

Improvement of Interfacial Bonding of WPC Based on Various Maleic Acid Anhydride Pre-treatments

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Keywords: Interfacial bonding, maleic acid anhydride, pre-treatment, wood polymer composites, WPC

ABSTRACT

Wood Polymer Composites (WPC) are a relative new group of hybrid materials, which consists of wood particles, thermoplastic polymers and various additives. The properties of WPC are influenced by various factors and parameters such as wood, wood content, polymer type, processing techniques and parameters as well as additives. Formulations based on Polyolefin's need the use of coupling agents to bridge the polarity differences between the wood particles and the polymer. Generally accepted and mainly used maleic acid anhydride (MAA or grafted on a polymer backbone, *e.g.* MAPP) is added as coupling agent. The estimation of the mode of action is that functional components of the maleic acid anhydride molecule react with the hydroxyl groups of the wood. The main objective of this research was to investigate and improve the interfacial bonding strength between the polymer matrix and pre-treated wood particles (dry-mixing, emulsified MAPP, direct extruded).

INTRODUCTION

Attention has been paid to improving the compatibility of the wood particle with the polymer matrix, by providing an interaction between the wood particle and the polymer. Generally, coupling agents markedly improve physical properties of the polymeric composite and its overall performance (Mahlberg *et al.* 2001, Balasuriya *et al.* 2002, Stark 2003, Richter 2004, Borysiak *et al.* 2006, Hill 2006, Radovanovic 2007, Grüneberg *et al.* 2008). In order to improve the compatibility between high surface energy lignocellulosic fibers and low-energy polyolefin matrix materials, extensive use has been made of coupling agents (Bledzki *et al.* 1998, Hill 2000, Lu *et al.* 2000, Richter 2004). The most commonly employed coupling agents are maleated polymers (*e.g.* maleic anhydride polypropylene (MAPP) or polymethylene polyphenylene isocyanate (PMPPIC) (Hill 2006). Coupling agents are added to the wood fibre/polymer ingredients and subjected to energetic mixing involving high shear in extruders or high speed mixers. Evidence has been represented indicating that the attached anhydride moieties are capable of reacting with the surface of the lignocellulosic fiber (Felix *et al.* 1991, Grüneberg 2006, Hill 2006).

MATERIAL AND METHODS

Particles of spruce (*Picea abies*), type Arbocel C320G (Rettenmaier, Rosenberg Germany) with a main particle size between 2.0-5.0 mm are used for the study. Powdered Polypropylene homopolymer is used as matrix material with a melt flow index of 26 [230 °C/2.16 kg], type HG 245 FB (Borealis, Denmark). Grafted Licocene

PPMA 7452 (Clariant, Gersthofen Germany) is used as coupling agent in various conditions (powdered, emulsified, and extracted) with a density of 0.91 g/cm³. The pre-palletized wood-particles have been separated in a water treatment and afterwards dried to a moisture content of 1-2%. The direct extruded material (R) is directly feeded into an extruder without any pre-treatment. A MAPP-dispersion (30%-stock solution, 70% emulsifier) is used to pre-treat the wood particles in the given concentrations (E). The wood particles are separated in cold water and treated with the dispersion; afterwards dried to a moisture content of u=1-2%. The dry-mixed material (T) is prepared in a free-fall horizontal mixer until the material is mixed homogeneously (75 [1-min]). The curing is done in a dry-chamber at a material temperature of 165°C for 15 minutes.

Table 1: Overview on modification methods

Abbreviation	Concentration (MAPP) [%]	Modification method
H ₂ O	-	without MAPP, water treated reference
R	1,3,9	direct extrusion no pre-treatment
E	1,3,4.5,6,9	pre-treated with dispersed MAPP
T	1,3,9	pre-treated with dry-mixing

After pre-treatment the wood particles were compounded with a ratio of 30% Polypropylene (PP), 61-70% wood and 1-9% MAA (depending on pre-treatments) in a co-rotating twin screw extruder (27 mm screw diameter). Test specimens were produced via injection molding according to the European standard EN 527-2. All samples are stored at 20 °C and 65% relative humidity for 21 days before testing. Mechanical properties (tensile strength according EN 527 ($v = 1$ mm/min), bending strength and Modulus of Elasticity (MOE) according ISO 178 ($v = 2$ mm/min) and impact bending according ISO 179) were measured.

