

MECHANICAL PROPERTIES OF THERMOPLASTIC MATRIX COMPOSITES WITH SILANE-TREATED WOOD FIBRE

A. Abdalla¹, K. L. Pickering² and A. G. MacDonald³

^{1,2}*Department of Materials and Process Engineering, University of Waikato
Private Bag 3105, Hamilton, New Zealand.*

Email ¹aa23@waikato.ac.nz, ²K.Pickering@waikato.ac.nz

³*Manufacturing, Forest Research, Private Bag 3020, Rotorua, New Zealand.*

SUMMARY: The effect of surface treating wood fibre with silane coupling agents on the mechanical properties of thermoplastic matrix composites was studied. Two different silane agents, Dichlorodiethylsilane (DCS) and Gamma-aminopropyltriethoxysilane (GS), were used to treat radiata pine (*Pinus Radiata*) wood fibre. In addition, the effect of pre-treatment with a 2% solution of sodium hydroxide (S) was studied. Composite sheets were produced by blending fibre (5, 10 and 20wt%) with polyethylene and extruding. An increase in strength was obtained at fibre contents of 5wt% for all treatments. This is believed to be mainly due to increased chemical bonding. However, there was no such improvement obtained at higher fibre contents. Here it is believed the effects of fibre agglomeration are limiting composite strength.

KEYWORDS: Wood Fibre, Silane Coupling Agent, Thermoplastic Matrix Composite, Polyethylene

INTRODUCTION

In recent years, considerable efforts have been made to develop light, strong, and inexpensive fibres to reinforce polymeric materials. Natural plant-based (cellulose) fibres, originating from renewable sources, are a potential alternative to conventional fibres [1]. Their low cost, low density and biodegradability constitute major incentives for their use as reinforcement. One problem with these fibres is their highly polar nature, which makes them incompatible with non-polar polymers, such as commodity thermoplastics [2]. This limits stress transfer at the fibre-matrix interface and therefore reduces the potential for reinforcement of the fibres. In addition, fibre-fibre interactions resulting from intermolecular hydrogen bonding, limits the dispersion of the fibre in such a matrix [3]. This situation calls for the development of strategies for surface treatment to facilitate the fibre dispersion and induce bond formation between the fibre and the polymer.

Stress transfer at the interface between the different components can be influenced by chemical modification. The term chemical modification is taken to include improvement in the efficiency of wetting by the matrix (termed compatibilization) and also the creation of chemical bonds (usually covalent) between the surface cell walls of the fibre and the matrix via a novel adduct [4].

The most common adhesion promoters are coupling agents based on silane molecules [5]. These are widely employed in systems involving glass or silica substrates, and more particularly in the case of polymer-based composites reinforced by glass fibre. Their use in systems involving cellulose fibres has not been extensively studied [3].

In this work, the effect of two different silane coupling agents on the mechanical properties of wood fibre reinforced thermoplastic matrix composites were examined. Results were considered taking into account the degree of silane uptake obtained from the different treatments and also the effect of a pre-treatment with sodium hydroxide [6].

EXPERIMENTAL DETAILS

Materials

Thermomechanical Pulp (TMP) wood fibre was supplied by Forest Research, New Zealand, Rotorua, procured from radiata pine (top log chips). These fibres had a length of between 1-3 millimetres and an average tensile strength of 107 MPa. Polyethylene powder (MD1030) was obtained from Clariant (New Zealand) Ltd, Auckland, New Zealand, quoted as having a tensile strength of 15MPa.

Pre-treatment

Approximately half of the wood fibre was treated with 2%w/w sodium hydroxide. To these ends, the wood fibre was immersed to about two hours in the sodium hydroxide solution and then rinsed with distilled water until a pH of 7 was attained.

