**Proceedings of the**
**International Conference on Mechanical Engineering 2007**
**(ICME2007) 29- 31 December 2007, Dhaka, Bangladesh**

**ICME07-AM-49**

# THE EFFECTS OF MECHANICAL FIBRE BEATING, REPROCESSING AND HYGROTHERMAL AGEING OF WOOD FIBRE REINFORCED POLYPROPYLENE COMPOSITES

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## ABSTRACT

In this study the effects of mechanical fibre beating, reprocessing and hygrothermal ageing of wood fibre reinforced polypropylene composites were investigated. Composites were produced using a twin-screw extruder followed by injection moulding. Coupling agent contents of 1, 2, 3, 4, 5, 7 and 10 wt% were used in composites, with 4 wt% was found to be most favourable, providing a 65% increase in tensile strength (TS) and 225% increase in Young's modulus (YM) compared to the matrix. Fibre beating brought about an increase of composite TS up to a certain point. During reprocessing, TS and YM were found to decrease with increased number of times the materials were reprocessed by up to 25% for TS and 17% for YM (after being reprocessed eight times). After hygrothermal ageing, composites without coupling agent showed higher water uptake and diffusion coefficient than those with coupling agent. Both TS and YM were found to decrease after hygrothermal ageing. However, the diffusion coefficient and the equilibrium moisture contents of composites decreased with increased number of times the materials were reprocessed.

**Keywords:** Reprocessing, Beating, Coupling agent, Hygrothermal ageing.

## 1. INTRODUCTION

In recent decades, growing environmental awareness has resulted in renewed interest in the use of natural materials for different applications. Increasingly more stringent environmental policies have forced industries such as the automotive, packaging and construction industries to search for new materials that can substitute traditional composite materials consisting of a plastic matrix and inorganic reinforcement [i]. Lignocellulosic fibres have many advantages, including that they are biodegradable and renewable, with acceptable specific properties compared to glass fibres. They also reduce dermal and respiratory irritation during handling, as well as tool wear. However, the main disadvantage of natural fibres is their hydrophilic nature, which results in incompatibility with hydrophobic polymeric matrices leading to poor composite mechanical properties [ii]. Moisture penetration into composite materials occurs by three different mechanisms. The main process consists of diffusion of water molecules inside the micro-gaps between polymer chains. The other mechanisms are capillary transport into the gaps and flaws at the interfaces between fibres and polymer due to incomplete wettability and impregnation, and transport by micro-cracks in the matrix, formed during the compounding process [iii,iv]. The capillary mechanism involves the flow of water molecules into the interface between the fibres and the matrix. It is particularly significant when the interfacial adhesion is weak and when the debonding of the fibres and the matrix has started. In addition, transport by micro-cracks includes the flow and storage of water in the cracks, pores or small channels in the composite structure. These imperfections can originate during the processing of the material, or due to environmental and service effects. The diffusion coefficient is the most important parameter for water absorption, as this shows the ability of solvent molecules to penetrate inside the composite structure. Over short times such that $M_t/M_\infty \leq 0.5$ the following equation can be used to determine the diffusion coefficient [v]:

$$\frac{M_t}{M_\infty} = \frac{4}{L}\left(\frac{D}{\pi}\right)^{0.5} t^{0.5} \quad (1)$$

where $M_t$ is the moisture content at time t, $M_\infty$ is the moisture content at the equilibrium, L is the thickness of the sample and D is the diffusion coefficient.
Rearranging equation (1) gives:

$$D = \frac{\pi L^2 (M_2 - M_1)^2}{16 M_\infty (t_2^{1/2} - t_1^{1/2})^2} \quad (2)$$

D can be obtained from the slope of the linear part of the plot of $M_t$ versus the square root of time t.

The generation of a stronger interface between matrix and reinforcement material could reduce the hygroscopicity of lignocellulosic-based materials by reducing access to hydroxyl groups and therefore improve moisture resistance [vi]. Coupling agents can be used in order to improve adhesion between cellulosic fibres and polypropylene (PP) to improve mechanical properties [vii]. An alternative approach to improve

interfacial bonding, widely used in paper making, involves mechanical beating of fibre. The process of beating has three main effects, namely:

(1) The fibres become shortened

(2) External fibrillation occurs, causing partial or sometimes total removal of the primary wall and causing fibrils to form on the surface of the fibre, thereby increasing the fibre surface area

(3) Internal fibrillation occurs, causing the fibres to become more conformable [viii].

