Influence of Various Wood Modifications on the Properties of Polyvinyl Chloride/Wood Flour Composites

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ABSTRACT: Aminosilane, melamine and acetic anhydride treated wood flour were added to polyvinyl chloride (PVC) in order to process improved PVC/wood flour composites. The influence of wood treatment on water absorption and mechanical properties were evaluated. Treatments with amino-alkyl functional oligomeric siloxane and melamine in suitable concentration as well as acetylated wood flour composites showed decreased equilibrium moisture content and reduced speed of water absorption. Tensile strength, elongation at break and unnotched impact strength were considerably improved by the aminosilane treatments. The increase in strength and elongation was mainly influenced by the chemical structure and concentration of the used aminosilanes.
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Key words: interfaces; poly(vinyl chloride); composites; renewable resources; mechanical properties

INTRODUCTION

During the last 30 years, extensive research is done on the development of wood polymer composites (WPC).[1] Depending on the particle geometry, wood is used as a filler or reinforcement in polymer matrices to improve selected composite properties.[2,3] Compared to mainly used polyolefin-based matrices, polyvinyl chloride (PVC) shows enhanced stiffness, creep behavior, weatherability, and flame retardancy.[4] Thus, PVC-based composites can be used in building construction applications such as doors, windows, or facades.[5] For such applications, the hydrophilic wood surface shows crucial limitations. On the one hand, the compatibility with the more hydrophobic PVC is limited, leading to poor interfacial adhesion. On the other hand, moisture absorption occurs causing material defects, voids, and low dimensional stability.[6,7] The hydrophilic nature of wood is due to the presence of free hydroxyl groups in all cell wall layers and chemical components. Blocking and/or minimizing these OH groups is the main goal of wood modification.[8–15] To use suitable processes and modifications for WPC, critical mechanical properties of the wood component, e.g., impact bending, have to remain unchanged after treatment. A promising method is the treatment with aminosilanes.[4,16–21] Alkylalkoxysilanes are able to form covalent bonds with the cell wall and condense to a three-dimensional network after hydrolysis. Since at least one alkyl group remains in the system, it is stable against hydrolysis.[14,22] Amino groups included in the silicon compound are able to interact with other polymers or chemicals. Concerning PVC, the surface energy of aminosilane-treated wood flour changes and becomes more hydrophobic.[17] Furthermore, wood has a more basic nature due to the amino groups and can interact with the acidic surface of PVC.[17,20,23] Thus, aminosilane-treated wood acts also as a promoter/coupling agent in PVC-based WPC.[16,19] The main interaction is suggested according to Lewis acid-base theory, where ionic bonds are formed between the amino groups of treated wood flour and the chlorine atoms of the PVC.[16,24,25] The penetration of aminosilanes into the cell wall during impregnation depends on molecular sizes as well as hydrolysis and condensation reactions.[14] Therefore, silanes with various degrees of condensation, molecular sizes, and amino group contents were used in this study. Compared to other studies, the influence of high silane contents on the composite properties was investigated. Hydrophobicity can also be achieved by using methylated melamine-formaldehyde resin.[26] Its ability to penetrate the cell wall structures has been investigated.[27,28] Curing of the resin depends on temperature and pH value. During curing melamine monomers condensation, whereas methanol, water, and formaldehyde molecules are split off.[29,30] As leaching effects are negligible, the thermoset remains in the cell wall.[31] The treatments with melamine formaldehyde resin improve

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dimensional stability and biological durability of solid wood.[32] The third modification method used in this study is the acetylation of wood with acetic anhydride. Acetylation causes a reaction of acetic anhydride with the hydroxyl groups of wood forming acetyl groups and acetic acid.[12] Several studies reveal positive effects on durability and dimensional stability properties.[10,11,13] The modification agents were selected to compare the impact of different mode of actions of wood treatment on the properties of WPC.

EXPERIMENTAL

Material

PVC with a *K* value of 63 was provided by Solvin SA in the form of powder. Wood flour particles were obtained from wood milling processes and supplied by JRS (Rosenberg). The average size of the wood flour particles was in a range of 50–150 μm. The following modification agents were used: γ-aminopropyltriethoxysilane (Ameo) has monomeric structure; Dynasylan HS 2909 is derived from complete hydrolysis and partial condensation of monomeric ethoxysilanes, containing amino as well as hydroxyl groups, which can be subject to further condensation. Aminosilanes were provided by Evonik AG, Essen. Furthermore, methylated melamine-formaldehyde resin was applied (Madurit MW840, Ineos melamines GmbH) with a solid content of 75% solved in water. For acetylation process, acetic anhydride (provided by Th. Geyer, Hamburg) was used in this study. To complete the formulation, the following additives were mixed with main components: Ca/Zn stabilizer, polyethylene-based wax, glycerin stearate, and aliphatic acid as lubricants and calcium carbonate as mineral filler.

