RTM HEMP FIBRE-REINFORCED POLYESTER COMPOSITES

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ABSTRACT

Hemp fibre-reinforced polyester composites were prepared using a Resin Transfer Moulding (RTM) technique and the flexural and impact behaviour investigated. Flexural stress at break and flexural modulus showed an increasing trend with fibre content. Impact strength was found to decrease at low fibre content, then gradually increase with further addition of fibres. A strong interfacial adhesion between hemp and polyester was obtained using chemically modified hemp. This modification consisted in introducing reactive vinylic groups at the surface of the fibres, via esterification of hemp hydroxyl groups, using methacrylic anhydride. Increased bonding between fibres and matrix did not affect the flexural stress at break of the composite but was detrimental to toughness. This behaviour was ascribed to a change in the mode of failure, from fibre pull-out to fibre fracture, resulting in a marked reduction in the energy involved in the failure of the composite, leading to a more brittle material.

INTRODUCTION

In the last few years, there has been growing interest in using plant fibres as reinforcement in polymer matrices. As economic and environmental pressures increase, the use of plant fibres as a substitute for synthetic fibres is worth considering. Advantages to using such fibres lie in their low cost, renewability, biodegradability, low specific gravity, abundance, and their high specific strength and stiffness.

Currently, a wide variety of agricultural species like straw, jute, bamboo, sisal or pineapple leaf, have been considered for use in the production of plant fibre-reinforced polyester composites (1-7). Although composites with increased mechanical properties were obtained (compared with neat resin), more basic research is required before plant fibres can compete with glass fibres, particularly in regard to impact behaviour. For instance, very little research has been done with hemp-polyester systems, although hemp is commonly quoted as being among the strongest and stiffest of the available agrofibres (8, 9).
Processing methods have also to be further developed to produce more efficient mixing systems, most of the samples studied in the literature being exclusively produced by wet hand layup or press-moulding techniques. Investigation into the utilisation of other techniques such as Resin Transfer Moulding (RTM) is rare (10). RTM is an industrially important process, used to produce thermosetting resin-based reinforced composites of all shapes, sizes and degrees of complexity. It's a flexible net-shape technique that involves a pre-catalysed resin injected under pressure into a pre-formed reinforcement, in a closed die mould. The reinforcement usually consists of synthetic fibres (mainly glass fibres) while polyester is widely used as the resin (due to its low cost).

Another issue relates to poor interfacial adhesion between fibres and matrix. It is generally believed that one critical barrier to obtaining valuable agrofibre-reinforced composites is the lack of adhesion between the hydrophilic lignocellulosic fibres and more hydrophobic matrices (6, 11, 12, 13). It is, however, possible to improve interfacial bonding by chemical modification of the fibre surface. Our approach relies on the grafting of reactive vinylic groups at the surface of the fibres, using methacrylic anhydride. Radical copolymerisation between these vinylic groups and the unsaturated bonds of the resin was then expected to occur, leading to an increased interfacial adhesion.

In this study, hemp fibre-reinforced polyester composites were prepared using a Resin Transfer Moulding technique and the flexural and impact properties determined as a function of fibre loading. The effect of enhanced compatibility between fibres and matrix was also investigated.

EXPERIMENTAL

The samples are labelled according to the type of fibres and chemical modification. Thus, composites prepared with unmodified hemp are labelled **UnH**; with methacrylic anhydride-treated hemp, **MeH**; pyridine-treated hemp, **PyH**; and glass fibres, **Gl**.

Hemp fibres (*Cannabis sativa*) were used in the form of nonwoven mats and the samples were moulded with a laboratory Hypaject MK II model machine (from Plastech, UK) connected to a 500 mm x 300 mm x 3 mm mould. The fibres were equilibrated in a climatic room, at 23 °C and 50% H.R., before moulding. Panels were produced according to an industrial process used by Concargo Composites (UK) for the manufacture of glass fibre-reinforced car parcel shelves. The resin used was the same unsaturated polyester resin Crystic PD9029 (from Scott Bader). This polyester was cured with 2% wt Trigonox 524 (mixture of acetyl acetone peroxide and tert-butyl peroxybenzoate, from Akzo) as catalyst and 0.6% wt of 1% cobalt solution (NL 49 ST, from Akzo) as accelerator. The mould temperature was 30 ^{0}C at the beginning of the resin injection which was performed at a pressure of 2 bar, with vacuum assistance. The composites were post-cured for 16 h at 80 ^{0}C before testing. These plant fibre-reinforced samples were compared with a glass fibre-reinforced composite produced in the same conditions, with Rovicore glass fibres (commercial glass fibres used in Concargo's parcel shelves).

