

COUPLING AGENT FOR NATURAL FIBRE COMPOSITES UTILISING THERMOSETTING RESIN SYSTEMS

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Keywords: natural fibres, thermosetting resins, interface optimisation

Abstract

Standard composite thermosetting resins are designed to be compatible with the sizing on a synthetic fibre. A natural fibre without surface modification will not create the desired interface in conjunction with these resin systems. This study examined the use of a coupling agent added directly to a suitable, cold curing urethane methacrylate resin system. Coupling agent concentrations of 0 wt%, 5 wt%, 10 wt% and 20 wt% of the total resin system were investigated. Using 20 wt% of coupling agent, a dried unidirectional twisted yarn hemp fabric laminate exhibited a tensile stiffness and strength increase of 31 % and 9 % respectively compared with a laminate that had no coupling agent.

1 Introduction

The development of green composites that can be economically competitive when compared with standard synthetic fibre composites is an important area of research. The common components for the manufacture of green composites are natural fibres and bio-based resin systems. Here the focus is on cellulosic fibres derived from vegetative feedstocks. The resin systems commonly used with natural fibre are bio-derived thermoplastics, often designed for temporary structures (food packaging). However, for (semi-)permanent, structural, structural components, a bio derived thermosetting resin may produce the optimum performance.

Depending on the features of the matrix and fibres, the resulting mechanical properties of the composite are determined by the chemical and associated mechanical characteristics of the interface [1]. Therefore, optimisation of the fibre matrix interface strength is crucial to obtain the best performance of a composite. Standard thermosetting resins are designed to develop chemical bonds with the sizing on the surface of a synthetic fibre. However, these resin systems will not be optimised for natural fibres that have not undergone some form of fibre surface treatment. The techniques available for interface optimisation are either fibre treatments or the addition of coupling agent directly to the resin system [2, 3]. The fibre treatment optimisation process aims to modify the surface in order to be compatible with the resin system whereas a coupling agent added directly to the resin system aims to modify the resin to be compatible with natural fibres.

Since the addition of a coupling agent to a resin system does not normally require a further fibre treatment, the coupling agent process could have simpler manufacturing requirements than the fibre treatment method of interface modification.

Through selection of the appropriate coupling agent for natural fibre composites, utilising thermosetting resins, it could be possible to improve the resin-fibre interface strength. This improvement in interface strength could increase the bulk mechanical properties of a composite. An optimised system would require less fibre and matrix in order for a component to achieve the same desired stiffness or strength; assuming that fibre volume fractions and fabric architectures are identical.

2 Scope

The current study examines the use of a coupling agent specifically designed to improve the interface strength between a natural fibre and a thermosetting resin system. The mechanical properties of the selected resin with the coupling agent were first evaluated in order to understand the effect of coupling agent on the base resin system. Resin plaques with 0 wt%, 5 wt%, 10 wt% and 20 wt% of coupling agent within the base resin were manufactured and mechanically tested. Natural fibre laminates were then manufactured and mechanically tested using these modified resin systems. The reason for selecting the coupling agent quantities, listed above, was to discover the optimum coupling agent addition to a resin system for a natural fibre composite to achieve the highest mechanical properties.

3 Materials and Methods

3.1 Designing the coupling agent for natural fibres

A synthetic fibre, which is tailored for composites, has a coating applied to the fibre's surface in order to promote adhesion between the inorganic, hydrophilic fibre and the organic, hydrophobic resin (and to protect the fibre during processing). A silane based coupling agent is an example of a fibre-resin adhesion promoter that has a hydrolysable functional group, which will react with the fibre surface to form a chemical bond, and a nonhydrolysable organic radical, which can react/cross-link with a resin system [4].

From understanding how a coupling agent was designed for a synthetic fibre, a coupling agent was developed to promote interface adhesion between the organic natural fibre and an organic thermosetting resin system. This coupling agent has two functional groups, one functional group will form a chemical bond with the –OH groups on the surface of a natural fibre and another with unsaturation for cross-linking with the polymer matrix. The coupling agent is a proprietary chemical developed and manufactured by Scott Bader Company Ltd.

