STIFFENING OF SUSTAINABLE CELLULOSE FIBRES FOR USE IN THE LIGHT-WEIGHTING OF SHEET MOULDING COMPOUNDS

P. Brookbank[a*], L. Savage[a]

[a] *College of Engineering, Mathematics and Physical Sciences, University of Exeter, Harrison Building, North Park Road, Exeter, UK, EX4 4QF*

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Abstract

Rayon (1.5g/cm^3) fibre offers a significant weight saving compared to E-glass (2.5g/cm^3) fibres. However, rayon is a mechanically inferior and flexible fibre in comparison to glass. Micromechanical tests have been used to assess the suitability and extent to which a cellulosic fibre may be stiffened via either acetylation or esterification of the surface structure. Results show that the elastic modulus of rayon can be stiffened chemically using formaldehyde and citric acid with varying efficiency. Rayon treated with citric acid showed an increase in E_F from 3.5GPa to 7.0GPa whilst rayon treated with formaldehyde increase from 3.5GPa to a maximum of 15.5GPa.

1. Introduction

Future developments in the automotive sector will be dominated by the requirement for low carbon vehicles, with highly efficient combustion engines or the use of alternative propulsion technologies such as hybrid-electric and all electric power-trains. Whatever the final solution, the light-weighting of vehicle structures will be an important requirement in upping fuel efficiency and range, where the 500kg car is a viable target for the industry[1].
Sheet Moulding Compound (SMC) is the largest type of thermoset composite used in the automotive industry today. SMC is typically a glass-reinforced short-fibre composite (25mm), incorporating a highly filled formulated matrix –where the thermoset used is typically orthophalic unsaturated polyester. SMC can be as cheap to produce as steel, offers excellent thermal compatibility with steel, adequate crash management and fatigue resistance but with a 40% weight saving. The short production cycle times of SMC's, and the ability of the material to be moulded to a so called "class A" surface finish, has allowed these materials to be frequently use for exterior body panels and other semi-structural components. SMC developers have tried to extend the current range of SMC to include grades based on carbon fibre for use where stiffness and weight saving is a key concern. These new carbon fibre SMCs can achieve flexural strength and modulii up to 792MPa and 45GPa respectively, but the increase in performance comes at a high financial cost [2]. In order to achieve flexural properties five times greater than of a standard glass SMC, manufacturers are using aerospace grade (3K) carbon fibre combined with vinyl ester resins in a 50% w/w ratio, totally removing mineral fillers from the SMC paste. The high fibre loadings in these CF SMCs is detrimental to flow during moulding where a mould coverage of >80% is often necessary. This reduces

the ability of these CF SMCs to form intricate shapes as flow is kept to a minimum making the process a hybrid between hand lay-up and compression moulding.
There is therefore a desire for a SMC material that possesses similar flow properties to glass SMCs but offers a clear reduction in density. This new material must be sustainable, easily recycled and should cost no more than current glass SMCs if it is to gain widespread acceptance in light weight vehicles and automotive manufacture in general.
To meet these challenges, developers have turned to natural alternatives to replace synthetic resins, fillers and reinforcing fibres where bio-derived alternatives often offer a weight saving. Many authors have published results where natural fibres such as hemp, jute and flax [3, 4] have been used as alternatives to e-glass reinforcement (with varying degrees of success). These natural fibre composites are often made from woven mats to maximise the performance of these mechanically inferior fibres, rather than the standard discontinuous glass and carbon. The use of mats prevents flow during moulding however, so these mat-reinforced grades are of limited utility. Natural fibre SMC materials often have poor mechanical performance due to the reduced strength of the fibre, uncontrolled aspect ratio and fibre orientation [3, 4, 6]. Recently, Savage and Evans (2014) have found that mechanically weak rayon fibres can be engineered so that they offer improved reinforcement. This is achieved by control of the fibre *meso*-structure within a composite [5, 6]. Rayon was used during experimentation by Savage and Evans because the reconstituted cellulose had a controlled fibre diameter and consistent fibre length unlike natural fibres. In their study it was shown that rayon fibres, though having inferior properties to many natural fibres, could outperform natural fibres when used in polyester SMCs. This increase in performance was the result of bundling fibres to form a bundle with increased strength and stiffness than that of the constituent fibres. The produced rayon SMCs demonstrated a significant improvement in toughness, a common failing in cellulosic composites. However, the reported flexural strength values of 60MPa and modulus 8GPa, were somewhat lower than a standard glass SMC (σ – 90MPa, E_f – 10GPa) [7]. The development of rayon fibres with increased strength and stiffness as reinforcement is therefore now necessary to improve the properties of these cellulosic SMCs to a level where they can compete with the current market standard.