Esterification of hemp was conducted at 100 °C for 48 h, using a solution of methacrylic anhydride in pyridine (1 g of dry hemp : 2.2 ml methacrylic anhydride : 6.5 ml pyridine). Prior to use, samples were extracted with toluene : acetone : methanol (2 : 1 : 1) and oven dried at 105 °C for 15 h. After reaction, samples were again extracted/oven dried and 10% weight percent gain (WPG) was obtained. In addition, the reaction was repeated in the absence of anhydride and the fibres obtained were used to produce **PyH**.

Flexural tests were performed according to BS 2782: Part 10: Method 1005: 1977, using an Instron universal testing machine Model 1195 (50 KN max. capacity), at a crosshead speed of 10 mm per minute. Flexural stress was calculated at rupture. Charpy impact strength of unnotched specimens were calculated according to BS 2782: Part 3: Method 359: 1984, using a Zwick pendulum impact tester.

Impact fracture surfaces of **UnH** and **MeH** were examined using a scanning electron microscope (SEM) Hitachi S-520. Samples were first mounted on aluminium stubs and gold coated using a Polaron SEM coating unit E5000.

Photomicrographs of unmodified hemp fibres were obtained with a Leitz Wetzlar microscope, under polarised light.

RESULTS AND DISCUSSION

Figures 1-3 represent the flexural and impact properties of hemp fibre-reinforced polyester composites as a function of fibre weight fraction (**UnH**) and fibre modification (**MeH** and **PyH**). These hemp composites were compared with a 15% wt glass fibre-reinforced composite corresponding to the commercial parcel shelf (**Gl**).
Error bars represent the mean value ± the maximum standard deviation observed with **UnH**, **MeH**, **PyH** and **Gl** respectively.

Effect of fibre content

With unmodified fibres (**UnH**), the polyester composites showed an increasing trend in the flexural stress at break and flexural modulus with fibre content (Figures 1 and 2). Addition of 36% wt fibres increased the flexural stress at break of pure polyester by 220 % and the flexural stiffness by 100%. With 15% wt fibres, the glass-reinforced composite (**Gl**) exhibited better flexural stress at break and flexural modulus than hemp-reinforced composites at identical loading. Similar flexural stress at break was however obtained with hemp, beyond 30% fibre weight fraction. The composite was then stiffer than the 15% wt glass product.

With regard to toughness, addition of 11% wt hemp was found to decrease impact strength (work of fracture) by 70% compared with neat polyester (Figure 3). However, further addition of fibres appeared to increase gradually the work of fracture. It is believed that at low loading levels, inclusion of fibres introduces a disproportionately high degree of critical defects to the composite structure, perhaps in the form of voids or poorly bonded interface regions. Such defects act to reduce impact strength. Only at higher fibre loading levels can the reinforcing nature of the cellulose, counterbalance the inclusion of defects and impart improved toughness. 14 KJ/m^2 impact strength was achieved with 36% wt hemp, which is 2 times more than for pure resin but remains poor, compared with glass composite.
This excessively low toughness might be partly explained by the presence of many pre-existing microcompressive defects along the fibres. These defects assume the form of small kinks in the microfibrillar structure, and because of the presence of crystalline regions in the cell wall it is possible to observe this feature using polarisation microscopy (Figure 5) (14). These microcompressive defects could act as loci of failure in the composite structure during impact.