Many thermosetting resin systems are sensitive to residual moisture within the natural fibre; this can have a detrimental affect on the final properties of the composite [5]. The coupling agent was specifically designed such that it does not develop water (condensation) from the reaction with the surface of the natural fibre.

3.2 Resin compatibility

As the coupling agent is highly reactive with any –OH groups, not solely with the natural fibre surface, careful selection of an appropriate resin system was required to ensure that the coupling agent reacted with the natural fibre as intended. It was determined that unsaturated polyesters (UP) and vinyl esters (VE) would not be an appropriate choice as the base resin system. This was because UPs are manufactured by condensation polymerisation (evolution of water) with a polyol excess (polymer chains are terminated with –OH groups). VEs form –OH groups along the polymer backbone due to ring opening of the epoxide molecule.

The type of resin that could be used in conjunction with the coupling agent was a urethane methacrylate resin system (UMa). Urethane methacrylates are manufactured using an addition polymerisation process and where sites of unsaturation are at the extremities of the molecule. The specific UMa selected had no –OH groups present within the polymer. The UMa resin system used within this investigation has no bio-derived content.

3.3 Modified resin systems

Using the UMa resin as the base resin, the coupling agent was added to the base resin system to form modified resin systems with 5 wt%, 10 wt% and 20 wt% of coupling agent. Plaques of solid resin were cast with these modified resin systems and specimens were manufactured from these plaques. In order to assist the analysis of these modified resin systems, specimens were manufactured from the base UMa resin (0 wt%), a typical UP and a typical VE. All of the resin systems were supplied by Scott Bader Company Ltd. The resin systems were cured and post cured according to the manufacturer's specification.

3.4 Natural fibre composites

A unidirectional hemp fabric, supplied by Engtex, was selected for the manufacture of natural fibre composites within this investigation. The fabric utilises yarns of hemp fibre held together in parallel with a low tex cotton cross stitch. The yarns have an approximate diameter of 0.75 mm and a twist of between 50 to 100 turns per metre. The fibres within the yarn are solely bast fibre and the fibres are adequately separated.

Unidirectional composites were manufactured by a vacuum assisted resin transfer process. The composites utilised the UMa resin systems with 0 wt%, 5 wt%, 10 wt% and 20 wt% of coupling agent. Four layers of the fabric were used in order to create a laminate thickness of 3 mm. The fabric was dried in an oven for two hours at 105 °C before lamination to remove residual moisture [5]. The cure system was adjusted so that all of the resin systems had a gel time of one hour by altering the catalyst and inhibitor quantities. After post cure, specimens were cut from these laminates.

3.5 Mechanical testing

The resin systems were tested in tension according to BS EN ISO 527 – Part 1: 1996 [6]. The composites were tested in tension according to BS EN ISO 527 – Part 4 : 1997 [7]. The longitudinal (0°) and transverse (90°) fibre directions were evaluated for this investigation. The reason for selecting these test procedures was to develop an understanding of how the coupling agent affects the resin system and the resulting composite mechanical performance.

The test procedures were conducted using an Instron quasi-static test machine (3392) with a 50 kN load cell and, where applicable, a clip-on extensometer (50 mm gauge length) to measure displacement (strain). The data was gathered using Bluehill2, Instron's proprietary software.

3.6 Fibre volume fraction determination

Since the standard methods of resin burn-off and acid digestion are not suited to natural fibre composites, the fibre volume fraction was determined by Archimedes density measurements. As natural fibres are hydrophilic, canola oil was selected as the immersion fluid. The density of the canola oil was measured using a density meter (Anton Paar DMA 4100M). Once the density of the fibres, solid resin and composite were measured, it was possible to calculate the fibre volume fraction for that composite. Five specimens were used to determine the fibre volume fraction for each of the laminates with the different resin systems. Once the fibre volume fractions were calculated for each laminate, it was possible to calculate the estimated fibre stiffness within the composite using the rule of mixtures.

4 Results and Discussion

4.1 Modified resin systems

The tension test results for the thermosetting resin systems can be seen in Figure 1 and 2. Figure 1 displays the tensile stiffness and Figure 2 displays the peak tensile strength. The error within the figures corresponds to the error in the mean for that result. From examining the results in Figure 1 and 2 it was observed that an increasing addition of the coupling agent increased the stiffness and strength compared with the UMa base resin system. For a 20 wt% of coupling agent the tensile stiffness and strength increased by 22 % and 25 % respectively compared with the unmodified UMa resin.