The aim of this study is to stiffen rayon material through the introduction of chemical cross-links along the fibre surface. Two process's used by the textile industry for imparting anti-crease properties to garments such as shirts and dresses, are a formaldehyde or carboxylic acid treatment; although the former has ceased to be used in recent years due to the growing health concerns with the use of formaldehyde and its salts. These treatments introduce acetyl or ester links between adjacent C_6 hydroxyl groups along the cellulose skeleton respectively [8, 9]. Changes in tensile properties of treated fibres have been assessed by single fibre tensile tests to calculate the ultimate strength and modulus.

A relatively new, high crystallinity reconstituted cellulosic material, BioMid, is reported to have inherently greater properties than rayon due to the highly crystalline nature of the material [10]. BioMid has also been evaluated in this study – offering a potential alternative to rayon but without the requirement of further post processing.

Halpin-Tsai and modified Halpin-Tsai models have been used to predict the tensile modulus and strength of discontinuous rayon and BioMid SMCs, as a means to conceptualise the effect of stiffening the base rayon fibre.

2. Materials

2.1. Rayon

High tenacity rayon (cellulose II), produced using a proprietary variation of the viscose process, was supplied by Cordenka GmbH. The fibre yarn received, was a 1540 dTex tow with a 500 filament count. The tow was examined by optical microscope and the nominal filament diameter was found to average14.6µm in a population of 50 samples.

2.2. BioMid

BioMid is a high crystallinity reconstituted cellulose fibre produced via a process dissimilar from that of rayon. A saturated cellulose solution is formed into fibres via a closed loop dry-jet-wet-spinning method that forms high crystallinity fibres. This process consumes less energy and uses environmentally favourably solvents compared to the viscose process. GC consulting (Burnaby, Canada) kindly supplied 1650 denier tow made from 900 filaments. The reported nominal filament diameter is 11µm however optical inspection of 50 samples found that the average filament diameter was 14.6µm.

2.3. Acetylation

Single fibres mounted on 10mm window cards were immersed in a dry cross-linking solution as given in Table 1. The figures represent the percentage of each reagent on a weight basis. The fibres were left to steep in solution for 10h at 40°C with occasional replenishment of vaporised solution. After steeping was complete the samples were washed in deionised water, a minimum of 5 times and left in a convection oven at 60°C to dry in advance of tensile testing.

Acetone	86.0
Formaldehyde	5.0
Hydrochloric	0.2
Water	7.0
Methanol	1.8

Table 1: Dry Cross-linking Solution – Formaldehyde

The reaction of cellulose with formaldehyde is acid catalysed and is believed to proceed according to Figure 1.