Methods

Wood flour treatment

Aminosilanes and melamine resin were solved in water and applied to wood flour in concentrations of 1 and 10 wt % (abbreviations: 1Ameo, 10Ameo, 1HS2909, 10HS2909, 1Mel, 10Mel). Acetylation was performed using a 40% acetic anhydride in a solution with ethanol (abbreviation: Acetyl). Solutions were sprayed onto oven-dried (48 h at 103°C) wood flour in a mixing drum. Afterward, the treated wood flour was first dried in a vacuum-heated chamber to moisture content below 1%. Subsequently, the temperature was raised to 120°C to obtain suitable reaction conditions. In addition, the untreated wood flour was used as reference (abbreviation: Ref). The Ref was treated with water in the same way to reduce the impact of the treatment process itself, e.g., particle destruction, on the results.

TABLE I
Composite Ingredients

Ingredients	pph
Suspension PVC	100
Ca/Zn Stabilizer	2.5
Polyethylene wax	0.15
Glycerin stearate	1.2
Aliphatic acid	0.2
Calcium carbonate	10
Wood flour (dried)	116

Processing of PVC wood flour composites

The treated and untreated wood flour, PVC, and additives were dry blended in a mixer (Reimelt Henschel, FM L 30 KM 85) until a product temperature of 120°C was reached. Composition details are listed in Table I. Dry blend was compounded to granulate by counter-rotating twin screw extrusion (Leistritz MICRO 27). The compounding parameters were adjusted to obtain an average mass temperature of 180°C at a screw rotating speed of 65 rpm. The composites were compression molded into panels ($4 \times 280 \times 340$ mm^3) using a hydraulic press (Joos, HP-S 200LAB) at 190°C and 60 bars for 5 min. The temperature was slowly reduced to allow compressed hardening of the composite.

Property testing

Water absorption of the composites was measured according to EN 62. Five replicates for each composite were selected and oven dried for 2 days at 103°C. The dried samples were weighed to a precision of 0.01 g and subsequently placed in distilled water. The water absorption was calculated at various submersion times using Eq. (1).

$$U(\%) = \frac{M_2 - M_1}{M_1} \times 100 \quad (1)$$

where water absorption U (%) is described by mass (g) of dried (M_1) and submersed (M_2) sample. The equilibrium moisture content (EMC) was calculated at the end of the test using Eq. (2).

$$\text{EMC}(\%) = \frac{M_{\text{end}} - M_1}{M_1} \times 100 \quad (2)$$

where M_{end} is mass (g) after 1680 h. In addition, the linear slope (m) of each absorption curve was calculated between the second (168 h) and the fifth (672 h) data point.

The mechanical properties of the composite were assessed by testing impact and tensile properties. Unnotched impact strength test was performed according to EN ISO 179-1/1eU by using a Ceast,

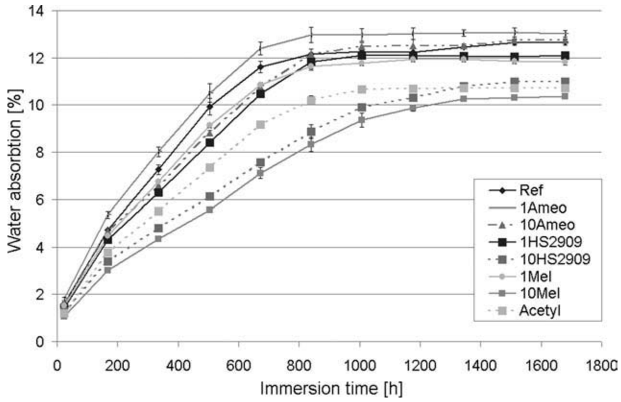

Figure 1 Water absorption versus immersion time of PVC/treated and untreated wood flour composites.

Resil Impact tester with hammer energy of 1 J for 15 replicates per composite. The tensile testing was conducted according to EN ISO 527 using a Zwick/Roell static testing material machine, model Z010 Allround Line. For each composite, 10 samples were tested at a cross head speed of 2 mm/min.