Treatment

The wood fibre was completely dried and then exposed to air until it acquired a moisture content of 10wt%. It has been shown [7] that the amount of water bound in fibres is critically important for hydrolysis of silane. At water contents greater than 10wt%, when silane is hydrolysed to produce silanol it tends to react with itself to produce polymerised silane which does not couple to the fibre. This tends to rest on top of the fibre and prevents the fibre from reacting with any unpolymerised silanol. It is noted that when silane is applied by immersing the wood fibre in a bath of silane solution with excess water, only low contents of silanol are observed in the final treated fibre. However, at moisture contents of less than 10wt%, incomplete mono-layers of silanol are coupled to the wood fibre.

Silane coupling agents, namely Dichlorodiethylsilane (DCS) and Gamma-aminopropyltriethoxysilane (GS), produced by Sigma Chemicals Co., St Louis, USA and Aldrich Chemicals Co., Milwaukee, USA, respectively, were dissolved to give a

concentration of 0.1% in an acetone/acetic acid mixture with a volume ratio of 19:1. The amount of solution used was just sufficient to wet the wood fibre to allow hydrolysis of silane to take place with water bound to the fibre. After immersion, the fibre was left for over an hour to dry in air and then oven dried at 60°C for 24 hours. The fibre was then thoroughly rinsed using pure acetone and then dried again for 24 hours.

The treated samples were analysed using X-ray Photoelectron Spectroscopy (XPS) to assess the amount of silane coupled to the fibre surface.

Extruding

The treated fibres were blended with polyethylene using a food processor to give fibre contents of 5, 10, and 20wt%, following which, the powder could be seen to be evenly distributed throughout the fibre, attached loosely on the fibre surface. These mixtures were then dried in the oven at 60°C for 24 hours, then transferred to a twin screw extruder set at 165°C and converted to composite sheets of approximately 1mm thick. These were then pelletised and re-extruded for maximum homogeneity. Samples were prepared for tensile testing according to ISO/R527-1966(Plastics, Determination of Tensile Properties).

RESULTS AND DISCUSSION

XPS spectra results for the different treatments are summarised Table (1). The analysed silicon mass concentration was 2.3%, 3.2%, 2.2%, and 0% for fibres treated with GS, DCS, DCS+S, and GS+S respectively. The mechanism by which silane reacts with the wood fibre is discussed by the authors elsewhere [6].

Table 1 XPS data results

	Mass Concentration %			Binding Energy		
	O	C	Si	O	C	Si
Untreated	37.9	62.1	-	536	289	-
GS	31.1	66.5	2.3	537	289	105
GS + pre-treated	37.9	62.1	-	536	289	-
DCS	30.3	66.4	3.2	536	288	105
DCS + pre-treated	35.5	62.1	2.2	536	288	105

The strength of composite materials reinforced with untreated wood fibre is shown in Fig. 1. Similar to other work [9,10], this shows an initial decrease in composite strength as the fibre weight percentage increases from 5wt% to 10wt%, followed by little change at a fibre content of 20wt%. The initial reduction of strength obtained on addition of untreated wood fibre was expected due to fibre-matrix incompatibility as described previously.

For fibre additions of 5wt%, silane treatment (Fig. 2 and Table 2) generally resulted in improvement in strength. This increase is expected to be due to increased chemical coupling between the fibre and the matrix. An alternative, however, may be due to the effect of the treatment on the strength of the fibres themselves. Other workers [8] have observed increases in fibre strength for flax after surface treatment. To resolve this, further work is required.

Similar increases in strength were not reflected at higher fibre contents. Here, there was a similar trend for 3 out of the 4 sample types (GS, DCS, DCS+S). For these samples, surface treatment gave little benefit in strength at 10wt% fibre content and at the highest fibre percentages, an actual reduction in strength was observed.

One explanation for the general reduction in the strength for the treated wood fibre as the fibre weight percentage increases (10wt% and 20wt%) could be related to fibre agglomeration, which, would be more likely at higher fibre contents. This is something that would need to be considered for the future processing of treated wood fibre.