Thus, it is believed that beaten fibres should exhibit increased fibre–matrix bonding in composites due to the increase in fibre surface area [ix].

Concern for the environment, both in terms of limiting the use of finite resources and the need to manage waste disposal, has led to increasing pressure to recycle materials at the end of their useful life. In the metals industries, for instance, materials recycling operations are already well established and are driven by economics [x]. Polymers are generally more difficult to recycle and the economic incentives to recycle have been less favourable, particularly when waste disposal in landfills is relatively cheap. However, waste management is now a high priority within the European Union. As a consequence, it is already illegal to landfill composites waste in many EU countries. The "End-of-Life Vehicle Directive" (Directive 2000/53/EC) regulates the disposal of vehicles and the requirements include that from 2015, 85% of the weight of all "End-of-Life" vehicles must be re-used or recycled, a further 10% may be subject to energy recovery with a maximum of only 5% of the vehicle allowed to be disposed of in landfill. As vehicles have a life expectancy of more than 10 years, vehicles currently being manufactured must meet the 2015 requirements [x]. As a consequence of increasing legislation, there is a need for recycling routes to be established [x]. Although there are governmental regulations in countries such as Germany, recycled materials are avoided, not only due to their physical properties, but mainly because of their surface appearance. Indeed, many designers are reluctant to use them as they can be rejected by the market. However, this is an attitude that can change [xi], as demonstrated in Brazil where around 15% of all rigid plastics and films consumed, are recycled and returned to industry [xii]. Some states in the US are also concerned with recycling. For example, in Michigan, the recycling rate is close to 100 % and proves the potential for recycling plastic waste as well as changes in market attitude [xiii].

Plastic waste management can be carried out using three different approaches namely, thermo-mechanical recycling, energy recovery and biological recycling. Thermo-mechanical recycling first involves mechanical recycling where the thermoplastics are granulated, followed by techniques as extrusion or thermoforming. Energy recovery can be performed in two distinct ways. One is incineration where the hydrocarbon polymers replace fossil fuels. The second approach is pyrolysis or by hydrogenation to low molecular weight hydrocarbons for use either as portable fuels or as polymer feedstock. Biological recycling takes advantage of polymer biodegradation, which is highly dependent on the polymer type and environmental conditions. However, this type of recycling most often involves not only high costs and complex procedures but also potential damage to the environment [xiv]. Of these three techniques, thermo-mechanical would be expected to involve the least energy in terms of the product "life cycle".

It may be considered that, to be economical, a thermo-mechanical recycling process must be designed in such a manner that the energy to recover the post-consumer materials plus the energy to reprocessing must be equal to the amount of energy needed to produce the virgin material plus the energy required to dispose of the material. This balance does not, however, take into consideration environmental benefits. When those environmental gains are considered, higher energy consumption could be allowed during thermo-mechanical recycling for which the increase in cost could be compensated by indirect costs due to reduction in landfill, for example.

The purpose of this investigation was to improve the interfacial bonding and to determine the extent to which wood fibre/PP composite materials are reprocessable.

## 2. EXPERIMENTAL

### 2.1 Materials

Radiata pine (*Pinus Radiata*) wood fibre (Kraft) was supplied by Tasman Pulp & Paper Co Ltd, New Zealand. The average fibre length was 2.36 mm. The matrix polymer was a standard polypropylene (PP) powder with a density of 0.9 g/cc supplied by the Aldrich Chemical Company, Inc and maleated polypropylene (MAPP -AC 950P) with a saponification value of 35-40 mg KOH/g, a density of 0.93 g/cc and free maleic anhydride content of less than 0.5% was supplied by Honeywell international, Inc, USA.

### 2.2 Methods

*Fibre beating:* Fibre was beaten using a Sprout-Waldron disc refiner with a specific edge load of 0.89 Ws/m for 10 minutes. The refiner was operated at 1450 rpm so that the disc peripheral velocity was in the range of 20-25 m/s. The plates used were Papro R³ plates, with a cutting length of 223 m/rev. Refined pulps were removed at regular intervals.