Statistical analysis

Origin 8G system was used for statistical analysis of the modification effects on the mechanical properties. One-way ANOVA and Turkey pairwise comparison at a 95% confidence interval were used to investigate differences between the composites. Significant differences are expressed with different letters in columns.

RESULTS AND DISCUSSION

Water absorption

The water absorption curves of the investigated composites are illustrated in Figure 1. Additionally, the calculated EMC and the gradient *m* of the linear slope of the absorption curves for each composite are listed in Table II. The speed of moisture absorption is considerably reduced for 10HS2909 and 10Mel, whereas EMC is reduced for 10HS2909,

TABLE II
Water Absorption Characteristics of PVC/Treated and Untreated Wood Flour Composites

Composites	EMC (%)	*m*
Ref	12.66	0.0154
1Ameo	13.03	0.0161
10Ameo	12.75	0.0137
1HS2909	12.10	0.0136
10HS2909	10.98	0.0094
1Mel	11.84	0.0143
10Mel	10.36	0.0090
Acetyl	10.72	0.0119

10Mel and Acetyl. All other composites did not show decisive differences to the Ref. The speed of uptake provides information about the hydrophilic nature of the wood flour. HS 2909 contains hydrophobic alkyl groups, which are required for effective water repellence. Moreover, it is reported that a higher long-term preservation is reached by multifunctional silane systems.[14] Ameo is neither changing the speed of absorption nor the EMC. This is an indication that Ameo does not alter the hydrophilic behavior of the wood. It can be assumed that the amount of unlinked amino and hydroxyl groups in Ameo-treated wood flour causes the observed effects. The treatment with methylated melamine-formaldehyde resin (10Mel) showed the lowest EMC value (10.36%) and speed of water absorption. Thus, it is possible to apply melamine-treated wood flour in PVC-based WPC processing to obtain suitable modification and hydrophobic conditions, respectively. The reduced EMC of 10Mel and Acetyl can be explained by the bulking of the cell wall, reducing the amount of water within the cell wall structure.[10,26]

Tensile properties

Tensile strength of PVC/treated and untreated wood flour composites are presented in Figure 2. HS2909 and Ameo-treated wood flour showed improved tensile strength values compared to the untreated Ref. An increase of the tensile strength by 40% was achieved after treatment with 10Ameo, for 10HS2909 the enhancement amounted to 34%. The treatments with low aminosilane content (1Ameo and 1HS2909) showed a slight improvement. In contrast to other studies, the strength values were improved by aminosilane concentrations above 1.5 wt %.[19] The coupling effect between amino groups and PVC seemed to be higher than the effect of self condensation reaction of hydrolyzed silane at the wood surface. With

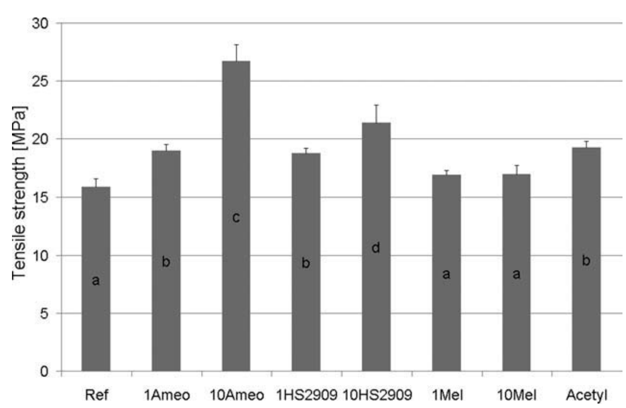

Figure 2 Tensile strength of PVC/treated and untreated wood flour composites. Data in columns with different letters have significant statistical difference.

increasing silane content, the interfacial adhesion between basic wood surface and acidic PVC surface was enhanced. In comparison to HS2909, Ameo contains more amino groups, which could be an explanation for the improvement of the tensile strength values at high contents. Melamine treatment exhibits no influence on the tensile strength of the composite. A minor improvement was observed for the acetylated wood flour composite. The interface is dominated by van der Waals forces between acidic polymer and acidic/neutral wood flour.[33] The wood content mainly influences the tensile modulus and was kept constant at 116 pph (50 wt %); therefore, the values ranged between 5103 MPa (Ref) and 5638 MPa (1Mel). Because of the low strain at test conditions, the tensile modulus is a rather unsuitable parameter to obtain information about the interfacial adhesion between PVC and treated wood flour.[16] The third tensile property evaluated was the percentage elongation at break (Fig. 3). The results are comparable to those from tensile strength values, whereas high aminosilane contents (10Ameo, 10HS2909) and Acetyl showed a significant improvement in elongation. Adding polypropylene (PP)-grafted maleic anhydride as coupling agent to PP-based composites showed improved elongation values,[34] as observed for composites with higher aminosilane content in this study. Acid-base interactions between PVC and treated wood flour indicate improved elongation properties of the composite.