Through conducting tensile experiments on the resin systems, it was observed that the tensile strain at break of the resin decreased proportionally to an increasing addition of coupling agent. The strain at break decreased from 6.8 % for the UMa (base) resin to 3.7 % for the UMa resin with 20 wt% of coupling agent. The reduction in strain at break was determined not be an issue for natural fibre composites, since preliminary testing of the composites using UD hemp fabric demonstrated a maximum tensile strain at break of 1.9 %. Owing to the increase in mechanical properties, due to the coupling agent, the effect of the resin system was taken into account when analysing the composites utilising the different resin systems.

Since the coupling agent was an unsaturated oligomer, the addition of the coupling agent to the base resin system created similar mechanical properties compared with the addition of styrene to the resin system. When extra styrene was added to the UMa resin the resulting modified resin had demonstrated an increase in stiffness and peak strength with a reduction in strain at break.

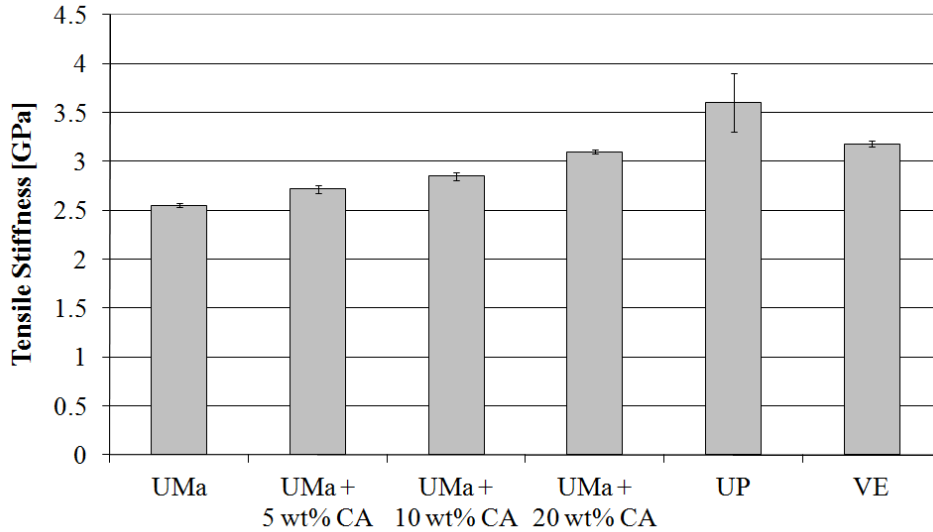


Figure 1. Tensile stiffness of modified resin systems compared with standard thermosetting resins

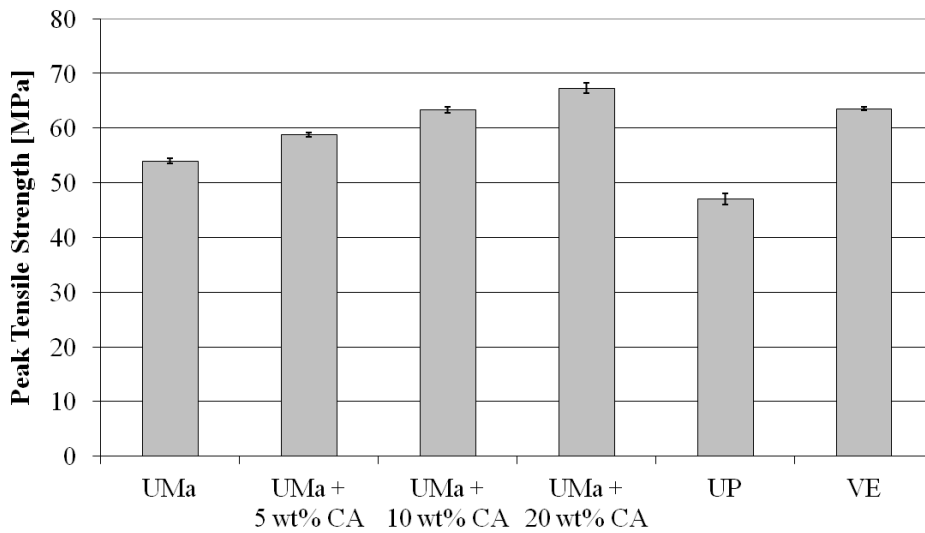


Figure 2. Peak tensile strength of modified resin systems compared with standard thermosetting resins