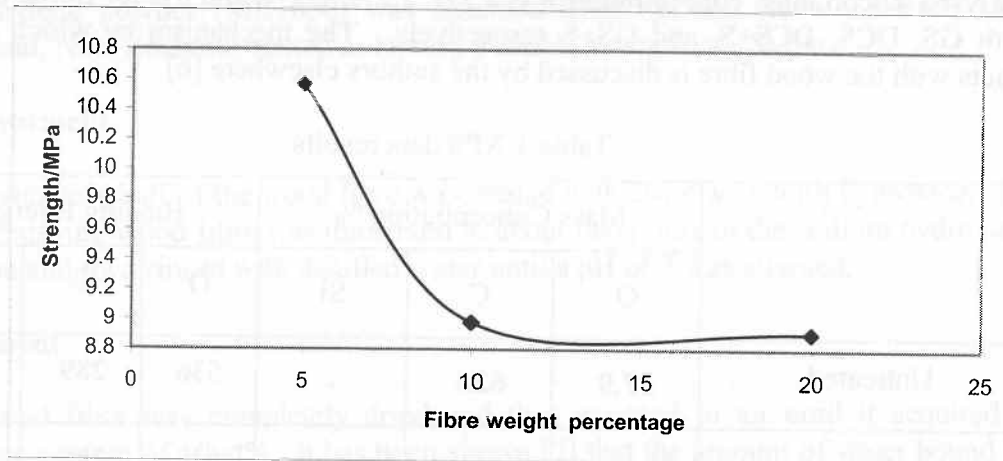


Figure 1 Composite strength versus fibre weight percentage for untreated wood fibre

Table 2 Average composite strengths for untreated and treated fibres

Fibre Weight Percentage	Untreated MPa	GS+S MPa	GS MPa	DCS MPa	DCS+S MPa	Pre-treated MPa
5	10.57	11.58	12.47	11.76	12.66	11.52
10	8.98	4.97	9.05	9.87	9.87	9.09
20	8.91	7.02	7.67	8.34	8.35	8.55

For GS+S treated samples, the strength was consistently lower at 10 and 20wt% fibre. However, as discussed elsewhere [6], for this particular set of samples, the treatment

regime was slightly different, resulting in a lack of silane coupled to the fibre. However, this seems to be in conflict with the improvement in strength observed at 5wt% fibre. Certainly this improvement cannot be explained by coupled silane leading to improved bonding. To understand this trend further, we must examine the effect of just the sodium hydroxide pre-treatment on composite strength as shown in Fig. 3.