*Composite fabrication:* Composites were fabricated with 40 wt% fibre with PP using a TSE-16-TC twin-screw extruder with a 15.6 mm screw blade diameter at 180°C (maintaining 5 different temperature zones 100, 130, 160, 180 and 175°C from feed zone to exit die) and a screw speed setting of 100 rpm. Prior to extrusion, wood fibre, PP and coupling agent were dried in an oven at 80°C for a minimum of 48 hours. Following extrusion, the material was pelletised into lengths of less than 5 mm and injection moulded into specimens for tensile testing using a BOY 15-S injection moulder. For reprocessing, specimens were randomly selected from approximately one hundred and fifty to evaluate the mechanical properties. The remaining specimens were granulated and injection moulded. Again specimens were randomly selected from these reprocessed materials for

physical and mechanical property evaluation. The procedure of injection moulding and granulation was repeated for a total of eight times.

*Water absorption:* Water absorption studies were performed following the ASTM D 570-98: Standard Test Method for Water Absorption of Plastics. Six specimens of tensile and bending from every batch were submerged in distilled water at 50$^{o}$C. The specimens were removed from the water after certain periods of time, weighed in a high precision balance to find the amount of water taken up and then resubmerged in water.

*Tensile testing:* Tensile testing was carried out according to the ASTM 638-03: Standard Test Method for Tensile Properties of Plastics. Test specimens were placed in a conditioning chamber at 23$^{o}$C ± 3$^{o}$C and 50 % ± 5 % relative humidity for 40 hours. The specimens were then tested using an Instron-4204 tensile testing machine fitted with a 5 kN load cell operated at a cross-head speed of 5 mm/min. An Instron 2630-112 extensometer was used to measure the strain. Six specimens were tested for each batch with a gauge length of 50 mm.

*Scanning electron microscopy (SEM):* The fractured surfaces of the tensile test specimens were examined using a Hitachi S-4000 field emission scanning electron microscope, operated at 5 kV. Samples were mounted with carbon tape on aluminium stubs and then sputter coated with platinum and paladium to make them conductive prior to SEM observation.

*Digital microscopy:* Following mounting, grinding and polishing, the fibre distribution and alignment of the fibre in the composites was observed using an Olympus B X 60 microscope.

*Extraction of fibre from composites:* Fibre was extracted by dissolving the matrix in hot xylene at 110$^{o}$C followed by soxhlet extraction in xylene for 72 hours.

*Fibre length measurement:* The length and fibre distribution of virgin and extracted fibre from the composites was measured using a Kajaani FS-200 electronic sequential fibre analyzer. Fibre count of about 15,000-20,000 was used to determine the fibre length distribution.

## 3. RESULTS AND DISCUSSION

### 3.1 Optimisation of coupling agent

The effects of MAPP on TS and YM of composites (40 wt% fibre with 1, 2, 3, 4, 5, 7 and 10 wt% MAPP) are presented in Fig. 1 and 2. No significant effect on TS and YM was found for MAPP addition to PP alone. For composites without the use of coupling agent, the TS decreased from 25 MPa for pure PP to 23 MPa for composites (Fig. 1). This suggests that the interfacial bonding between the fibre and the matrix is poor [xv], which is supported by SEM micrographs (Fig. 3a); fibre pull-out and debonding predominate at the fracture surface.

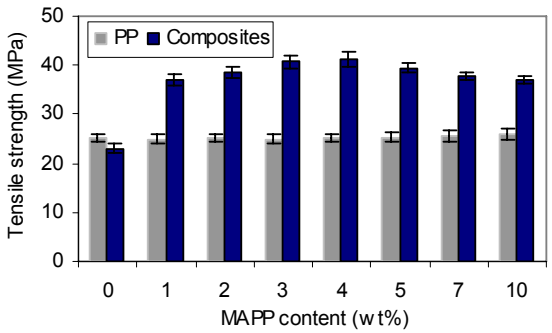



Fig 1: Tensile strength versus coupling agent content in composites (40 wt% fibre).

The TS increased dramatically on addition of 1 wt% MAPP (similar to that found for other wood fibre [xvi]), followed by further more gradual increases of TS up to 4 wt% MAPP (Fig. 1), which appeared to be due to better interfacial bonding between the fibre and the matrix (Fig. 3b). A slight reduction of TS was observed for 5 wt% MAPP, and the extent of the reduction increased for 7 and 10 wt% MAPP. Reduction of TS at higher MAPP content has been attributed to self-entanglement among the coupling agents chains rather than with the polymer matrix, thus resulting in slippage [xvii,xviii].

