

Effect of Maleic Anhydride Content and Ethanol Dilution on the Polymerization of Furfuryl Alcohol in Wood Veneer Studied by Differential Scanning Calorimetry

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The polymerization kinetics of furfuryl alcohol in wood veneer were studied using differential scanning calorimetry (DSC) and were compared with weight gains of treated wood veneers. Maleic anhydride was used as the reaction initiator. DSC data were obtained for samples of the veneers that had been impregnated with neat furfuryl alcohol or with furfuryl alcohol diluted with ethanol, and using two ratios of maleic anhydride to furfuryl alcohol. The high ratio of maleic anhydride to furfuryl alcohol (1:9) favoured rapid polymerization at a lower temperature, whereas the lower ratio (1:19) resulted in a relatively slower rate of polymerization, which required higher temperatures to affect the reaction. A higher temperature also led to an increase in furfuryl alcohol evaporation from the prepared veneers. The DSC data was compared with data obtained from furfuryl alcohol impregnated wood veneers but without the addition of maleic anhydride. DSC data is in good agreement with weight percentage gains (WPGs) obtained for samples impregnated with differently composed solutions. While higher maleic anhydride contents led to higher WPGs, ethanol dilution inhibits polymer formation, resulting in lower WPG.

Keywords: Differential scanning calorimetry; Furfuryl alcohol; Maleic anhydride; Modified wood veneer; Wood enhancement; WPG

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INTRODUCTION

The polymerization of furfuryl alcohol in wood is a well-known process for wood preservation and wood property enhancement. The modification process is based on dry wood impregnation with furfuryl alcohol and a reaction initiator, followed by polymer formation at elevated temperature. Early investigations used zinc chloride and organic acids for initiating furfuryl alcohol polycondensation reactions (Goldstein and Dreher 1960). However, more recently, Schneider (2002) and Westin (2004) implemented the use of cyclic carboxylic anhydrides, mainly maleic anhydride, to improve the stability of impregnation solutions with a preferable environmental impact. The complex chemical reactions that occur during the curing step lead to polymeric material comprised of several molecular structures. The resulting furfuryl alcohol polymer resides predominantly in the wood cell walls and gives the treated wood a dark brown colour.

Extensive research has been carried out on the determination of these reactions, as well as on the mechanisms and characterization of the polymer products obtained (Barr and Wallon 1971; Choura *et al.* 1996; Gandini 2009; Gonzalez *et al.* 1992; Guigo *et al.* 2007; Milkovic *et al.* 1979; Principe *et al.* 2000). On furfurylation, physical-mechanical and biological wood properties are significantly modified. Epmeier *et al.* (2004) have reported improved dimensional stability, substantially reduced impact bending strength, increased hardness, and reduced equilibrium moisture content for furfurylated wood specimens. These results generally agree with those obtained by Lande *et al.* (2004) and Esteves *et al.* (2010), who also verified an increased durability of treated samples against *Poria placenta* and *Coniophora puteana*. The degree of property modification depends on the weight percentage gain (WPG) and the polymer content inside the wood cell walls (Hadi *et al.* 2005, Lande *et al.* 2004) with the exception of durability. Alfredsen and Westin (2009) and Venås and Felby (2009) found no significant changes in mass loss and wood moisture content during field tests for WPGs higher than 20% and 25%, respectively. In order to realize different WPGs, Westin diluted furfuryl alcohol using different solvents such as methanol or ethanol evaporated from wood prior to the curing step (Westin 2004).

Little has been reported on the role of maleic anhydride content and ethanol dilution on reaction kinetics and its effects on the polymer yield and weight gains of wood samples during furfurylation. Wewerka (1968) stated that the initial reaction rate was a function of pH. The source of protons required to provide the low pH for reaction initiation is the labile half-ester, obtained from the reaction of maleic anhydride and furfuryl alcohol, isolated by Pelter and Singaram (1983) from chloroform solution. Wewerka (1968) could not find any effect of the initiator's concentration on the end product's chemical constitution. In contrast, Gonzalez *et al.* (1992) reported polymers with differing structures obtained by using different curing temperatures and concentrations of trifluoroacetic acid dissolved in furfuryl alcohol to affect the polymerization, a conclusion consistent with earlier differential scanning calorimetry (DSC) measurements obtained by Kelley *et al.* (1982). These studies suggest a great impact of maleic anhydride on the polymerisation reactions. Extensive chemorheological analyses on furfuryl alcohol polymerization have been carried out by Guigo *et al.* (2007) using neat furfuryl alcohol and water-dissolved maleic anhydride. These authors studied the effect of different heating ramps and isothermals during DSC on the extent of furfuryl alcohol conversion.