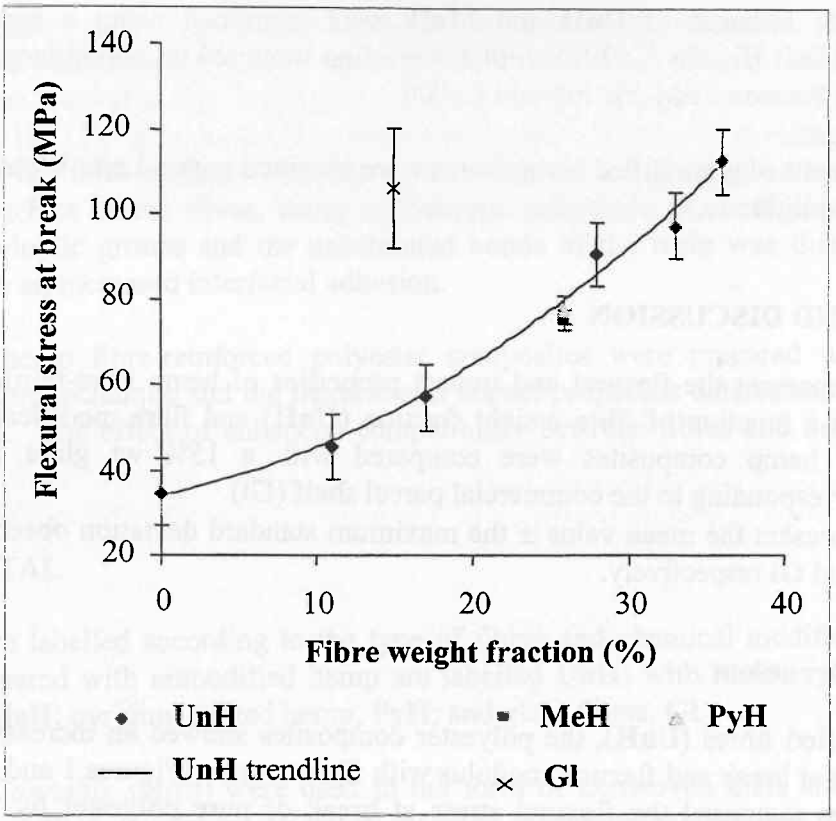

Figure 1 – Flexural stress at break as a function of fibre weight fraction.

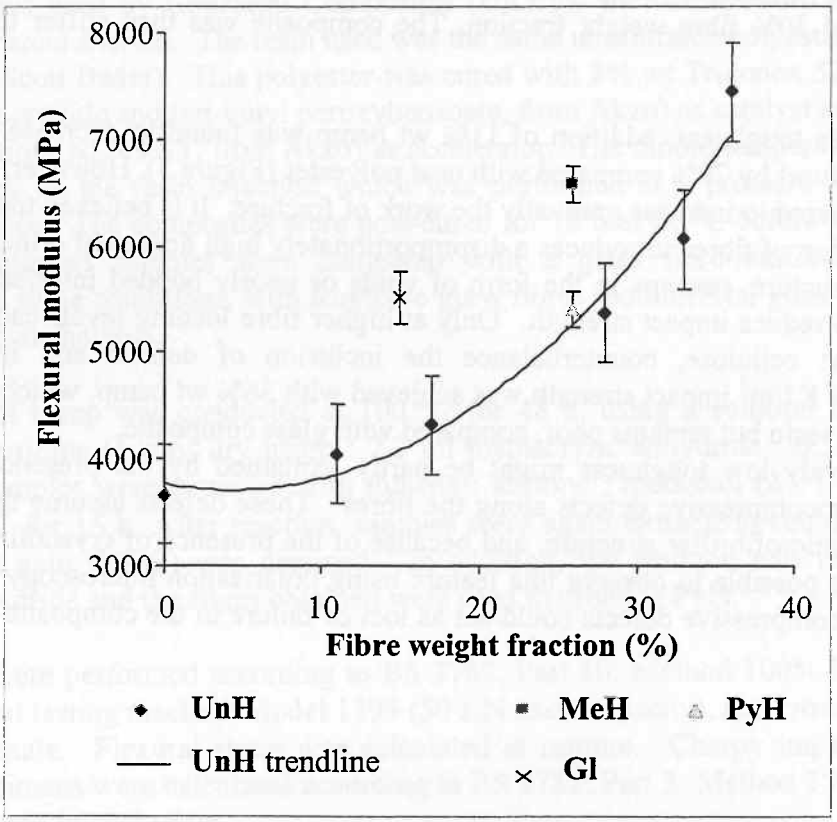

Figure 2 – Flexural modulus as a function of fibre weight fraction.

