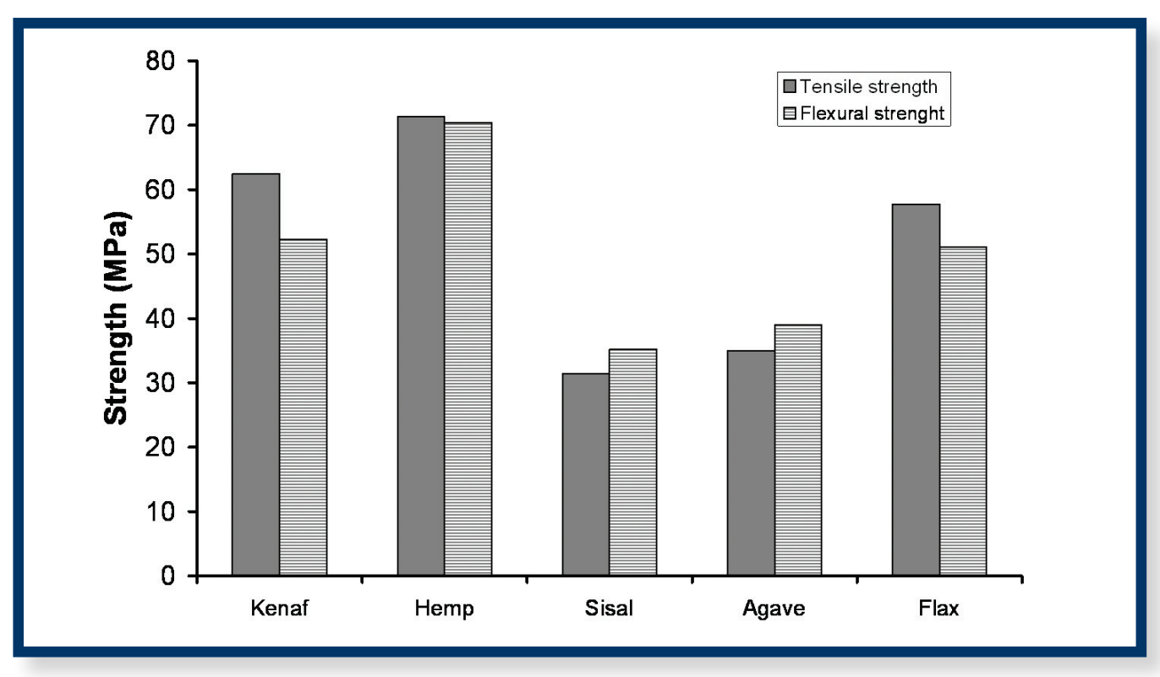


Figure 7: Effect of different fibres on the tensile and flexural strength of the acrylic acid modified polypropylene composite

The hemp fibre composite showed the highest tensile and flexural strength (71 MPa and 71 MPa) while sisal fibre composite showed the lowest (31 MPa and 35 MPa).

The tensile and flexural modulus of the agave fibre composite was very low (1.4 and 1.0 GPa) compared to hemp-reinforced composites that gave excellent tensile and flexural modulus (5.4 and 4.7 GPa).

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

CSIR researchers are investigating natural fibres as an environmental alternative for the automotive and aerospace industries.

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/m2)
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)

CONCLUSION

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.

Of the different fibres used to reinforce acrylic acid modified polypropylene composite, hemp gave the highest mechanical properties.

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