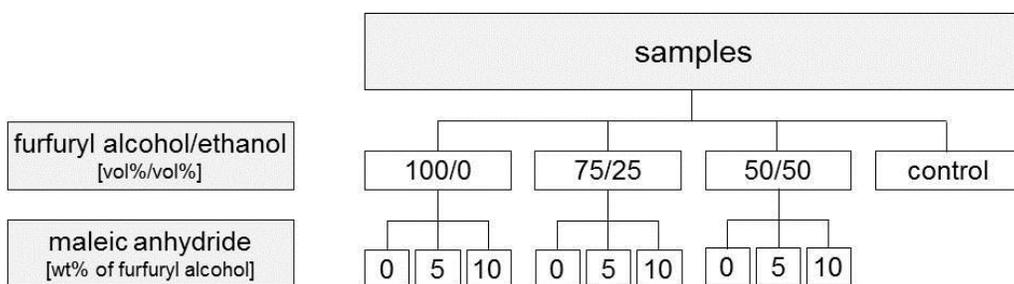
However, in order to understand, adjust, and control the wood furfurylation process, it is of interest to determine the impact of different maleic anhydride contents on the polymerization reactions regarding the degree, optimum temperature, and duration of polymerization within the wood. For this purpose DSC has been carried out on wood veneer samples impregnated with furfuryl alcohol/ethanol solutions containing different amounts of maleic anhydride. Furthermore, the WPGs were determined on larger-scale samples cured for 4 h at 120 °C and related to results obtained from DSC.

EXPERIMENTAL

Preparation of Specimens

All analyses were conducted on veneer samples taken from maple (*Acer sp.*). The veneer was provided by Furnierwerk Prignitz GmbH und Co. KG. All specimens were

cut from a single sheet of veneer, which was produced as a crown-cut veneer. The dimensions of the samples were about 20 mm (T) × 25 mm (L) with a thickness of 0.53 to 0.57 mm for unmodified samples. The prepared veneer specimens were kiln dried at 80 °C when placed in a mounting bracket inside a desiccator under low pressure (100 mbar) to evacuate the wood cells. After 30 min, the samples were lowered into the modification solution and impregnated for 3 h at 100 mbar, allowing maximum uptake. The solutions used were prepared as shown in Scheme 1. Maleic anhydride was dissolved in furfuryl alcohol (by wt%). The furfuryl alcohol/maleic anhydride solution then was blended with ethanol (by vol%) as a variable to control the extent of furfurylation (Westin 2004). After impregnation was completed, the specimens were kept enclosed in aluminium foil envelopes to soak for 24 h. Residual ethanol was removed under low pressure (100 mbar). Furfuryl alcohol (> 98 vol%) was provided by International Furan Chemical B.V., Rotterdam, the Netherlands. Maleic anhydride (P.A.) and ethanol (96 vol%) were obtained from Merck KGaA, Darmstadt, Germany.



Scheme 1. Furfuryl alcohol and maleic anhydride composition of the impregnation solutions used in preparing modified veneer specimens.

DSC Measurements

The DSC measurements were performed on a TA instruments Q1000 DSC under a nitrogen atmosphere. Samples were cut from the veneer specimens into small squares (5 to 6.5 mg) and placed in standard aluminium pans. For DSC measurements, two different experiments were run: a ramp with a heating rate of 10 °C/min from 20 to 200 °C and isothermal temperature profiles at 80, 100, 120, and 140 °C with an initial ramp of 100 °C/min (according to DIN EN ISO 11357-1:2009).

WPG

To determine the weight uptake due to formation of furfuryl alcohol polymer during the furfurylation process, six samples per charge were prepared as indicated and cured at 120 °C for 4 h in a laboratory kiln under self-generated atmosphere. The samples were weighed in absolute dry condition after soaking and removal of residual ethanol, and finally after curing. From those weights, the mass uptake was determined as WPG using Equation (1),

$$WPG = \frac{(W_t - W_u)}{W_u} * 100 \quad (1)$$

where *WPG* is the weight percentage gain of the sample after curing [%], *W_t* is the weight of the sample after curing [g], and *W_u* is the weight of the absolutely dry sample [g].

Results are shown as mean with the standard deviation.

RESULTS

DSC Experiment 1: Heating Ramp

DSC thermograms of treated veneer specimens (Figs. 1 to 4) show the distinct effects of maleic anhydride on furfuryl alcohol polymerization. Figure 1 shows the changes of the cure profiles in relation to different amounts of maleic anhydride for undiluted furfuryl alcohol treatment. The application of veneer treated with furfuryl alcohol and 10 wt% maleic anhydride led to a single exothermic peak with an onset at *ca.* 101 °C and a maximum at 122 °C. Employing the veneer treatment of furfuryl alcohol with 5 wt% maleic anhydride concentration led to a formation of two exothermic peaks, the first at 122 °C and the second at 147 °C. Both peaks had a relatively lower intensity than the single exothermic peak displayed by the samples treated with 10 wt% maleic anhydride in undiluted furfuryl alcohol. No exothermic reaction was observed in the absence of maleic anhydride, with an endothermic peak at 154 °C attributed to the evaporation of furfuryl alcohol.