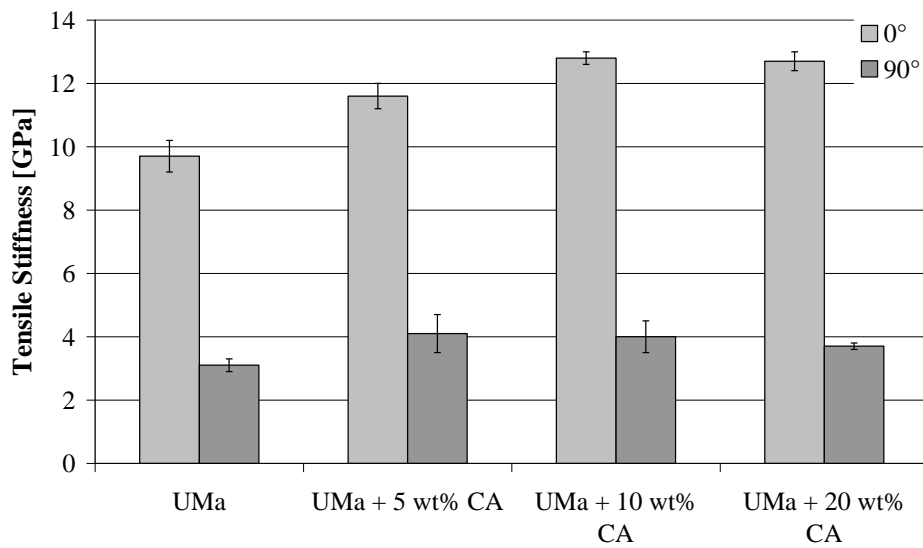


Figure 3. Tensile stiffness of unidirectional hemp laminates with modified resin systems

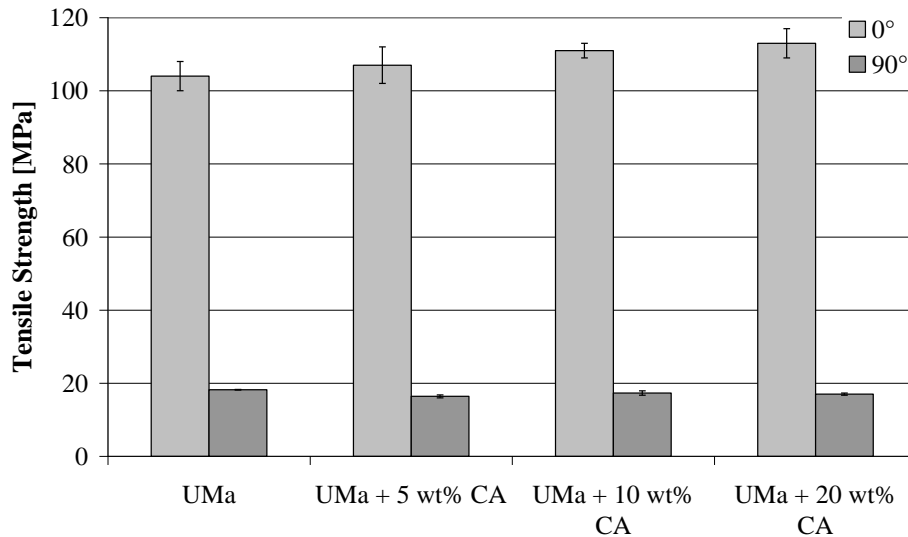


Figure 4. Tensile strength of unidirectional hemp laminates with modified resin systems

4.2 Natural fibre composites

The tension test results for the unidirectional hemp laminates using the modified resin systems can be seen in Figure 3 and 4. Figure 3 displays the tensile stiffness and Figure 4 displays the tensile strength. The error within the figures corresponds to the error in the mean for that result.