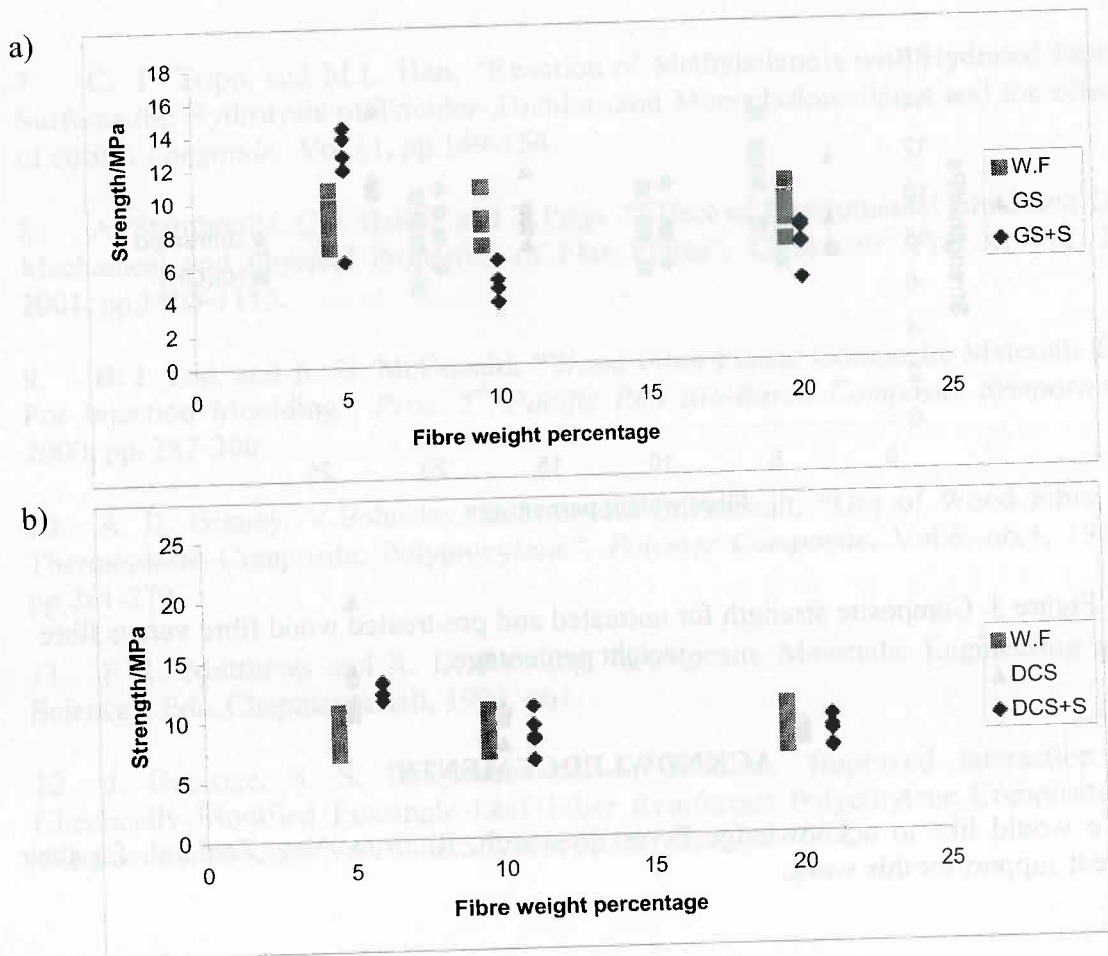


Figure 2 Comparison of composite strength versus fibre weight percentage for untreated fibre samples compared to samples with a) fibre treated with DCS and DCS+S, b) fibre treated with GS+S

It can be seen that the strength of the samples pre-treated with sodium hydroxide has increased at the fibre content of 5wt% similar to that seen for GS+S. This can be explained by mechanical interlocking [11] assisting bonding as a result of the sodium hydroxide pre-treatment which changes the topography of the fibre [12]. However, this is less effective at higher fibre weight percentages, which again could be due to fibre agglomeration.

CONCLUSIONS

Surface treatment using silane coupling agents was found to improve the strength of composites containing 5wt% fibre, suggesting silane to be assisting in interfacial

bonding. An alternative possibility is that the treatment is increasing the strength of the fibres themselves. This is to be examined in future work. Surface treatment gave little benefit in strength at 10wt% fibre content, and at the highest fibre content, an actual reduction in strength was observed. It is believed that the effects of agglomeration at higher fibre weight percentages masks the advantages of interfacial bonding obtained with 5wt% fibre.