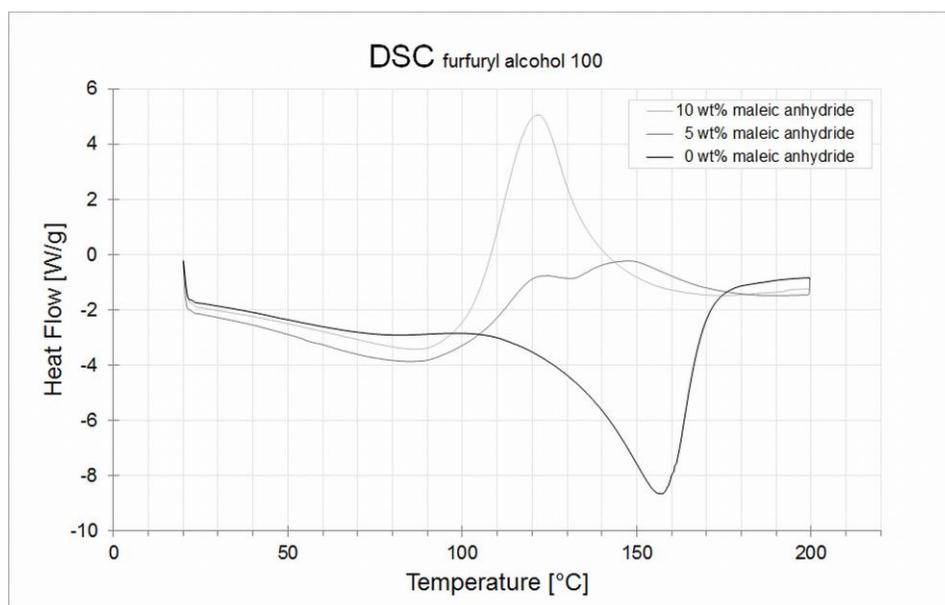


Fig. 1. DSC heating ramp: 10 °C/min; veneer samples impregnated with neat furfuryl alcohol and different amounts of maleic anhydride

In Figs. 2 to 4, the DSC thermograms compare veneer samples treated with differing furfuryl alcohol/ethanol combinations and the same ratio of maleic anhydride. Figure 2 shows the distinct effect on the polymerization reaction with increasing amounts of ethanol as diluent and with the same ratio of maleic anhydride to furfuryl alcohol (10 wt%). The thermogram of the undiluted sample (neat furfuryl alcohol) showed a single peak at 122 °C (Fig. 1). Dilution of furfuryl alcohol to 75 vol% in ethanol caused a broadening of this exothermic peak and a shift towards a higher temperature, with the maximum of this peak at 147 °C and a shoulder at 124 °C. The DSC thermogram of the most diluted furfuryl alcohol (50 vol%) demonstrated the cure profile splitting into two distinct exothermic peaks, with the greater at 155 °C and with the second, lower peak at *ca.* 122 °C.

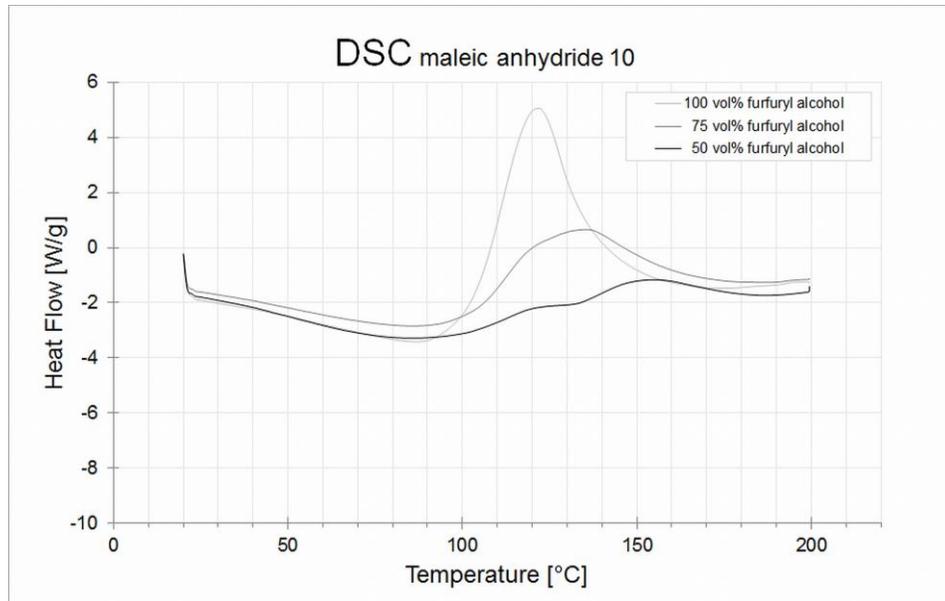


Fig. 2. DSC heating ramp: 10 °C/min; veneer samples impregnated with 10 wt% maleic anhydride and different dilutions of furfuryl alcohol in ethanol

In contrast to the thermogram results from ethanol dilution of the furfuryl alcohol solutions containing 10 wt% maleic anhydride, the thermogram profiles of the veneer specimens treated with diluted and neat furfuryl alcohol solutions containing 5 wt% maleic anhydride displayed polymerization occurring at a higher temperature with increasing ethanol content (Fig. 3). In the absence of ethanol, two exothermic peaks (124 °C and 147 °C) were observed from 5 wt% maleic anhydride (Fig. 2). In the presence of ethanol, the higher temperature exotherm peak shifted to 162 °C when furfuryl alcohol was diluted to 75 vol%. Upon 50 vol% dilution, this exotherm peak shifted to 168 °C. Also evident in Fig. 3 was the diminishing exothermic peak at 122 °C, which was relatively small when compared to the exotherm from treated veneer samples containing 10% maleic anhydride (Fig. 2).