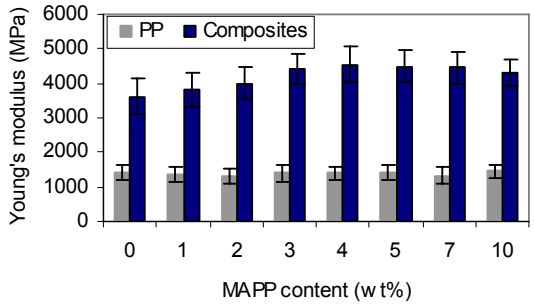
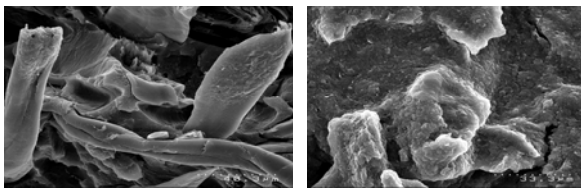



Fig 2: Young's modulus versus coupling agent content in composites.



Without MAPP With 4 wt% MAPP

Fig 3: SEM of composites fracture surfaces (40 wt% fibre) with and without MAPP.

The influence of MAPP content on YM of composites was less than that on TS (Fig. 2). The YM of composites without MAPP was found to be higher than that of matrix PP. However, the YM gradually increased with increasing MAPP content up to 4 wt% which could be due to better interfacial bonding as discussed previously. A small decrease was found for further addition of MAPP, which could be due to the excess MAPP that was not bonded with wood fibre. As TS and YM were both found to be highest with 4 wt% MAPP, 4 wt% MAPP was

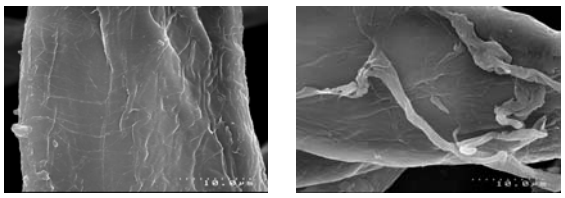
considered to be optimum and used for the rest of this study.

### 3.2 Effects of fibre beating

The TS and YM of composites (40 wt% fibre with 4 wt% MAPP) prepared with beaten fibre are presented in Table 1. TS increased from 41 MPa up to 45 MPa with increased beating time up to 5.5 minutes, which could be due to the improvement of interfacial bonding between the fibre and the matrix resulting from the formation of micro fibrils (Fig. 4) and increased surface area; TS then decreased upon further beating, probably due to fibre damage and reduced of fibre length [xix]. YM was found to gradually decrease with increased beating time which may be due to the reduction of fibre length.

Table 1: Tensile properties of composites (40 wt% fibre and 4wt% MAPP)

| Proper -ties | Beating time (minutes) | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 1.5 | 4 | 5.5 | 6.5 | 7.5 |
| TS (MPa) | 41.1 | 42 | 43.5 | 45 | 43.5 | 41.5 |
| YM (MPa) | 5453 | 4300 | 4179 | 4161 | 4100 | 4000 |



Unbeaten 5.5 minutes beaten

Fig 4: SEM of beaten and unbeaten fibre surfaces.

### 3.3. Effects of reprocessing

Reprocessing was carried out for 40 wt% fibre (with 4 wt% MAPP) reinforced composites. Very little change on TS and YM was found for PP during reprocessing (Figs. 5 and 6). The TS and YM of composites decreased with increased number of times the materials were reprocessed in a linear fashion. The virgin composites showed an average TS of 41 MPa and YM of 4553 MPa which reduced after being reprocessed 8 times to 31 MPa and 3800 MPa respectively.

One of the reasons for the changes in mechanical properties is likely to be due to the fact that reprocessing resulting some fibre damage. The average fibre length was found to decrease from 2.36 mm for virgin fibre to 0.37 mm for the fibre extracted from the 40 wt% fibre composites reprocessed 8 times (Fig. 7). The shorter fibre lengths and the increased fines percentage with reprocessing were also observable by light microscopy (Fig. 8). The reductions of fibre length would be expected to reduce reinforcing efficiency, leading to the observed reduction in TS, YM [xx].

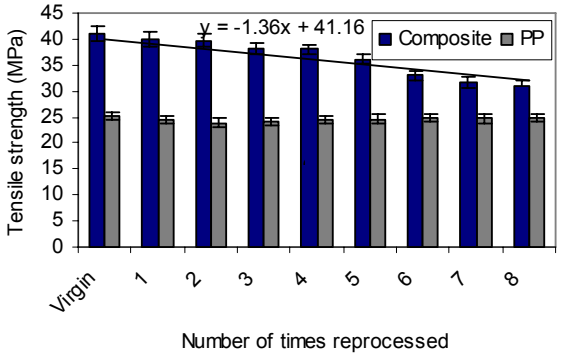



Fig 5: Tensile strength of composites versus number of times the materials were reprocessed.