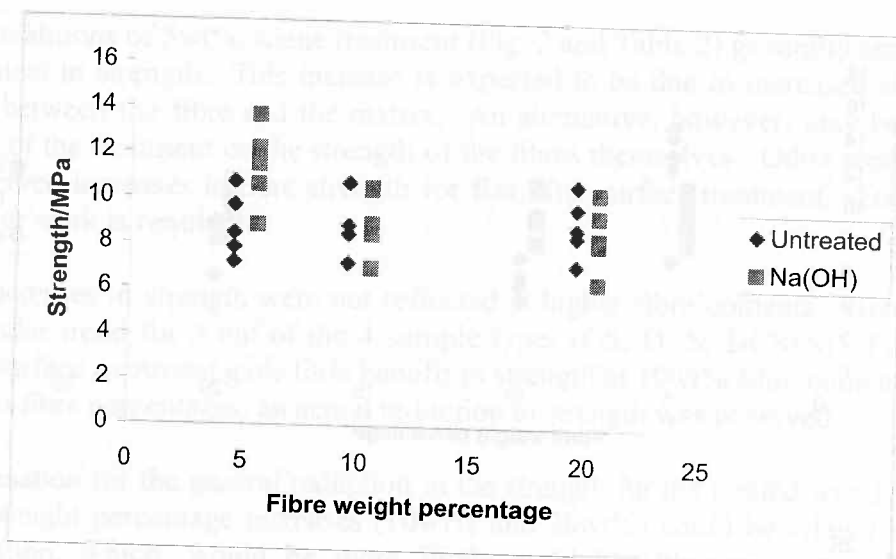


Figure 3 Composite strength for untreated and pre-treated wood fibre versus fibre weight percentage

ACKNOWLEDGEMENTS

We would like to acknowledge Forest Research, Rotorua, New Zealand, for their great support for this work.

REFERENCES

1. D. N. Saheb and J.P. Jog, "Natural Fibre Polymer Composite: A Review", *Advances in Polymer Technology*, Vol. 18, no.4, 1999, pp.351-363.
2. R. Gauthier, C. Joly, A. C. Coupas, H. Gauthier and M. Escoubes, "Interfaces in Polyolefin/Cellulosic Fiber Composites: Chemical Coupling, Morphology, Correlation with Adhesion and Aging in Moisture", *Polymer Composites*, Vol.19, no.3, 1998, pp.287-300.
3. L. M. Matuana, J. Balatinecz, C. B. Park and R. N. S. Sodhi, "X-ray Photoelectron Spectroscopy Study of Silane Treated Newsprint-Fibers", *Wood Science and Technology*, Vol.33, 1999, pp.260-270.
4. A. Kelly and C. Zweben, "Comprehensive Composite Materials", Vol.1, Eds.Elsevier, 2000, pp.303-325.

5. E. P. Pluedmann, "Silane Coupling Agent in Reinforced Plastics", Eds. John Wiley & son, Inc. 1970, pp.95-106.
6. A. Abdalla and K. Pickering, "XPS Study Of Wood Fibre Treated With Silane Coupling Agent For Use In Thermoplastic Matrix Composites", *Proc. New Zealand Engineering and Technology Postgraduate Conference*, August 2001, pp.33-48.
7. C. P. Tripp, and M.L. Hair, "Reaction of Methylsilanols with Hydrated Silica Surfaces: the Hydrolysis of Trichlor-, Dichlor-, and Monochlorosilanes and the effect of curin", *Langmuir*, Vol.11, pp.149-154.
8. A. Stamboulis, C.A Baillie and T. Peijs, "Effect of Environmental Condition On Mechanical and Physical Properties of Flax Fibres", *Composite :Part A*, Vol. 32 2001, pp.1105-1115.
9. B. J. Lee, and A. G. McDonald, "Wood Fibre-Plastic Composite Materials for For Injection Moulding", *Proc. 5th Pacific Rim Bio-Based Composite Symposium*, 2000, pp. 287-300.
10. A. D. Beshay, V. Bohuslav, Kokota and C. Daneault, "Use of Wood Fibre in Thermoplastic Composite: Polypropylene", *Polymer Composite*, Vol.6, no.4, 1985, pp.261-270.
11. F. L. Matthews and R. D. Rawling, "Composite Materials: Engineering and Science", Eds. Chapman & Hall, 1994, p61.
12. J. George, S. S. Bhagawan and S. Thomas, "Improved Interaction In Chemically Modified Pineapple Leaf Fiber Reinforced Polyethylene Composites", *Composite Interfaces*, Vol. 5, no.5, 1998, pp.201-223.

KEYWORDS: Composite, Pineapple Leaf Fiber, Polyethylene, Injection Moulding, Matrix, Frequency