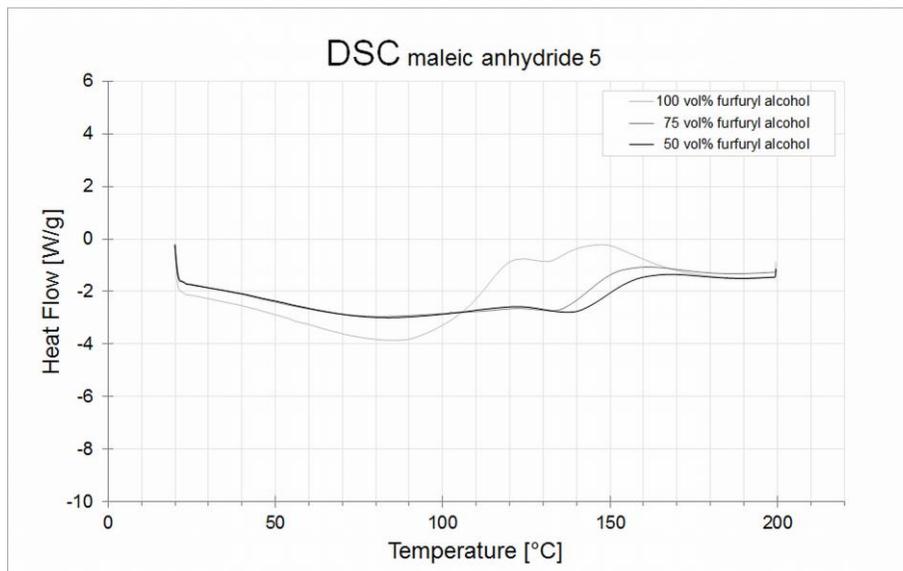


Fig. 3. DSC heating ramp: 10 °C/min; veneer samples impregnated with 5 wt% maleic anhydride and different dilutions of furfuryl alcohol in ethanol

Dilution of neat furfuryl alcohol treatment solution with ethanol had little impact on cure profiles. Across the samples measured, the maximum of the endothermic peak was between 154 and 157 °C, attributed to evaporation of furfuryl alcohol (Fig. 4).

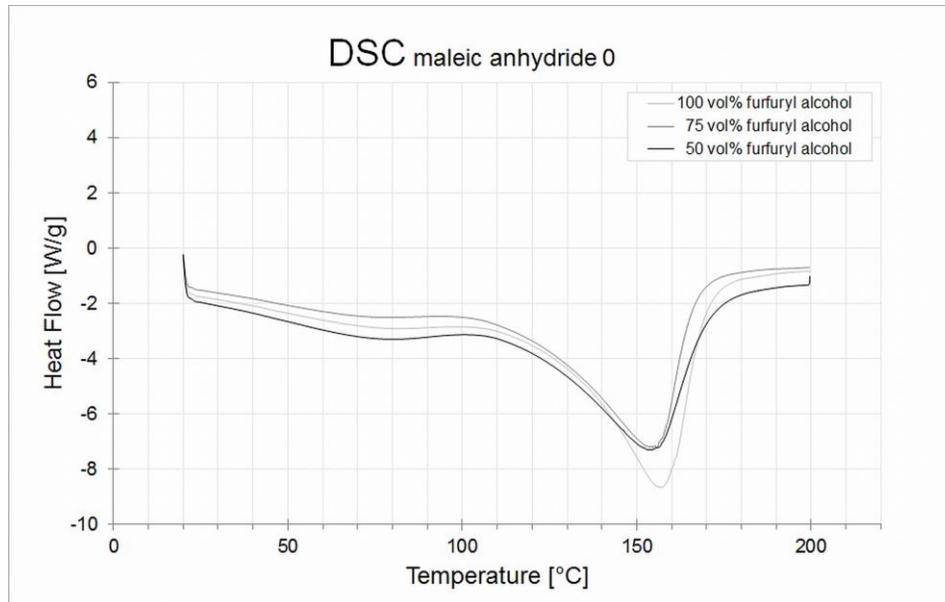


Fig. 4. DSC heating ramp: 10 °C/min; veneer samples impregnated with different dilutions of furfuryl alcohol in ethanol

The DSC data obtained from the thermal profiles in Figs. 1 to 4 are summarized in Table 1.

Table 1. DSC Peak Temperatures for the Treated Veneer Specimens Described in Scheme 1

Samples			Peak I (at ~122 °C) [°C]	Peak II [°C]
Furfuryl alcohol [vol%]	Ethanol [vol%]	Maleic anhydride [wt% of FA]		
100	0	0	-	157 (endotherm)
100	0	5	124	147
100	0	10	122	122
75	25	0	-	156 (endotherm)
75	25	5	123	162
75	25	10	124 (shoulder)	135
50	50	0	-	154 (endotherm)
50	50	5	122	168
50	50	10	122	155

DSC Experiment 2: Isothermal Temperature Profiles

The DSC experiments using isothermal temperature profiles reflect the impact of differing temperature (80, 100, 120, and 140 °C) on the polymerization kinetics and reaction duration. The differing isothermal cure profiles are exemplified in Fig. 5 for samples impregnated with undiluted furfuryl alcohol and 10 wt% maleic anhydride.