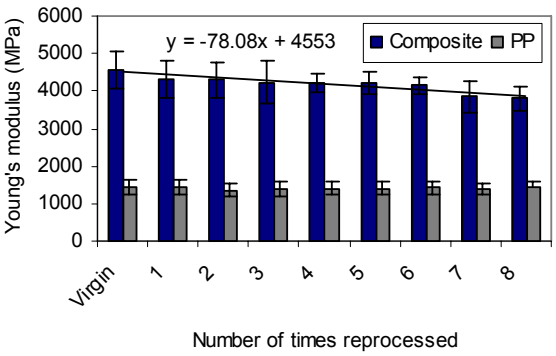



Fig 6: Young's modulus of composites versus number of times the materials were reprocessed.

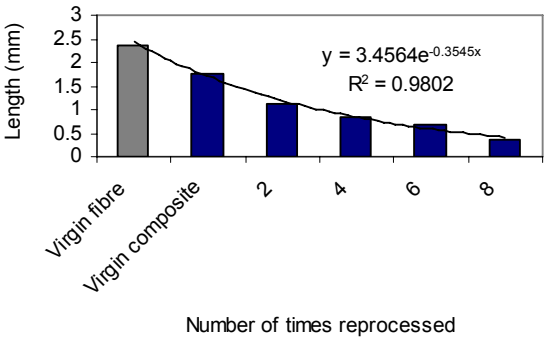
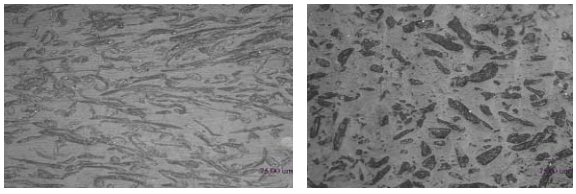



Fig 7: Average fibre length of virgin and reprocessed composites.



Virgin 8 times reprocessed

Fig 8: Fibre distribution in virgin and reprocessed composites.

### 3.4 Effects of Hygrothermal ageing

Moisture absorption increased with increased soaking time for all composites until saturation at about 5 months (Fig. 9). As no significant weight gain was found for PP

during this period, it seems likely that moisture only penetrated into the composites through the fibre and fibre matrix interface.

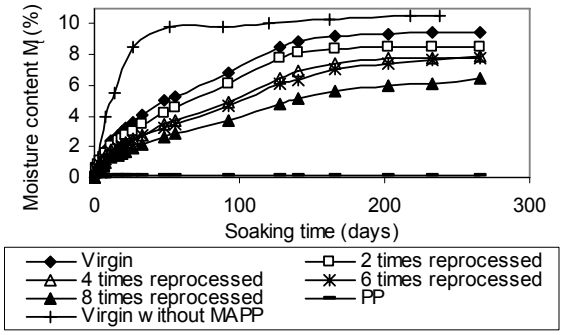



Fig 9: Moisture content of composites and PP versus hygrothermal ageing time.

The diffusion coefficient of moisture absorption was calculated using equation (2) from the plot of $M_t$ versus the square root of time (t) and presented in Table 2. Both the equilibrium moisture content and diffusion coefficient was found to be higher for composites without coupling agent than those with coupling agent. A higher diffusion coefficient for composites without coupling agent is likely to be due to poor interfacial bonding, evident from SEM (Fig. 3).

Both the equilibrium moisture content and diffusion coefficient decreased with increased number of times the materials were reprocessed (Table 2) from 9.42% and $2.54 \times 10^{-13}$ $m^2/s$ respectively for virgin composites to 6.41% and $1.01 \times 10^{-13}$ $m^2/s$ for composites reprocessed 8 times.