RESULTS

The tensile strength for the samples made from water treated wood particles (H₂O) a value of 18.25 N/mm² was measured. The direct extruded references showed the highest values in the tensile strength. R 3 with 46.54 N/mm² has a higher value than R1 and R9. The samples made from emulsified wood particles (E) showed a slight increase of the tensile strength compared to the water treated, up to 24.77 N/mm² with 1% MAPP (E1), however E9 showed a strong decrease down to 10.32 N/mm². The value of the dry-mixed wood fibers (T), showed an increase of the tensile strength up to 46.64 N/mm² for T3 and slightly lower values for T1 39.95 N/mm² and for T9 38.29 N/mm². The Modulus of elasticity (MOE) for water treated wood particles is 6114 N/mm². In all formulations, except for E9 6078 N/mm², the MOE is increased, the highest value is measured for T1 7528 N/mm². The values for the load of work showed similar results to the tensile strength. Water treated wood particles reached a value of 32,07 [N/mm²], the strongest decrease is measured at E9 (25.69 N/mm²). The highest values are R3 8085 N/mm² and 79.25 N/mm² with slight decreases in the R1 and R9 as well as T1 and T9.

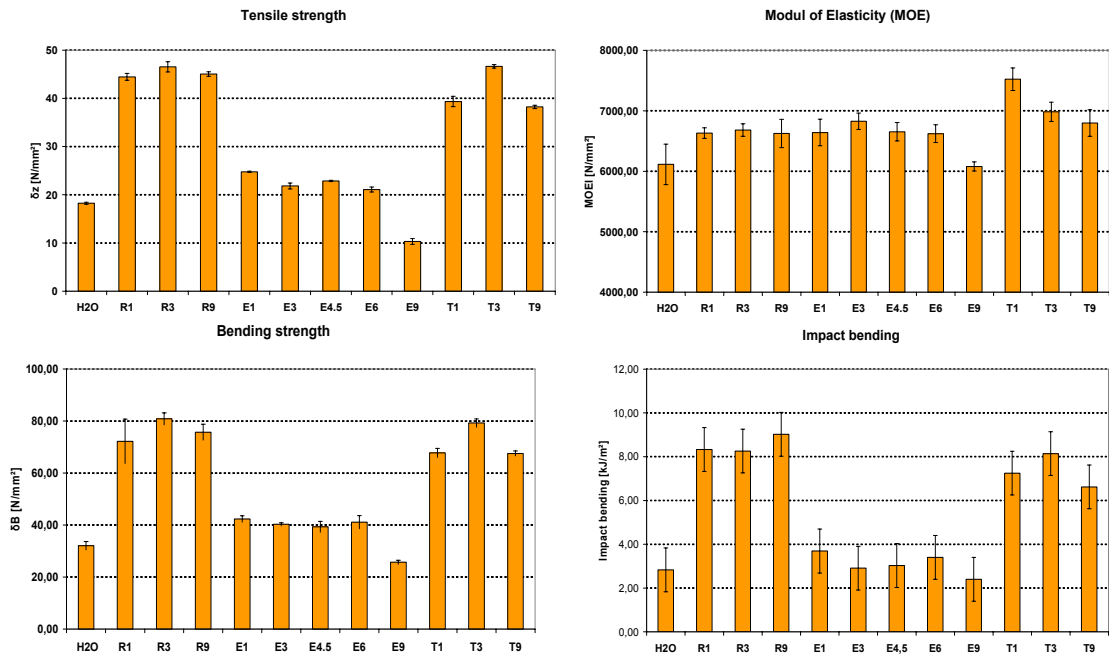


Figure 1: Mechanical properties of various pre-treated wood particles ($n=15$)

The impact bending showed the highest values in the direct extruded wood particles (R9 9,02 [KJ/m²]) and the lowest for E9 2,40 [KJ/m²]. Compared to the pure plastic reference, no break during test, all formulations with added wood fibers showed a strong decrease of the impact bending energy.

