Amine Treatment of Polyvinyl Chloride/Wood Flour Composites

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ABSTRACT: Ethanolamine and L-arginine treated wood flour were added to polyvinyl chloride (PVC) in order to improve the interphase between PVC and wood. The influence of the treatment on pH-value changes and nitrogen fixation of the wood and mechanical properties of the composite were evaluated. The treatments changed the pH of wood from acidic to basic. The highest nitrogen fixation was measured for monoethanolamine and L-arginine treated wood flour at high concentrations. Tensile strength, elongation at break, and unnotched impact strength were improved by ethanolamine and L-arginine treatments considerably. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4542–4546, 2012

Key words: mechanical properties; biofibers; poly(vinyl chloride) (PVC); composites; renewable resources

INTRODUCTION

Polyvinyl chloride (PVC) based wood flour composites become more important in research and industrial applications during the last decades.[1] Compared to the widely used polyolefin based wood-plastic composites (WPC), formulations containing PVC as matrix show enhanced stiffness, creep behavior, weatherability, and flame retardancy.[2] Still, the compatibility of the components is limited. The poor interfacial adhesion between the hydrophilic wood surface and the hydrophobic PVC leads to weak mechanical properties.[3,4] Several studies showed enhanced strength values because of wood flour pretreatment using aminosilanes.[5–8] It is reported that amino groups included in the silicon compound are able to interact with the matrix.[9] The nature of the wood surface changes and becomes more basic. Acid–base interactions occur between the treated wood flour and the acidic polymer, whereas different bonding mechanisms are possible.[6,10–12] The main interaction suggested is based on the Lewis acid–base theory, where ionic bonds are formed between the amino groups of treated wood flour and the chlorine atoms of the PVC.[11,13–14] Furthermore an improvement in flexural strength and unnotched impact strength was achieved by wood flour treatment using copper-amine.[15,16] Copper-amine complexes are commonly used as wood preservatives. The amine serves as a fixation agent for the copper-ion, which has a high effectiveness against wood decay fungi.[17] The objective of this study is to investigate the influence of various ethanolamines and amino acid treatments, on the mechanical properties of PVC based WPC. A potential application of the composite is for window frames, where mechanical properties, especially impact strength are important. Several studies indicated that, ethanolamine chemically reacts with hemicelluloses (carbonyl groups) and lignin.[18–20] Elemental analyses of nitrogen were used to determine the fixation as an indicator of the treatment success. An additional advantage is that ethanolamines have a lower price than aminosilanes, and contain no heavy metals such as copper-amine complexes. Ethanolamines and the used amino acid are nontoxic but produce irritant and corrosive effects.

EXPERIMENTAL

Material

PVC with a *K*-value of 63 was provided by Solvin SA in the form of powder. The *K*-value describes the inherent viscosity and molecular mass of the PVC, respectively. The *K*-value increases with increasing molecular mass. Wood flour C100 (*Picea abies*) were

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obtained from wood milling processes and supplied by JRS GmbH + Co. KG. The average size of the wood flour particles was in a range of 50–150 μm. Monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and L-arginine (LAR) were used as treatment agents and were purchased from Th. Geyer GmbH, KG. The chemicals had the purity level "for analysis." To complete the formulation, 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

The LAR and the ethanolamines were solved in distilled water and applied to wood flour in concentrations of 2.5 and 5 wt % (wood flour). Solutions were sprayed onto oven dried (48 h at 103°C) wood flour in a mixing drum. Afterwards treated wood flour was first dried in a vacuum heated chamber to moisture content below 1%. Subsequently, the temperature was raised to 110°C for 24 h in order to fix the agents. In addition, untreated (water sprayed) wood flour was processed in the same way (abbreviation: Ref).