The thermograms showed a single, intense exothermic peak when the polymerization reaction was carried out at 140 °C. Two sequential peaks were observed from polymerization at 120 °C. Thermograms at 100 and 80 °C show little exothermic activity with no measurable change in heat flow after approximately 5 min at these isothermal temperatures.

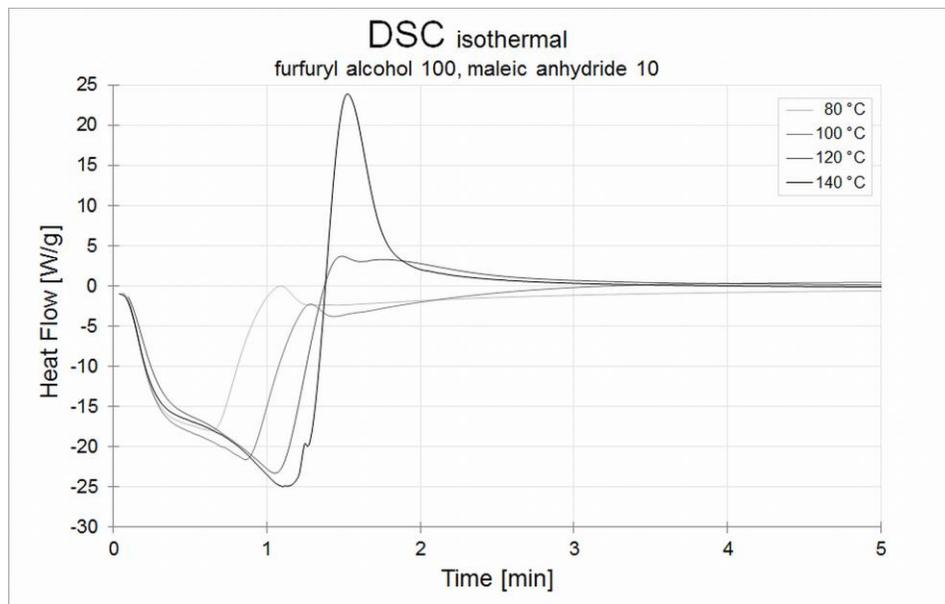


Fig. 5. DSC isothermal temperature profiles at 80, 100, 120, and 140 °C with an initial ramp of 100 °C/min; veneer samples impregnated with neat furfuryl alcohol and 10 wt% maleic anhydride

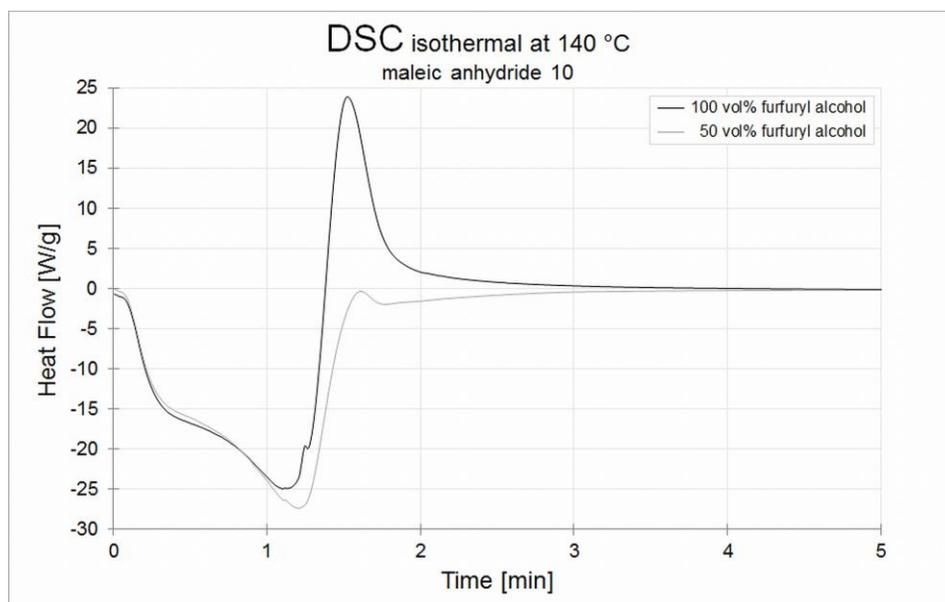


Fig. 6. DSC isothermal temperature profile at 140 °C, initial ramp 100 °C/min; veneer samples impregnated with 50 vol% (in ethanol) and neat furfuryl alcohol and 10 wt% maleic anhydride

A comparison of samples impregnated with 50 vol% furfuryl alcohol in ethanol or neat furfuryl alcohol (with 10 wt% maleic anhydride) at an isothermal temperature of 140 °C indicated a lower rate of reaction was achieved (Fig. 6). Figure 6 illustrates the thermogram for a specimen impregnated with diluted furfuryl alcohol (50 vol%), which showed a broad exotherm peak, comparable in intensity with that observed for the sample treated with neat furfuryl alcohol and 10 wt% maleic anhydride reacted at 100 °C.