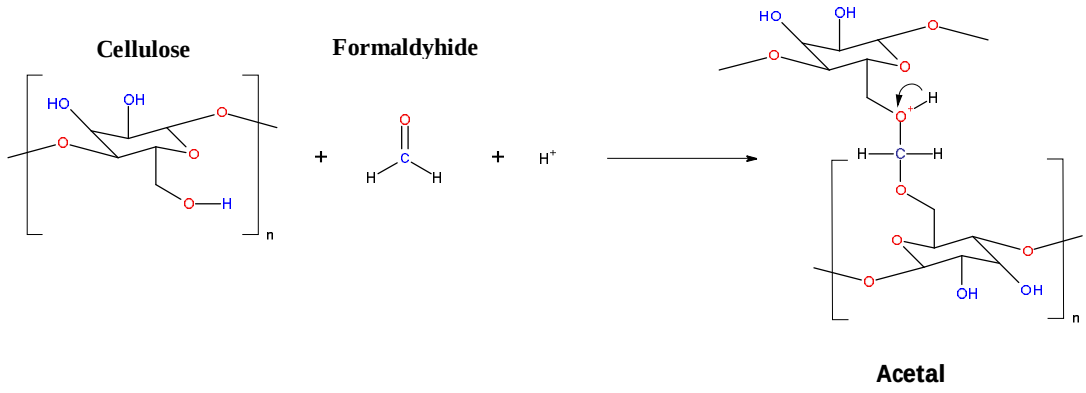

Figure 1: Acetyl Formation at Cellulose Surface

2.4. Esterification

Single fibres mounted on 10mm window cards were immersed in a citric acid cross-linking solution as given in Table 2 and represents the percentage of each reagent on a weight basis. The fibres were left to steep in solution for 10h at 40°C. After steeping was complete the samples were washed in deionised water a minimum of 5 times and in a convection oven at 60°C to dry in advance of tensile testing.

Citric Acid	4.7
Sodium Hydroxide	0.7
Sodium Hypophosphite	1.2
Water	93.4

Table 2: Carboxylic Cross-linking Solution

The reaction of cellulose with citric acid is catalysed by sodium hypophosphite and is believed to proceed according to Figure 2.

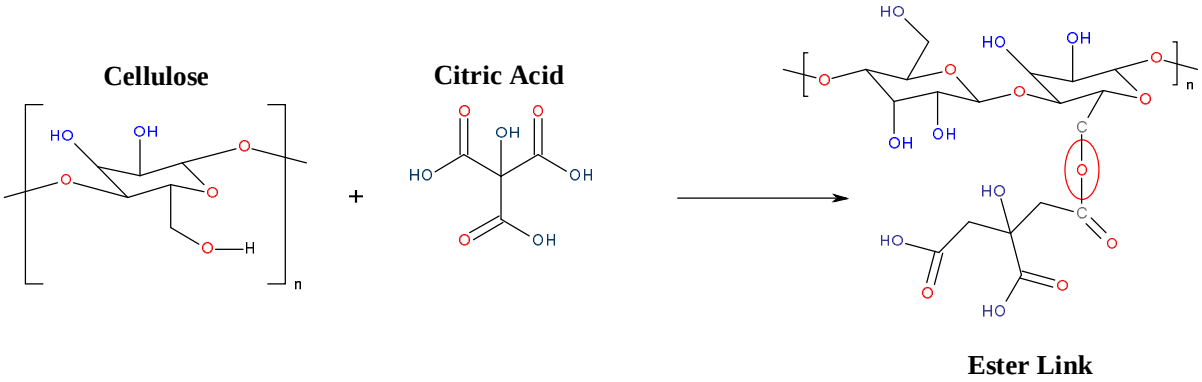

Figure 2: Ester Formation at Cellulose Surface

3. Testing

The mechanical testing procedure used is an adaptation of ASTM D2256 – Standard Test Method for Tensile Properties of Yarns by the Single-Strand Method. This standard was followed explicitly with the exception of the gauge-length and cross-head speed. The use of a smaller gauge length and cross-head speed was due to test equipment limitations. The gauge length and cross-head speed specified by this standard were 250±3 mm and 300±10 mm/min respectively.

3.1. Sample Mounting

Single filaments were removed from their respective tow's and mounted on a mounting tab with a gauge length of 10mm. The fibre samples were mounted in place using a slow cure bisphenol-A epoxy resin with an amine hardener.