Wood flour analysis

To get information about the fixation of nitrogen in the wood flour and the changes in pH-value, a leaching process was implemented. Ten gram of treated and untreated wood flour were mixed with 500 mL distilled water and stirred for 24 h at 80°C in a water bath. The suspensions were filtered and oven dried. Thus, two different groups were classified. The first group is the nonleached wood flour samples, representing the wood flour as it behave in the composite and the second group is the leached wood flour samples, which only contains the bound part of the chemical. For every treatment and the reference the pH-value and nitrogen content were measured nonleached and leached. The pH-values were determined by mixing and stirring 2.5 g of each sample (leached and nonleached) with 100 mL distilled water. pH-values were measured with a calibrated pH-meter (WTW InoLab pH Level 2 P). The nitrogen content was measured with an elemental analyzer (Heraeus, Elementar Vario EL). For each sample (leached and nonleached) ~ 5 mg were used to load the combustion cell. The materials were completely oxidized at a temperature of 1000°C and the nitrogen was quantified by a thermal conductivity detector. The nitrogen fixation was calculated using eq. (1)

$$\mathrm{Nf}[\%] = \frac{\mathrm{Nc}_l}{\mathrm{Nc}_{\mathrm{nl}}} \times 100$$

TABLE I
Composite Ingredients

Ingredient	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

where nitrogen fixation Nf (%) is described by nitrogen content (mg) of leached (Nc_l) and nonleached ($\mathrm{Nc}_{\mathrm{nl}}$) samples.

Processing of PVC wood flour composites

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. In this study the wood content was kept constant at 50% by weight. Composition details are listed in Table I. The dry blend was compounded to granulate by counter-rotating twin screw extrusion (Leistritz MICRO 27). Compounding parameters were adjusted to obtain an average mass temperature of 180°C at a screw rotation speed of 65 rpm. The composites were compression molded into panels (4 × 280 × 340 mm^3) using a hydraulic press (Joos, HP-S 200LAB) at 190°C and 60 bar for 5 min. Temperature was slowly reduced to allow hardening of the composite under pressure.

Mechanical properties

The mechanical properties of the composite were determined by testing impact and tensile properties. Unnotched impact strength test was performed according to EN ISO 179-1/1eU by using a Ceast, Resil Impact tester with hammer energy of 1 J for 20 replicates per formulation. The tensile testing was conducted according to EN ISO 527 using a Zwick/Roell static material testing machine, model Z010 Allround Line. For each formulation 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 treatment effects on the mechanical properties. One-way ANOVA and Turkey pair wise comparison at a 95% confidence interval were used to investigate differences between the formulations. Significant differences are expressed with different letters in columns.

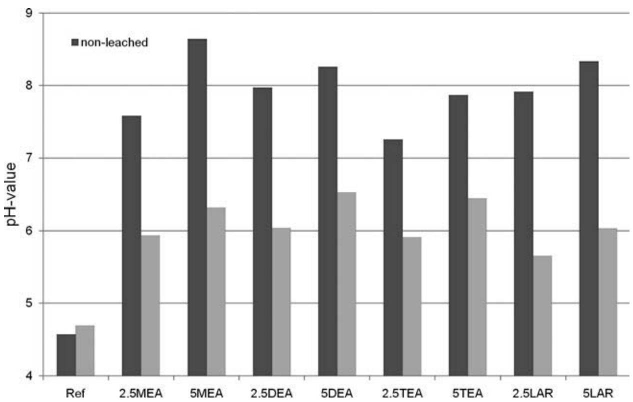

Figure 1 pH-values of leached and unleached wood flour treatments.