WPG

Results reveal the impregnated samples lose at least 58 % of unreacted furfuryl alcohol during the curing step. This was mainly due to furfuryl alcohol evaporation and water release from the condensation reaction. However, the loss of furfuryl alcohol and retention of reacted furfuryl alcohol depend strongly on the maleic anhydride content of the impregnation solution as well as on the ethanol dilution (Fig. 7). From these results there is a linear relationship between WPG and maleic anhydride. Moreover, WPGs also demonstrate an inhibiting effect by ethanol on the extent of polymer formation and weight retention. Diluting furfuryl alcohol with ethanol (3:1 and 1:1) leads to reduced WPG by ~49% and ~78%, respectively, for the same maleic anhydride ratios.

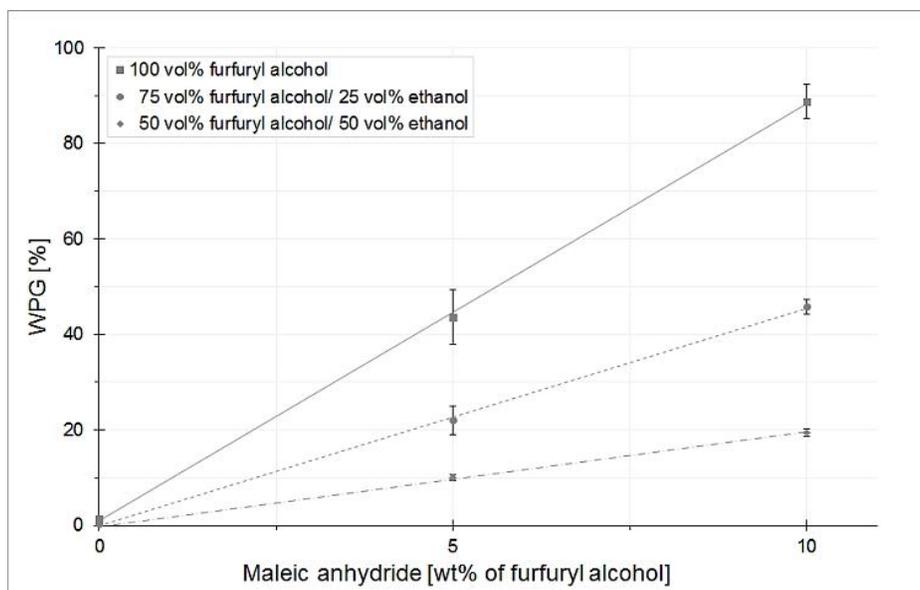


Fig. 7. WPG of samples impregnated with different ethanol dilutions of furfuryl alcohol (100, 75, and 50 vol%) in relation to the maleic anhydride content (0, 5, and 10 wt% of furfuryl alcohol) in the impregnation solutions

DISCUSSION

The use of neat furfuryl alcohol for treating wood veneer led to a single endothermic peak that indicated the vaporization of furfuryl alcohol with little or no evidence of any exotherm, indicative of polymerization having taken place at elevated temperature (Guigo *et al.* 2007). Interestingly, this endotherm had a broad onset and maximum at *ca.* 154 °C, while DSC measurements of neat furfuryl alcohol displayed a narrow endothermic peak at *ca.* 185 °C. This shift of the evaporation peak to lower

temperatures compared to the corresponding liquid was noticed for all treated veneer samples, irrespective of the ethanol content. These shifts to lower temperatures are a result of the wood ultrastructure and resulting capillary forces affecting the physical properties of furfuryl alcohol. The same effect is known to occur for water in porous material (Schreiber *et al.* 2001) and can be utilized for wood cell size and diameter determination by thermoporometry (Zauer 2012).

For veneers impregnated with neat furfuryl alcohol and maleic anhydride, only exothermic peaks were observed. No endotherm corresponding to evaporating furfuryl alcohol was detected, though furfuryl alcohol losses of at least 58% were shown to occur during larger-scale experiments. At least two exothermic reactions were apparent, as evidenced by peaks shown in Table 1. It is noteworthy that the intensity of the lower temperature exotherm (*ca.* 122 °C) determined the intensity and onset temperature of the second, higher temperature exotherm peak. This effect, resulting from polymerization reactions, was also dependent on the amount of maleic anhydride used. Increased maleic anhydride content in the impregnating solution activated more furfuryl alcohol, leading to an intense, lower temperature exothermic reaction. This was exemplified with the sample impregnated with furfuryl alcohol and 10 wt% maleic anhydride. Lower maleic anhydride proportions led to a reduced intensity of the first exothermic peak (122 °C) and the emergence of a second exothermic reaction at a higher temperature (above 134 °C). From these results, it can be deduced that the second exotherm is a result of polymerization reactions that require a minimum rate of energy to be initiated. Milkovic *et al.* (1979) also observed that furfuryl alcohol reactions occur at lower temperatures when the concentration of maleic anhydride is increased. Kelley *et al.* (1982) attributed the low temperature exothermic peak to condensation reactions between the methylol groups and the 5-position hydrogens, leading to methylene ether bridges between the furan rings. The second exothermic peak was attributed to several subsequent reactions, including the rearrangement of methylene ether linkages, resulting in chains of furan rings linked by methylene bridges. This assertion could be supported by spectroscopic analysis of dichloromethane extracts of samples cured at 140 °C for 30 minutes. Results showed that the extract colour was darker when lower amounts of maleic anhydride were used. This finding suggests that condensed and chromophoric furfuryl alcohol polymeric structures were already formed in all samples, but vary in branching or linkage when treated with low amounts of maleic anhydride.