Impact properties

Unnotched impact strength of PVC/treated and untreated composites is presented in Figure 4. Modified wood flour composites with high silane content (10Ameo and 10HS2909) revealed that the highest increase in impact strength and low concentrations did not significantly change that property. The impact strength indicates the ability of the composite to achieve a rapid transfer of stress/strain into the bulk material without critical stress peaks. This fact is mainly attributed to the interphase behavior. This is an indication for an enhanced interphase between treated wood and PVC. Advanced impact strength due to adding of various silane-structures and/or adding coadditives to the formulation was shown by other authors.[19,20] Obviously, the use of high silane contents enhances the interphase between PVC and wood flour. Melamine treatment showed no effect on the impact strength of the composite, whereas acetylated wood flour leads to a slight increase.

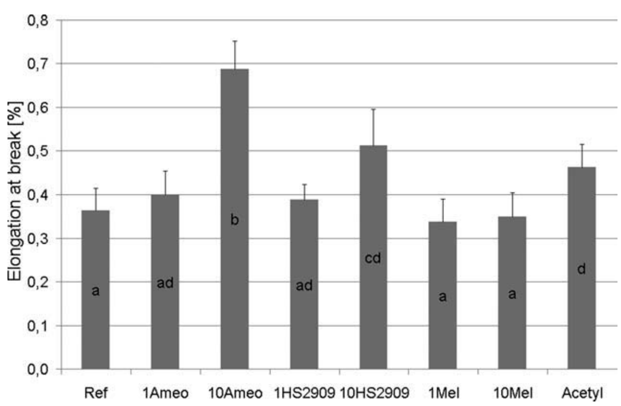

Figure 3 Elongation at break of PVC/treated and untreated wood flour composites.

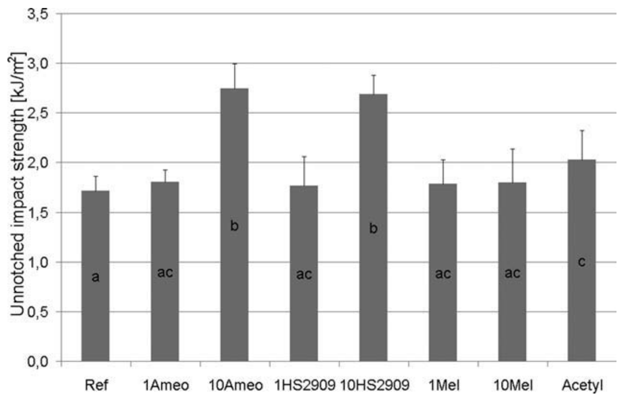

Figure 4 Unnotched impact strength of PVC/treated and untreated composites.

CONCLUSIONS

Two aminosilanes with different chemical structure, melamine-formaldehyde resin, and acetic anhydride were used in various concentrations for the treatment (modification) of wood flour that was compounded with PVC. Depending on the treatment, water absorption behavior and/or mechanical properties were improved compared to untreated references. With regard to water absorption behavior, treatments with melamine, aminosilane HS2909, and acetic anhydride showed a decrease in EMC and speed of water absorption. Hydrophobic properties, known from modified solid wood, remain stable in a composite with PVC. Thus, the processing of PVC-based WPC did not influence the effects of the wood flour treatments. Tensile strength, elongation at break, and unnotched impact strength were improved by treatments with high aminosilane contents. A higher amount of amino groups in the molecular structure of the silane leads to higher mechanical properties of the composite. Acetylated wood flour composite showed improved tensile strength, elongation, and impact strength, whereas the reasons for the enhancements are not clear. Independent of the application, various modification systems are helpful to meet a given requirement.