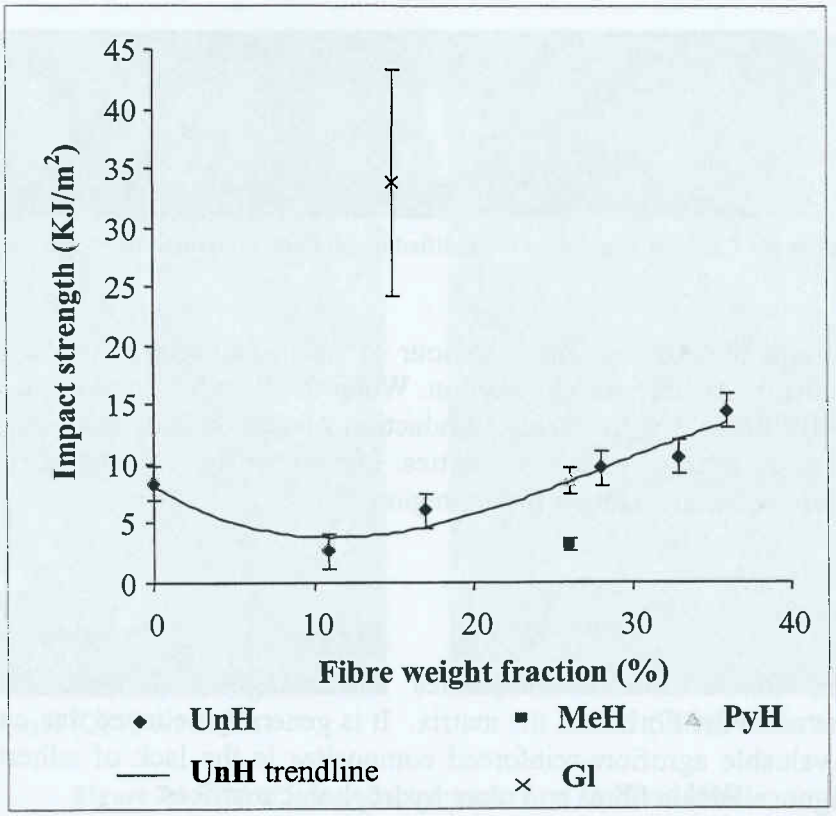

Figure 3 – Unnotched impact strength as a function of fibre weight fraction.

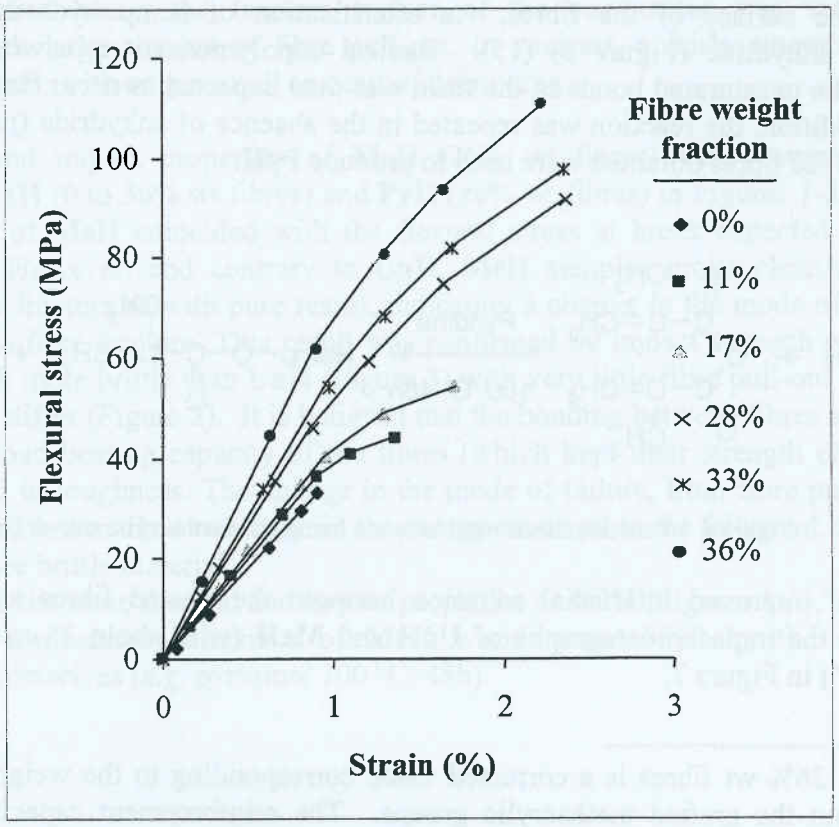

Figure 4 – Variation of **UnH** flexural stress at break with strain and varying fibre content.

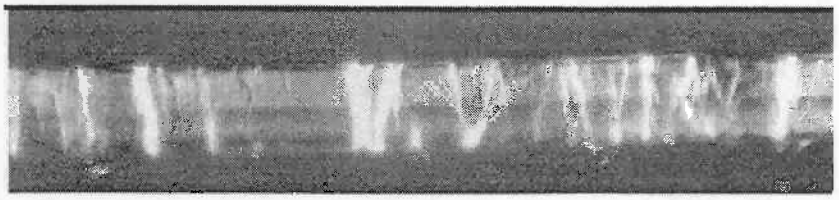

Figure 5 – Photomicrograph of unmodified hemp fibre, under polarised light (x 100).

Figure 4 represent the stress-strain behaviour of hemp-polyester composites (**UnH**) under flexure as a function of fibre weight fraction. When the flexural stress of neat polyester resin increased strictly linearly with strain, introduction of unmodified hemp fibres imparted the material with some form of plastic properties. Increase in fibre content led to an enhanced limit of proportionality and a larger plastic region.