In addition, dilution with ethanol leads to a further reduction of the degree of polymerization. The thermograms in Figs. 2 and 3 substantiate a decreasing intensity of the first exothermic peak and a shift of the second exothermic peak to higher temperatures with increasing ethanol content. Simultaneously, higher temperatures favour furfuryl alcohol evaporation, leading to less polymer formation as shown in Fig. 7. The reduced polymerization may be caused by relatively lower amounts of furfuryl alcohol dispersed within the wood veneer. Moreover, this reduction can be caused by acid-catalysed esterification of ethanol and maleic anhydride, forming diethyl maleate. An excess of ethanol and elevated temperatures are reported to favour the formation of diethyl maleate (Yadav and Thathagar 2002) and reduce the maleic anhydride content available for initiating furfuryl alcohol polymerization

Overall, these findings gained from DSC were in accordance with sample weight gains due to this veneer modification process. As shown in Fig. 7, weight gains were strongly dependent on the maleic anhydride content used in samples cured at 120 °C. A lower maleic anhydride content contributed to smaller sample weight gains. Likewise,

samples impregnated with ethanol-diluted furfuryl alcohol/maleic anhydride solutions showed smaller weight gains compared to samples impregnated with solutions of furfuryl alcohol and the same ratio of maleic anhydride.

Furthermore, sample weight gains recorded for impregnated and cured samples could generally be related to the DSC thermograms, in which a shift to higher temperature exotherms was a result of lower maleic anhydride concentrations in the treatment solutions and ethanol dilution of the impregnation solutions. Therefore, polymerization of furfuryl alcohol in veneer samples using low ratios of maleic anhydride conducting reactions at 120 °C will result in longer reaction times and potentially lead to incomplete reactions. Furthermore, this process was complicated by the volatilization of furfuryl alcohol from the treated wood veneers so that less cured polymer is deposited in the wood cells, together with reactions requiring more time.

The different isothermal temperature cure profiles depicted in Fig. 5 show a single intense exotherm at 140 °C and a broader, lower intensity exotherm at 120 °C, with only weak exotherms observed at 100 and 80 °C isothermal treatments. At both 140 and 120 °C, polymerization appeared to be relatively quick, reaching completion within 5 min (Fig. 5). This apparent rapid reaction at elevated temperatures is not inconsistent with the findings for furan resins and other methylol chemical systems polymerization, such as formaldehyde adhesives (Wang *et al.* 1994), and is in good accordance with results from Guigo *et al.* (2007). In contrast, relatively little reactivity was evident below 100 °C over the initial 30 min reaction period. The extent of the initial cure exotherm at 140 °C was also dependent on the ratio of maleic anhydride used in the veneer modification solution (Fig. 6). This was consistent with findings from heating ramp thermograms (Figs. 1-4). These differences in exotherm intensity observed across Fig. 5 and Fig. 6 are also related to polycondensation reactions taking place. Comparisons of sample mass on polymerization at 120 and 140 °C do not show that any significant differences in the treatment weight gains affecting treatment and polymer formation. This indicated that the furfuryl alcohol must be retained in approximately the same amounts in the wood veneer specimens.

The results from DSC measurements, using the heating ramp method, indicated reactions are initiated above 100 °C, particularly from *ca.* 120 °C, with differing polymerization reaction temperatures greater than 160 °C. Reactions were dependent on the maleic anhydride content and its availability to initiate polycondensation reactions, and on furfuryl alcohol dilution with ethanol. Isothermal cure profiles provided further information in terms of duration and enthalpy of the polycondensation reactions, indicating that they were relatively rapid, but dependent on temperatures greater than 100 °C and maleic anhydride content.

CONCLUSIONS

1. Wood veneer furfurylation modification using maleic anhydride as the furfuryl alcohol polymerization initiator significantly influenced polymerization kinetics and polymer formation. Modification using treatment solutions with low maleic anhydride content require a higher temperature to affect the same degree of polymerization.
2. Dilution of the furfuryl alcohol/maleic anhydride treatment mixture with ethanol retarded the polymerization reaction resulting in lower WPGs, which may be due to

both side reactions of ethanol with maleic anhydride and diluting the reactants within the wood.

3. High curing temperatures (120 to 140 °C) led to a more rapid, exothermic cure, whereas temperatures less than 100 °C were below the polymerization threshold onset temperature, resulting in low rates of polycondensation and potential for furfuryl alcohol loss through evaporation.
4. DSC assessments of polymerization reactions were in good agreement with results regarding the WPG of reacted polymer inside the veneers. Both DSC assessments and polymer gain are affected by ratio of maleic anhydride and furfuryl alcohol dilution with ethanol.

ACKNOWLEDGMENTS

The authors are grateful for the financial support of the German Research Foundation (DFG, Grant No. PF 686/4-1), AiF (16735 BR), and COST (STSM-RA - New Zealand-06283). We are also greatly appreciative for the supply of furfuryl alcohol by International Furan Chemicals B.V.