3.2. Micro-tensile testing

A Biax micro-tensile tester fitted with a 10N load cell and precision linear variable differential transformer (LVDT) driving system was used at a cross-head speed of 0.01mm/s

(0.6mm / min) to induce failure in 60 ± 5 seconds. Data was exported as a 1,000 point .txt file for computation of tensile strength and modulus according to ASTM D2256.

3.3. Halpin-Tsai Model

3.3.1. Tensile Strength

The tensile strength of discontinuous short fibre composites may be predicted using a modification of the Halpin-Tsai equation performed by Neilson [11]. The modified Halpin-Tsai equation is given in Eqn. 1

$$T_C = \frac{T_M}{5T_M}\left(\frac{1 + A\eta V_F}{1 - \eta\psi V_F}\right) \qquad (1.0)$$

where

$$\eta = \left(\frac{T_F}{T_M} - 1\right) \div \left(\frac{T_F}{T_M} + A\right) \qquad (1.1)$$

$$\psi = 1 + \left(\frac{1 - \phi_{\max}}{\phi_{\max}^2}\right) V_F \qquad (1.2)$$

$$A = \frac{2l}{d} \qquad (1.3)$$

Where, T_C, T_F and T_M are the strength of the composite, fibre and matrix respectively. The parameter ϕ_{max} is the maximum packing fraction of reinforcement and has a value of 0.82 for random packing in 2 dimensions. *l* and *d* are fibre length and diameter and *l/d* is the aspect ratio.

3.3.2. Tensile Modulus

The tensile modulus of discontinuous short fibre composites may be predicted using the Halpin-Tsai equation. The Halpin-Tsai equation is given in Eqn.2

$$\frac{E_L}{E_M} = \frac{1 + \left(\frac{2l}{d}\right)\eta_L V_F}{1 - \eta_L V_F} \qquad (2.0)$$

$$\frac{E_T}{E_M} = \frac{1 + 2\eta_T V_F}{1 - \eta_T V_F} \qquad (2.1)$$

$$E_{Random} = \frac{3}{8}E_L + \frac{5}{8}E_T \qquad (2.2)$$

where

$$\eta_L = \frac{\left(\frac{E_F}{E_M}\right) - 1}{\left(\frac{E_F}{E_M}\right) + 2\left(\frac{l}{d}\right)} \qquad (2.3)$$

$$\eta_T = \frac{\left(\frac{E_F}{E_M}\right) - 1}{\left(\frac{E_F}{E_M}\right) + 2} \qquad (2.4)$$

Where, $E_L$and E_T are the composite modulus in longitudinal and transverse loading directions respectively. E_M is the modulus of the matrix or filled matrix for the case of traditional SMCs. E_{Random} is the modulus of a randomly orientated short fibre composite.

4. Results and Discussion

4.1. Micro-Tensile Test

Figure 3 shows the tensile strength (MPa) and Modulus (GPa) from BioMid and rayon fibres having undergone treatment with citric acid and formaldehyde. Fibre strength was found to decrease in the following order: BioMid > Formaldehyde ≥ virgin rayon > citric acid. The relatively high crystallinity of BioMid meant that it required the greatest amount of force to cause failure in the fibre. The formaldehyde treatment had little effect on rayon fibre strength. The citric acid treatment had a detrimental effect, decreasing the strength from 492MPa to 333MPa. The modulus of treated rayon fibres increased compared to the virgin rayon value of 3.47GPa with formaldehyde treated samples increasing to 15.47GPa. BioMid has an intrinsic modulus of 9GPa, greater than virgin rayon (3.47GPa) and citric acid treated rayon (7GPa) but less than formaldehyde treated rayon (5.5GPa).