RESULTS AND DISCUSSION

Wood flour analysis

The pH-values of nonleached and leached wood flour treatments are represented in Figure 1. Compared to the reference an increase in pH-value was detected for all listed treatments. The nature of the wood flour changes from acidic to basic for the nonleached treatments. Independent of the agent used the pH-value increases with increasing ethanolamine/amino-acid concentration. The highest increase for the nonleached treatments was measured at 5MEA, whereas the differences to the remaining treatments at high concentration are minor. The results suggested that no obvious ethanolamine evaporation took place during the treatment process.[19,20] Same observation was made for LAR treatment in this study. Leaching of the samples considerably lowered the pH-values; nevertheless the values were higher related to the untreated reference. The results imply that a certain amount of the treatment agent was not fixed in the wood structure and therefore leached by water. Information concerning the fixation and the nitrogen content of nonleached and leached wood flour treatments are illustrated in Figure 2. As expected the nitrogen content of the nonleached wood flour depends on the nitrogen content of the treatment agent. LAR had the highest amount, followed by MEA, DEA, and TEA. Thus, higher contents were measured with increasing concentration of the agent. With regard to the treatment success the percentage fixation of nitrogen of each treatment had to be compared. 5MEA and 5LAR had the highest nitrogen fixation and TEA the lowest. With the exception of DEA, the fixation increases with increasing concentration of the agent. However, amino groups of MEA and LAR seemed to be more effective at wood fixation than DEA and TEA.

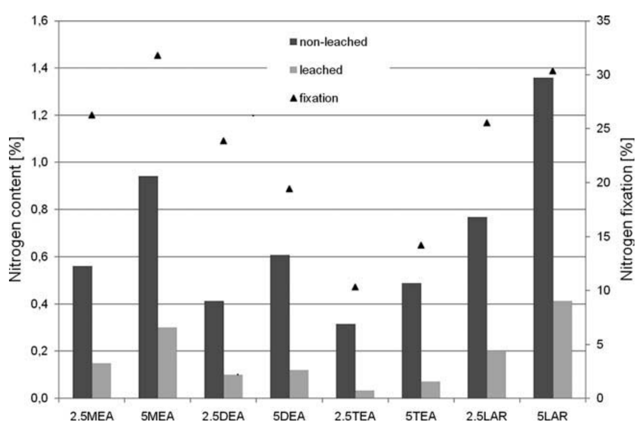

Figure 2 Nitrogen content and fixation of nonleached and leached wood flour treatments.

Mechanical properties

Tensile properties

Tensile strength of PVC/treated and untreated wood flour composites are presented in Figure 3. Each of the treated wood flour composites showed a significant improvement of tensile strength compared to the untreated reference. Same observations were made for aminosilane treated PVC/treated wood flour composites in previous studies.[5,7,11] The results suggest an improvement of the interphase between basic modified wood surface and acidic matrix.[8–10,12] With an increase of 83%, the strongest improvement was achieved by the treatment with 5LAR. For the ethanolamine treatment increases of 66 and 56% for 5MEA and 5DEA were measured, respectively. With the exception of TEA treatment, tensile strength increased with increasing concentration. The LAR treatment showed the highest increase with increasing concentration. The minor increase for TEA treatment is probably related to the poor nitrogen fixation. In contrast, 5DEA showed strength values comparable to 5MEA, although nitrogen content and fixation of 5DEA were much lower. The wood content, mainly influencing

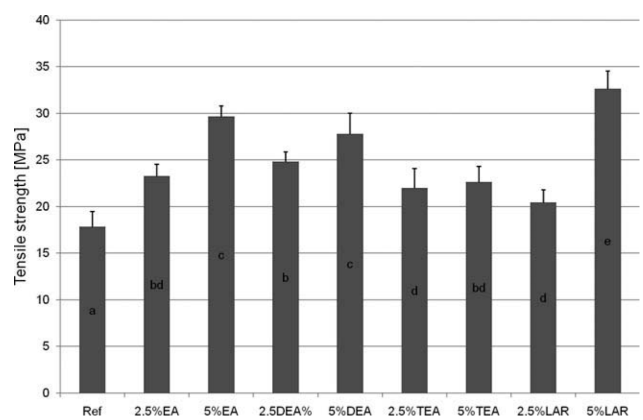

Figure 3 Tensile strength of PVC/treated and untreated wood flour composites. Data in columns with different letters differ significantly.