Effect of fibre modification

Properties of fibre-reinforced composites are strongly dependent on the interfacial interactions between the fibres and the matrix. It is generally believed that one critical barrier to obtaining valuable agrofibre-reinforced composites is the lack of adhesion between the hydrophilic lignocellulosic fibres and more hydrophobic matrices.
In the present work, a strong interfacial adhesion between hemp and polyester was obtained using chemically modified hemp. This modification consisted in introducing reactive vinylic groups at the surface of the fibres, via esterification of hemp hydroxyl groups using methacrylic anhydride (Figure 6) (15). Radical copolymerisation between these vinylic groups and the unsaturated bonds of the resin was then expected to occur during moulding of **MeH**. In addition, the reaction was repeated in the absence of anhydride (just pyridine/ 100 ^{0}C/ 48h) and the fibres obtained were used to produce **PyH**.

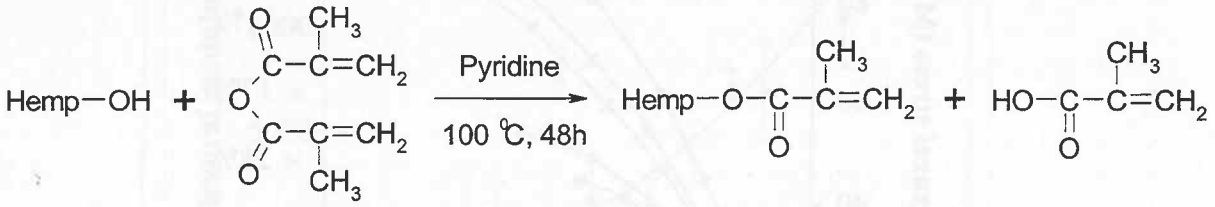

Figure 6 – Reaction mechanism between hemp and methacrylic anhydride.

Evidence of improved interfacial adhesion between the treated fibres and the matrix is reflected by the impact fractographs of **UnH** and **MeH** (with about 28 and 26% wt fibres respectively*) in Figure 7.

* For **MeH**, 26% wt fibres is a corrected value corresponding to the weight fraction of the fibres without the grafted methacrylic groups. The reinforcement capacity of these non-fibrous groups was neglected when the properties of **MeH** and **UnH** were compared (the actual fibre weight fraction, including the grafted groups, was 29%).

UnH (28% wt fibres) **MeH** (26% wt fibres*)

Figure 7 – SEM of Impact fracture surfaces of **UnH** and **MeH**.

With unmodified hemp, the fracture surface of the composites was very fibrous in appearance, with large amount of fibre pull-out. In contrast, a fairly smooth surface was observed for **MeH**, with only a small amount of debonding.

The flexural and impact properties of **MeH** (26% wt fibres) were compared with the properties of **UnH** (0 to 36% wt fibres) and **PyH** (26% wt fibres) in Figures 1-3. The flexural stress at break of **MeH** coincided with the flexural stress at break expected without fibre modification. However, and contrary to **UnH**, **MeH** samples broke cleanly apart under flexure (similar fracture as with pure resin), indicating a change in the mode of failure, from fibre pull-out to fibre fracture. This result was confirmed by impact strength measurements. **MeH** was much more brittle than **UnH** (Figure 3) with very little fibre pull-out (Figure 7). It was also much stiffer (Figure 2). It is believed that the bonding between fibres and matrix did not affect the load bearing capacity of the fibres (which kept their strength efficiency), but was detrimental to toughness. The change in the mode of failure, from fibre pull-out to fibre fracture, resulted in a marked reduction in the energy involved in the failure of the composite, leading to a more brittle material.

PyH exhibited the same flexural and impact properties as **UnH** (Figures 1-3), indicating that the particular mechanical behaviour of **MeH** wasn't engendered by the conditions of esterification themselves (e.g. pyridine/ 100 ^{0}C/ 48h).

CONCLUSION

The results of this study showed that Resin Transfer Moulding could be used to produce hemp fibre-reinforced polyester composites with good flexural properties.
Impact properties of hemp composites, however, remained insufficient to really compete with glass in structural applications. This excessively low toughness was partly explained by the presence of many pre-existing microcompressive defects along the fibres.
The improvement of interfacial adhesion between fibres and matrix did not increase the mechanical properties as expected; leading, on the contrary, to a very low composite toughness. Consequently, fibre pull-out appeared to be the principal mechanism controlling the toughness of hemp-polyester composites.

ACKNOWLEDGMENTS

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