DISCUSSION

Of all tested pre-treatments the direct extruded samples showed the highest values, except for the MOE. A clear correlation between the concentration and the resulting mechanical properties was not found. The samples made from dry-mixed wood particles showed similar values than the direct extruded samples; an increase in the measured MOE values, especially for E1 was observed. The emulsified MAPP treated fibers showed a strong decrease of all mechanical properties. A reason for the low values of emulsified wood particles can be the higher presents of OH groups in the solution and the presents of the emulsifying agent. Microscopy investigations showed a strong mechanical stress through the single wood particle, which deformed the cells and either filled the cell lumina with polymer or compressed it. Overall the samples showed a strong orientation due to the particle distribution across the sample geometry. The tested pre-treatments showed no significant improvement of the measured mechanical properties compare to direct extruded wood particles. Partly a slight increase, e.g. MOE T1, was achieved.

ACKNOWLEDGEMENT

The company Clariant AG, Gersthofen (Germany) is gratefully acknowledged for supporting the work and providing materials.

REFERENCES

- Balasuriya, P.W., Ye, L., Mai, Y.W. and Wu, J. (2002), Mechanical properties of wood flake-polyethylene composites. II. Interface modification. *Journal of Applied Polymer Science*, **83**, 2505-2521
- Bledzki, A.K., Reihmane, S. and Gassan, J. (1998), Thermoplastics reinforced with wood fillers: a literature review. *Polymer and Plastic Technology*, **37**, 451-468
- Borysiak, S. and Doczekalska, B. (2006), Influence of chemical modification of wood on the crystallisation of polypropylene. *Holz als Roh- und Werkstoff*, **64**, 451-454
- Felix, J.M. and Gatenholm, P. (1991). "The nature of adhesion in composites of modified cellulose fibers and polypropylene", *Journal of Applied Polymer Science*, **42**, 609-620
- Grüneberg, T. (2006). Untersuchung zur verbesserung der verbundeigen-schaften von holz-polymer-verbundwerkstoffen auf basis von poly-propylen. *Masterarbeit Fachhochschule Rosenheim, Fachbereich Holztechnik (geschützt)*
- Grüneberg, T., Mai, C., Militz, H., Kurda, K., Kretschmer, K. and Radovanovic, I. (2008). Holz und kunststoffe – die eigenschaften der grundstof-fe für WPC. *Holztechnologie*, in press
- Hill, C.A.S. (2000). Wood-Plastic Composites: strategies for compatibilising the phases. *Journal of the Institute of Wood Science*, **15**, 140-146
- Hill, CAS (2006), *Wood Modification – Chemical, Thermal and other Processes*, John Wiley & Sons, Ltd, Chichester, UK.
- Lu, JZ, Wu, Q and McNabb, HS (2000). Chemical coupling in wood fiber and polymer composites: a review of coupling agents and treatments. *Wood and Fiber Science*, **32**, 88-104
- Mahlberg, R., Paajanen, L., Nurmi, A., Kivisto, A., Koskela, K. and Rowell, R.W. (2001). Effect of chemical modification of wood on the mechanical and adhesion properties of wood fiber/polypropylene fiber and polypropylene/veneer composites." *Holz als Roh- und Werkstoff*, **59**, 319-326
- Radovanovic, I. (2007). Verarbeitung und Optimierung der Rezeptur von Wood Plastic Composites (WPC). *Dissertation Universität Osnabrück*
- Richter, E. (2004). Additives for Wood-Plastic Composites. *5th Global Wood and Natural Fiber Composites Symposium, 27-28 April 2004, Kassel, Germany, Proceedings*
- Stark, N.M., Rowlands, R.E. (2003). Effects of wood fiber characteristics on the mechanical properties of wood/polypropylene composites. *Wood Fiber Science*, **35**, 167-174