the tensile modulus, remained constant at 116 pph (50 wt %). The values ranged from 5679 MPa (Ref) to 6063 MPa (5MEA) without any significant differences. 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.[11] The elongation at break (Fig. 4) showed same trends as the tensile strength, whereas the enhancements were much higher. 5LAR showed an increase in elongation of 157%. For 5MEA and 5DEA an improvement by 107 and 96% was obtained. For WPC it is reported that a coupling agent effect between wood and polymer leads to increased elongation values as observed for amine treated composites in this study.[21]

Changes of pH-value and fixation were similar for 5LAR and 5MEA. Nevertheless, the amino acid showed obviously higher strength and elongation values than MEA at high concentration. LAR provides more free amino groups than ethanolamines, which could be a reason for a better interaction with the polymer. In Cu-amine preservative systems MEA is a more effective fixation agent as compared to DEA and TEA.[22] Concerning fixation in wood, similar assumptions were made for MEA, DEA, and TEA. However, the results indicate that the treatment with the mentioned chemicals changed the nature of wood from acidic to basic. Thus, chemical bonding between the components occurs, leading to increased strength and elongation values. In addition the fixation of treatment agent in wood seems to be necessary to obtain an improved interphase. Still, the detailed reactions and interactions between basic-modified wood flour and PVC matrix were not identified and have to be investigated in further studies.

Impact strength

Unnotched impact strength of PVC/treated and untreated composites are presented in Figure 5.

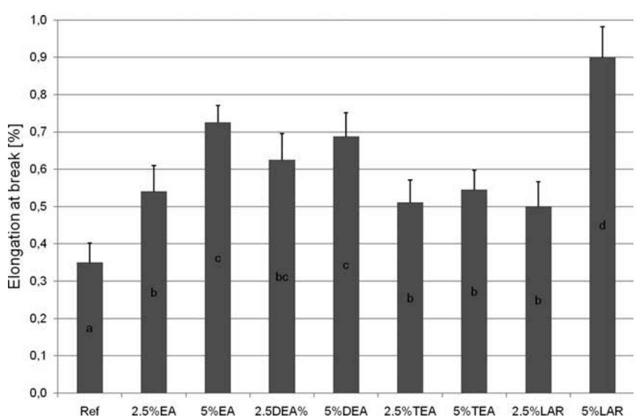

Figure 4 Elongation at break of PVC/treated and untreated wood flour composites.

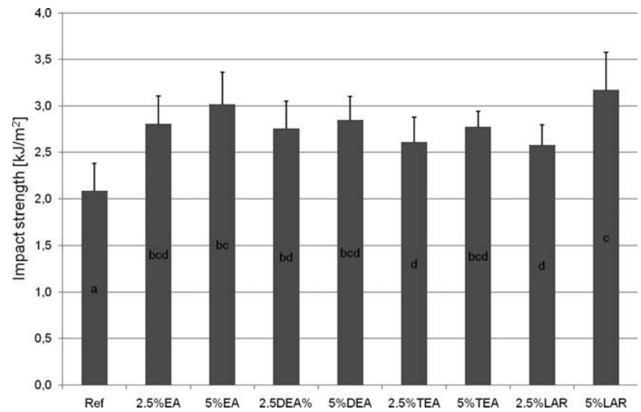

Figure 5 Unnotched impact strength of PVC/treated and untreated wood flour composites.

Each treatment showed improved impact strength values as compared to the untreated reference. Comparable results were achieved for Cu-amine based systems in a previous study.[15] Except the LAR treatment, no significant differences between the concentrations were measured. The same observation was made for high concentrated treatments. Compared to the tensile test values (strength and elongation) standard deviation was higher; this explains the reduced differences in the significance test. It is reported that an increase in wood content leads to decreased impact strength of the composite.[23] Because of more voids, gaps, and agglomeration occurring with increasing wood content, stress transfer between matrix and wood flour is reduced, resulting in decreased impact strength.[24] The use of a highly filled matrix (116 pph wood) in this study could have caused the higher deviation. However, impact strength was improved after the treatment with the mentioned agents.