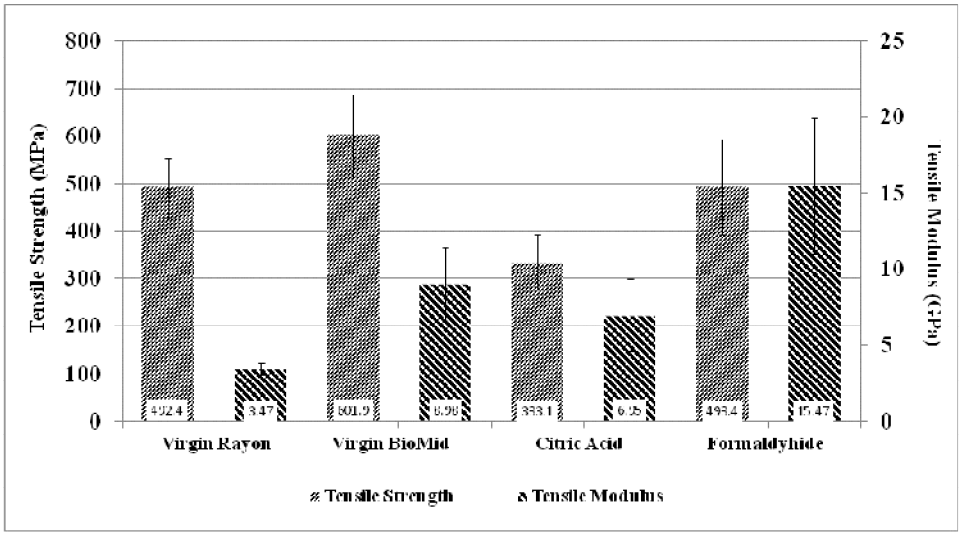

Figure 3: Tensile Strength and Modulus from Micro-Tensile Tests

4.2. Halpin-Tsai Model

Values of E_f, E_m, σ_F and σ_M, used during modelling are shown in Table 3. The fibre length (*l*), diameter (*d*) and volume fraction remained constant throughout calculation. Values of 25mm, 15µm and 20% were used for fibre length, diameter and volume fraction respectively.

	Tensile Strength (MPa)	Tensile Modulus (GPa)
Matrix	62.0	7.1
Rayon	492.4	3.5
BioMid	601.9	9.0
Citric Acid	333.1	7.0
Formaldehyde	493.4	15.5

Table 3:Matrix and Fibre Tensile Strength and Modulus Values

Figure 4 shows the tensile strength (MPa) and modulus (GPa) for random, discontinuous short fibre composites predicted by the Hapin-Tsai model. The results from the model reflect the findings in Figure 3 with BioMid obtaining the greatest strength and formaldehyde treated rayon being the stiffest. Assuming a good prediction has been achieved with the Halpin-Tsai models it can be seen that, unless modulus is the driving composite property, the most suitable material to manufacture cellulosic SMC from is BioMid. BioMid requires no post treatment with potentially harmful chemicals and obtains similar composite properties to those manufactured from formaldehyde treated rayon.

The model can be used to obtain an approximate value of Vf that would be required to obtain properties similar to a standard glass SMC. A volume fraction of 50% would be necessary to obtain a similar stiffness to glass SMC (10GPa) using formaldehyde treated rayon. Manufacturing SMC with 50% Vf rayon would present a technical challenge because high volume fractions of rayon fibre would be extremely difficult to wet-out using a normal SMC manufacturing route where paste viscosities are of the order ≈5,000cP.