It was observed that, for laminates tension tested in the longitudinal (0°) fibre direction, the coupling agent increased the tensile stiffness of the laminate to a maximum at a 10 wt% of coupling agent (Figure 3). The addition of more coupling agent over the 10 wt% demonstrated no increase in tensile stiffness. Comparing this result with the laminate using UMa base resin system demonstrated a tensile strength increase of 32 %. The tensile strength results showed a gradual increase in strength for increasing coupling agent content (Figure 4). By using an UMa resin with 20 wt% of coupling agent the laminate tensile strength increased by 9 % compared with a laminate using the UMa base resin.

A method for interpreting the effect of the coupling agent on interface strength was to analyse the tension results for the transverse fibre direction (90°). The tensile stiffness of the laminate reached its peak at a 5 wt% of the coupling agent, with no improvement at greater coupling agent concentrations. Using the UMa resin with 5 wt% of coupling agent, the laminate tensile stiffness increased by 32 % compared with a laminate using the UMa base resin. All of the laminates that utilised the coupling agent demonstrated no noticeable improvement in tensile strength compared with a laminate using the UMa base resin. However, there was a notable improvement in the yield strength of approximately 15 %.

4.3 Fibre volume fraction determination

The results from the density investigations of the resin, fibre and composites as well as the resulting fibre volume fraction of these composites are listed in Table 1. From knowing the resin stiffness, composite stiffness and fibre volume fraction it was possible to calculate the effective stiffness contribution of the fibre to the composite laminate.

Coupling Agent wt%	Fibre Volume Fraction	Composite Stiffness [GPa]	'Effective' Stiffness of Fibre [GPa]	Stiffness Gain of Fibre [%]
0	0.29	9.7	27.2	0
5	0.30	11.6	32.2	18
10	0.33	12.8	33.0	21
20	0.30	12.7	35.2	29

Table 1. Fibre volume fraction and calculated fibre stiffness of using rule of mixtures for laminates using modified resin systems

The calculations for the fibre volume fractions assume that there was no porosity within the composites. Any voids within the composite will affect the composite's density, which in turn affects the calculated fibre volume fraction. Assuming that there was porosity within the laminates, this porosity would have decreased the measured density of composite, which would have decreased the calculated fibre volume fractions. It means that there was a potential for the calculated fibre volume fraction for each laminate to be an underestimate of the true fibre volume fraction. Through microscopy examinations of the cross-section of these composites (Figure 5), it was determined that as there was no noticeable porosity within the laminates. Therefore, the calculated fibre volume fractions in Table 1 were close to the true value.

The calculated fibre stiffness, as seen in Table 1, is lower than recorded in literature for single hemp fibre (70 GPa [8]). This is because the composites within this investigation utilised a twisted yarn. Even though the yarns are perpendicular, the twist means that not all of the fibres are perpendicular to the yarn direction. The fibres at the extremities of the yarn have a greater twist angle (Figure 5). An increase in the twist angle will reduce the yarn stiffness within a composite [9]. However, a twist is necessary in order for the yarn to be processed.