REFERENCES CITED

- Alfredsen, G., and Westin, M. (2009). "Durability of modified wood – laboratory vs field performance," *Proceedings of the 4th European Conference on Wood Modification 2009*, Stockholm, Sweden.
- Barr, J. B., and Wallon, S. B. (1971). "The chemistry of furfuryl alcohol resins," *J. Appl. Polym. Sci.* 15(5), 1079-1090.
- Choura, M., Belgacem, N. M., and Gandini, A. (1996). "Acid-catalyzed polycondensation of furfuryl alcohol: Mechanisms of chromophore formation and cross-linking," *Macromolecules* 29(11), 3839–3850.
- EN ISO 11357-1 (2009). *Kunststoffe – Dynamische Differenz-Thermoanalyse (DSC) – Teil 1: Allgemeine Grundlagen*.
- Epmeier, H., Westin, M., and Rapp, A. (2004). "Differently modified wood: Comparison of some selected properties," *Scand. J. Forest Res.* 19(Suppl. 5), 31-37.
- Esteves, B., Nunes, L., and Pereira, H. (2011). "Properties of furfurylated wood (*Pinus pinaster*)," *Eur. J. Wood Wood Prod.* 69(4), 521-525.
- Gandini, A. (2010). "Furans as offspring of sugars and polysaccharides and progenitors of a family of remarkable polymers: A review of recent progress," *Polym. Chem.* 1(3), 245-251.
- Goldstein, I., and Dreher, W. (1960). "Stable furfuryl alcohol impregnating solutions," *Ind. Eng. Chem. Res.* 52(1), 57-58.
- Gonzalez, R., Martinez, R., and Ortiz, P. (1992). "Polymerization of furfuryl alcohol with trifluoroacetic acid: the influence of experimental conditions," *Makromol. Chem.* 193(1), 1-9.
- Guigo, N., Mija, A., Vincent, L., and Sbirrazzuoli, N. (2007). "Chemorheological analysis and model-free kinetics of acid catalysed furfuryl alcohol polymerization," *Phys. Chem. Chem. Phys.* 9(39), 5359-5366.

- Hadi, Y. S., Westin, M., and Rasyid, E. (2005). "Resistance of furfurylated wood to termite attack," *For. Prod. J.* 55(11), 85-88.
- Kelley, S. S., Young, R. A., Rammon R. M., and Gillespie, R. H. (1982). "Bond formation by wood surface reactions part Iv analysis of furfuryl alcohol, tannin and maleic acid bridging agents," *J. Wood Chem. Technol.* 2(3), 317-342.
- Lande, S., Westin, M., and Schneider, M. H. (2004). "Properties of furfurylated wood." *Scand. J. Forest Res.* 19(Suppl. 5), 22-30.
- Milkovic, J., Myers, G. E., and Young, R. A. (1979). "Interpretation of curing mechanisms of furfuryl alcohol resins," *Cell. Chem. Technol.* 13, 651-672.
- Pelter, A., and Singaram, B. (1983). "The reactions of furfuryl alcohols with maleic anhydride," *J. Chem. Soc. Perk. T. 1*, 1383-1386.
- Principe, M., Martinez, R., Ortiz, P., and Rieumont, J. (2000). "The polymerization of furfuryl alcohol with p-toluenesulfonic acid: Photocross-linkable feature of the polymer," *Polímeros* 10(1), 08-14.
- Schneider, M. H. (2002). "Furan polymer impregnated wood, method for preparing the polymer and uses thereof," Patent WO/2002/030638.
- Schreiber, A., Ketelsen, I., and Findenegg, G. H. (2001). "Melting and freezing of water in ordered mesoporous silica materials," *Phys. Chem. Chem. Phys.* 3(7), 1185-1195.
- Venås, T. M., and Felby, C. (2009). "Enzymatic hydrolysis of furfurylated Scots pine sapwood (*Pinus sylvestris*, L.)," *Proceedings of the 4th European Conference on Wood Modification 2009*. Stockholm, Sweden, 53-60.
- Wang, X.-M., Riedl, B., Christiansen, A. W., and Greimer, R. L. (1994). "Differential scanning calorimetry of the effects of temperature and humidity on phenol-formaldehyde resin cure," *Polymer* 35(26), 5685-5692.
- Westin, M. (2004). "Furan Polymer Impregnated Wood," Patent WO/2004/011216.
- Wewerka, E. M. (1968). "An investigation of the polymerization of furfuryl alcohol with gel permeation chromatography," *J. Appl. Polym. Sci.* 12(7), 1671-1681.
- Yadav, G., and Thatthagar, M. (2002). "Esterification of maleic acid with ethanol over cation-exchange resin catalysts," *React. Funct. Polym.* 52(2), 99-110.
- Zauer, M. (2012). *Untersuchung zur Porenstruktur und kapillaren Wasserleitung im Holz und deren Änderung infolge einer thermischen Modifizierung*. Schriftenreihe Holz- und Papiertechnik, Band 10, Technische Universität Dresden, Germany.

Article submitted: August 15, 2012; Peer review completed: Sept. 29, 2012; Revised version received: January 1, 2013; Accepted: January 3, 2013; Published: January 10, 2013.