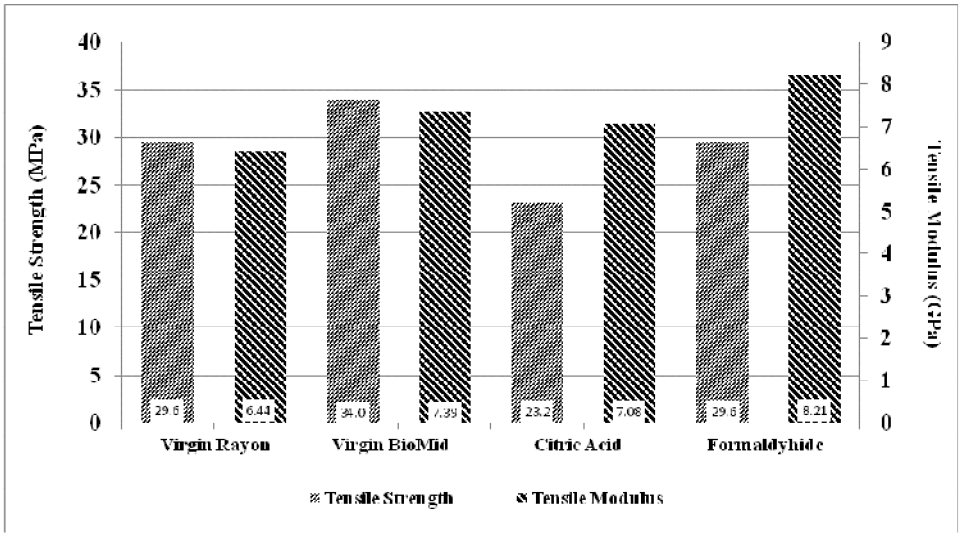

Figure 4: Halpin-Tsai Prediction of Strength and Modulus for Cellulosic Fibres

6. Conclusion

Rayon has been successfully treated with citric acid and formaldehyde in order to generate ester and acetyl cross-links on the fibre surface. The use of citric acid is detrimental to fibre strength but does cause an increase in overall modulus. Formaldehyde provided the most successful cross-linking solution. Samples produced from steeping in formaldehyde showed no change in strength compared to virgin rayon but realised a significant increase in modulus of 12GPa from 3.5GPa to 15.5GPa. The highly crystalline BioMid fibres offer an alternative to viscose rayon fibres and showed promising results. BioMid had the highest strength of all the fibres tested and when used in a SMC material, was predicted to demonstrate a modulus of 7.4GPa. Based on this study, the most viable fibre for manufacture of a stiff cellulosic SMC would be formaldehyde treated rayon or BioMid. However, formaldehyde treated fibres present additional health and safety difficulties because of potential exposure to potentially carcinogenic chemicals.

7. References

[1] N Meilhan. (2013) Why the car of the future only weighs 500 kg [Online]. Available at: http://www.slideshare.net/FrostandSullivan [Accessed on 12th February 2014].
[2] Quantum Composites (2014). Thechnical Data Sheet – AMC 8592, 126-76-86 Engineered Structural Composite (ESC) Molding Compound [Online]. Available at: http://www.quantumcomposites.com/pdf/datasheets/amc/Quantum-AMC-8593%20126-76-118.pdf [Accessed on 18th March 2014]
[3] D. Nabisaheb and J P Jog. Natural Fiber Polymer Composites: A Review. *Adv Polym Tech*, 18 (4): 351–363, 1999
[4] R. Newman. Development of non-wood natural fibre-fibre composites. In: *Properties and performance of natural-fibre composites*. K. L. Pickering (editor). Pp 193 – 208 Woodhead Publishing Limited, 2008
[5] M. R. Piggott. Debonding and friction at fibre-polymer interfaces. I: Criteria for failure and sliding. *Comp Sci* 30(4): 295-306, 1987
[6] L. Savage, K. E. Evans. The Importance of the Mesostructure in Toughening Cellulosic Short Fibre Composites. *Comp Sci* 93: 97-105, 2014
[7] Menzolit (2014) Menzolit SMC 0400 [Online] http://www.menzolit.com/templates/rhuk_solarflare_ii/pdf/list_smc/SMC_0400.pdf [Accessed on 13th February 2014]
[8] M. Lewin (editor) *Handbook of fibre chemistry*, CRC Press, 2006
[9]C. M. Herron. D. J. Cooper. T. R. Hanser. B. S. Hersko. Preocess for preparation of individualized polycarboxylic acid crosslinked fibres. US Patent N° 5190563, 1993
[10] M. LeGault (2013) Bio-composites update: Beyond eco-branding In: composites world http://www.compositesworld.com/articles/biocomposites-update-beyond-eco-branding
[11] L. E. Nielson. *Mechanical properties of polymer and composites*, Marcel Dekker, New York, 1974