CONCLUSIONS

Various concentrations of mono-, di-, and triethaniolamine as well as LAR were used to treat wood flour before compounding it with PVC. Each of the treatments was expected to change the nature of wood from acidic to basic in order to improve the interphase with the polymer. Concerning fixation in wood of the used chemicals, MEA, and LAR showed the highest values. This could be explained by the more effective interaction of amino groups and cell wall components. Thus, tensile strength and elongation at break were considerably improved for LAR at high concentration, followed by MEA and DEA treatment. Compared to the ethanolamines, LAR had more free amino groups to interact with the matrix resulting in increased tensile strength and elongation. In addition, unnotched impact strength was improved by the treatment, whereas the differences to the untreated reference were not as high as in the tensile test. The study showed that it is possible to improve mechanical behavior of PVC based WPC with the chemicals mentioned. This is because of an enhancement of the interphase between wood and PVC.

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References

1. Clemons, C. Forest Prod J 2002, 52, 10.
2. Jiang, H. H.; Kamdem, D. P. J Vinyl Additive Technol 2004, 10, 59.
3. Kokta, B. V.; Maldas, D.; Daneault, C.; Beland, P. Polym Plast Technol Eng 1990, 29, 87.
4. Matuana, L. M.; Park, C. B.; Balatinecz, J. J. J Vinyl Addit Technol 1997, 3, 265.
5. Müller, M.; Radovanovic, I.; Grüneberg, T.; Militz, H.; Krause, A. J Appl Polym Sci, to appear.
6. Matuana, L. M.; Balatinecz, J. J.; Park, C. B. Polym Eng Sci 1998, 38, 765.
7. Sombatsompop, N.; Chaochanchaikul, K. J Appl Polym Sci 2005, 96, 213.
8. Kokta, B. V.; Maldas, D.; Daneault, C.; Béland, P. J Vinyl Technol 1990, 12, 146.
9. Matuana, L. M.; Balatinecz, J. J.; Park, C. B.; Sodhi, R. N. S. Wood Sci Technol 1999, 33, 259.
10. Walinder, M. E. P.; Gardner, D. J. J Adhes Sci Technol 2002, 16, 1625.
11. Matuana, L. M.; Woodhams, R. T.; Balatinecz, J. J.; Park, C. B. Polym Compos 1998, 19, 446.
12. Matuana, L. M.; Balatinecz, J. J.; Park, C. B.; Woodhams, R. T. Wood Fiber Sci 1999, 31, 116.
13. Chung, F. H. J Appl Polym Sci 1991, 42, 1319.
14. Shah, H. L.; Matuana, L. M. J Vinyl Additive Technol 2005, 11, 160.
15. Jiang, H. H.; Kamdem, D. P. J Vinyl Addit Technol 2004, 10, 70.
16. Jiang, H. H.; Kamdem, D. P. Appl Surf Sci 2010, 256, 4559.
17. Lee, M. J.; Cooper, P. Holzforschung 2010, 64, 653.
18. Humar, M.; Petric, M.; Pohleven, F.; Despot, R. Holz als Roh-Werkstoff 2003, 61, 29.
19. Humar, M.; Petric, M. International Research Group on Wood Preservation, Kona, Hawaii, USA, 00–05-14/19, 2000, p 10.
20. Humar, M.; Pohleven, F.; Kesnar, Š.; Kalan, P. International Research Group on Wood Preservation, Cardiff, Wales, UK, 02–05-12/17, 2002, p 10.
21. Hristov, V. N.; Krumova, M.; Vasileva, S.; Michler, G. H. J Appl Polym Sci 2004, 92, 1286.
22. Lee, M. J.; Cooper, P. Holzforschung 2010, 64, 659.
23. Mengeloglu, F.; Matuana, L. M.; King, J. A. J Vinyl Addit Technol 2000, 6, 153.
24. Joshi, P. S.; Marathe, D. S. J Reinforced Plast Compos 2010, 29.