Table 2: Equilibrium moisture content and diffusion coefficient of 40 wt% fibre virgin (with and without MAPP) and reprocessed composites (made with 4 wt% coupling agent)

| Composites | Equilibrium moisture content $M_\infty$(%) | Diffusion coefficient D ($m^2/s$) |
|---|---|---|
| Virgin Without MAPP | 10.51 | $5.70 \times 10^{-13}$ |
| Virgin (with 4 wt% MAPP) | 9.42 | $2.54 \times 10^{-13}$ |
| 2 times reprocessed | 8.46 | $1.53 \times 10^{-13}$ |
| 4 times reprocessed | 7.93 | $1.19 \times 10^{-13}$ |
| 6 times reprocessed | 7.75 | $1.10 \times 10^{-13}$ |
| 8 times reprocessed | 6.41 | $1.01 \times 10^{-13}$ |

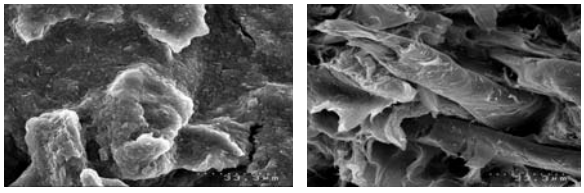
The decrease in moisture content and diffusion coefficient with increased number of times the materials were reprocessed can be explained by a number of effects. As the fibre length decreased with increased number of times the materials were reprocessed, it would have been more difficult to form finite clusters which serve as passages for water molecules to travel through the lattice from one side to another [xxi].

TS and YM decreased after hygrothermal ageing for all composites (Table 3), and it can be seen that the extent of reduction in properties decreased with increased number of times the materials were reprocessed. After ageing, reductions in TS of 33% and YM of 40% were found for virgin composites compared to reductions for both TS and YM of 27% for composites reprocessed 8 times. This may be due to the equilibrium moisture content decreasing with increased number of times the materials were reprocessed, and therefore having less effect on behaviour.

Table 3: Mechanical properties of 40 wt% fibre virgin (with and without MAPP) and reprocessed composites (made with 4 wt% coupling agent)

| Composites | TS (MPa) | | YM (MPa) | |
|---|---|---|---|---|
| | Unaged | Aged | Unaged | Aged |
| Without MAPP | 23 | 17.5 | 3619 | 1226 |
| With 4 wt% MAPP | 41 | 27.7 | 4553 | 2734 |
| 2 times reprocessed | 40 | 26.3 | 4295 | 2776 |
| 4 times reprocessed | 38 | 25.2 | 4215 | 2847 |
| 6 times reprocessed | 33 | 23.5 | 4148 | 3002 |
| 8 times reprocessed | 31 | 22.7 | 3800 | 2769 |

SEM of aged composite fracture surfaces clearly showed the loss of adhesion between fibre and matrix after ageing, characterised by the apparition of voids and fibre pull out (Fig. 10b) compared to better interfacial bonding for the composites fracture surface before ageing (Fig. 10a).



Unaged Aged

Fig 10: Effects of hygrothermal ageing showing SEMs of a) fracture surface of an unaged virgin composite, b) fracture surface of an aged virgin composite.

## 4. CONCLUSIONS

Both TS and YM increased on addition of coupling agent in composites. For 40 wt% fibre composites, 4 wt% coupling agent (MAPP) was found to be optimum, providing a 64% increase in TS and 220% increase in YM compared to the matrix PP. Fibre pre-treatment by beating increased the TS of composites from 41 MPa for unbeaten fibre composites to 45 MPa for 5.5 min beaten fibre composites, but upon further beating, TS was found to decrease. For 40 wt% fibre reinforced composites

reprocessed 8 times, a 25% reduction in TS and 16% reduction in YM was found. The reduction of TS, YM was considered to be due to fibre damage that occurred during reprocessing as evaluated by the associated reduction of the average fibre length from 2.36 mm for virgin fibre to 0.37 mm for the fibre extracted from the composites reprocessed 8 times. After hygrothermal ageing composites without coupling agent showed higher water uptake and diffusion coefficient than those with coupling agent. Both TS and YM were found to decrease after hygrothermal ageing. However, the diffusion coefficient and the equilibrium moisture contents of composites decreased with increased number of times the materials were reprocessed.

## 5. NOMENCLATURE

| Symbol | Meaning | Unit |
|---|---|---|
| $M_\infty$ | Equilibrium moisture content | (%) |
| t | Time | (s) |
| D | Diffusion coefficient | ($m^2$/s) |
| TS | Tensile strength | (MPa) |
| YM | Young's modulus | (MPa) |

## 6. ACKNOWLEDGEMENTS

The authors would like thanks to the Foundation for Research Science and Technology, New Zealand for their financial support of this project.

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