References

1. Clemons, C. Forest Prod J 2002, 52, 10.
2. Migneault, S.; Koubaa, A.; Erchiqui, F.; Chaala, A.; Englund, K.; Wolcott, M. P. Compos Pt A-Appl Sci Manuf 2009, 40, 80.
3. Wolcott, M. P.; Englund, K. Presented at 33rd International Particleboard/Composite Materials Symposium; Pullman, Washington, 1999; pp 103.
4. Jiang, H. H.; Kamdem, D. P. J Vinyl Addit Technol 2004, 10, 59.
5. Smith, P. M.; Wolcott, M. P. Forest Prod J 2006, 56, 4.
6. Bledzki, A. K.; Reihmane, S.; Gassan, J. Polym Plast Tech Eng 1998, 37, 451.
7. Klyosov, A. A. Wood Plastic Composite 2007.
8. Hill, C. A. S.; Farahani, M. R. M.; Hale, M. D. C. Holzforschung 2004, 58, 316.
9. Donath, S.; Militz, H.; Mai, C. Wood Sci Technol 2004, 38, 555.
10. Brelid, P. L.; Simonson, R.; Bergman, O.; Nilsson, T. Holz Roh- Werks 2000, 58, 331.
11. Takahashi, M.; Imamura, Y.; Tanahashi, M. International Research Group on Wood Preservation: Lappeenranta, Finland, 89-05-22/26, 1989; pp 16.
12. Beckers, E. P. J.; Militz, H.; Stevens, M. International Research Group on Wood Preservation: Nusa Dua, Bali, Indonesia, 94-05-29/06-03, 1994; pp 11.
13. Rowell, R. M.; Imamura, Y.; Kawai, S.; Norimoto, M. Wood Fiber Sci 1989, 21, 67.
14. Donath, S. Treatment of wood with silanes, Dissertation, Georg-August Universität, 2004.
15. Krause, A. Holzmodifizierung mit N-Methylolvernetzern, Dissertation; Georg-August Universität Göttingen: Göttingen, 2006.
16. Matuana, L. M.; Woodhams, R. T.; Balatinecz, J. J.; Park, C. B. Polym Compos 1998, 19, 446.
17. Matuana, L. M.; Balatinecz, J. J.; Park, C. B. Polym Eng Sci 1998, 38, 765.
18. Matuana, L. M.; Balatinecz, J. J.; Park, C. B.; Sodhi, R. N. S. Wood Sci Technol 1999, 33, 259.
19. Sombatsompop, N.; Chaochanchaikul, K. J Appl Polym Sci 2005, 96, 213.
20. Kokta, B. V.; Maldas, D.; Daneault, C.; Béland, P. J Vinyl Tech 1990, 12, 146.
21. Matuana, L. M.; Balatinecz, J. J.; Park, C. B.; Woodhams, R. T. Wood Fiber Sci 1999, 31, 116.
22. Sebe, G.; Brook, M. A. Wood Sci Technol 2001, 35, 269.
23. Walinder, M. E. P.; Gardner, D. J. J Adhesion Sci Tech 2002, 16, 1625.
24. Shah, H. L.; Matuana, L. M. J Vinyl Addit Technol 2005, 11, 160.
25. Chung, F. H. J Appl Polym Sci 1991, 42, 1319.
26. Lukowsky, D. Holzschutz mit Melaminharzen, Dissertation; Universität Hamburg: Hamburg, 1999.
27. Rapp, A. O.; Bestgen, H.; Adam, W.; Peek, R. D. Holzforschung 1999, 53, 111.
28. Gindl, W.; Zargar-Yaghubi, F.; Wimmer, R. Biores Tech 2003, 87, 325.
29. Lukowsky, D. Holz Roh- Werks 2002, 60, 349.
30. Jones, F. N.; Chu, G. B.; Samara Weera, U. Prog Org Coat 1994, 24, 189.
31. Rapp, A. O.; Peek, R.-D. International Research Group on Wood Preservation: Guadeloupe, France, 96-05-19/24 1996, pp 4.
32. Inoue, M.; Ogata, S.; Nishikawa, M.; Otsuka, Y.; Kawai, S.; Norimoto, M. Mokuzai Gakkaishi 1993, 39, 181.
33. Schreiber, H. P. The Interfacial Interactions in Polymeric Composites; Kluwer Academic Publishers: Netherlands; 1992, pp 21.
34. Hristov, V. N.; Krumova, M.; Vasileva, S.; Michler, G. H. J Appl Polym Sci 2004, 92, 1286.