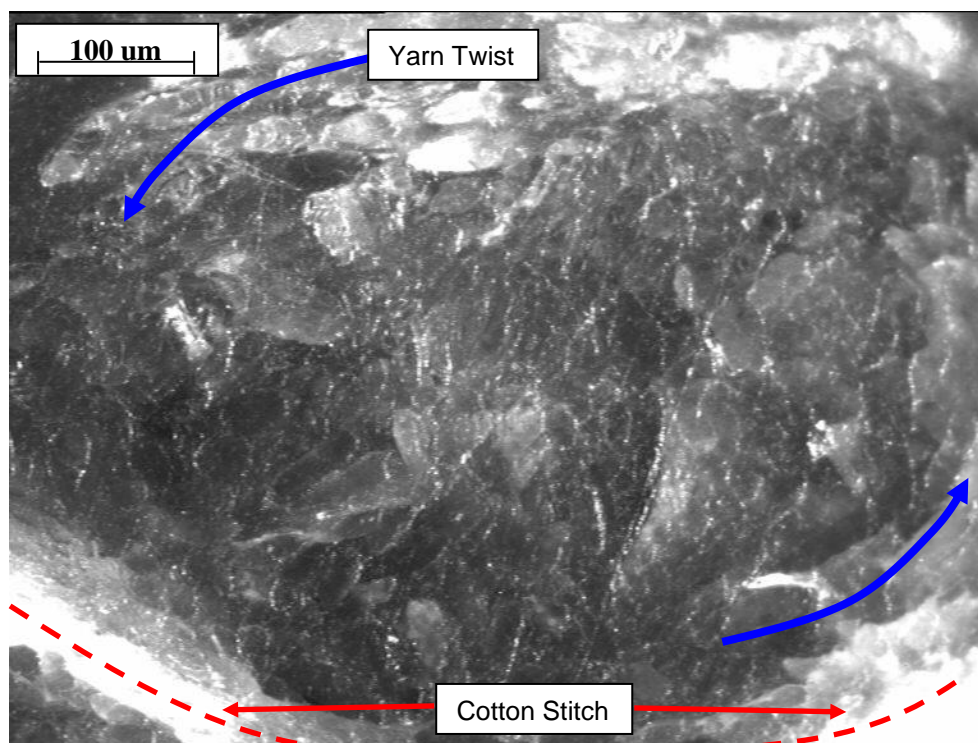


Figure 5. Cross section of a unidirectional hemp/urethane methacrylate composite showing a single yarn and the cotton cross stitch

5 Concluding Remarks

The development of green composites is important for reducing the environmental impact of composites. The current (and ongoing) research has demonstrated that through the correct selection of the coupling agent for a thermosetting resin system, it is possible to improve the stiffness and strength of a natural fibre composite without the requirement for advanced fibre treatment processes. This development has been achieved through consideration of the resin formulation and the requirements of the fibre-matrix interface. Through improving the strength and stiffness of a natural fibre composite it will signify a reduction in the mass of material required for a component to meet specific stiffness and strength requirements. Reducing the amount of material required is the most preferred method for waste prevention [10]. This research has improved the viability of natural fibre polymer composites as a potential replacement for synthetic fibre polymer composites.

Since the research has demonstrated the benefits of this coupling agent with the UMa resin system, the future aim of this research will be to optimise the current coupling agent as well as investigate other types of coupling agent for thermosetting resins.

References

- [1] Matthews F.L., Rawlings R.D. *Composite Materials: Engineering and Science*. Woodhead Publishing Limited, Cambridge, England (2003).
- [2] Zafeiropoulos N.E. *Engineering the fibre-matrix interface in natural-fibre composites* in “Properties and performance of natural-fibre composites”, edited by Pickering K.L. Woodhead publishing in Materials, Cambridge, England, pp. 127-162 (2008).
- [3] Pickering K.L., Beckermann G.W., Alam S.N., Foreman N.J. Optimising industrial hemp fibre for composites. *Composites: Part A*, **38**, pp. 461-468 (2007).
- [4] Gelest, Inc. *Silane Coupling Agents: Connecting Across Boundaries*. Version 2.0 (2006)
- [5] Chard J.M. *Green Composites: Sustainability and Mechanical Performance* in Proceeding of 18th International Conference on Composite Materials. Jeju Island, Korea, (2011).
- [6] BS EN ISO 527 – Part 1: *Plastics – Determination of Tensile Properties – General Principles* (1996)
- [7] BS EN ISO 527 – Part 4: *Plastics – Determination of Tensile Properties – Test Conditions for Isotropic and Orthotropic Fibre-Reinforced Plastic Composites* (1997)
- [8] Huda M.S., Drzal L.T. *Natural-fiber composites in the automotive sector*. in “Properties and performance of natural-fibre composites”, edited by Pickering K.L. Woodhead publishing in Materials, Cambridge, England, pp. 221-268 (2008).
- [9] Madsen B. *Properties of plant fibre yarn polymer composites – An experimental study*. Ph.D thesis, Technical University of Denmark (2004).
- [10] EU Waste Framework Directive 2008/98/EC