

Full Length Research Paper

Acetylation of wood components and fourier transform infra-red spectroscopy studies

Nihat Sami Cetin* and Nilgul Ozmen

Faculty of Forestry, Kahramanmaraş Sutcu Imam University, Kahramanmaraş, Turkey.

Accepted 21 March, 2011

In this study, the reactivity of wood components with acetic anhydride or vinyl acetate was studied. It was found that the reactivity of wood components was virgin wood flour > holocellulose >> α -cellulose. Acetylation of Turkish pine or cedar wood flour with acetic anhydride was significantly improved in the presence of potassium carbonate at 100°C. Maximum of about 20 and 18% weight percentage gain (WPG) values were obtained with Turkish pine (*Pinus brutia*) and cedar (*Cedrus libani*) wood flour after 3 h reaction at 100°C, respectively. The two modification methods and the effect of wood components on vinyl acetate (VA) or acetic anhydride (AA) modification, were characterised by infrared analysis in detail. As an apparent advantage of this new method, acetaldehyde was formed as by-product which is non-acidic was removed easily after the reaction due to low the boiling point of acetaldehyde [b.p. (760 mm Hg) = 21 °C].

Key words: Acetic anhydride, vinyl acetate, holocellulose, α -cellulose, FTIR, chemical modification

INTRODUCTION

The chemical modification of wood has been the subject of research for many decades. It has been reported that the physical and chemical properties of wood has been improved by chemical modification (Stamm and Tarkow, 1947; Rowell, 1983; Banks and Lawther, 1994; Kumar, 1994; Cetin, 2000; Ozmen and Cetin, 2002; Hill, 2006; Rowell, 2006). The most favoured modification reaction involves the acetylation of wood with acetic anhydride. In previous studies (Cetin, 2000; Hill, 2006; Obataya and Minato, 2009; Cetin et al., 2010), various catalysts such as pyridine, dimethyl amino pyridine, dimethyl formamide, potassium acetate, etc. were used in acetylation of wood with acetic anhydride in order to increase the reaction rate. Nowadays, acetylated wood is a commercial product in Europe (Hill, 2006). Reacted acetate provides dimensional stability by bulking the cell wall polymers and reduces further swelling when the woods come into contact with water. In addition, chemical modification also provides biological resistance (Hill and Jones, 1996; Rowell, 1991, 2006). It is not only the amount of bonded acetate in the cell wall polymers that is important for

biological resistance, but also, the types of the cell wall polymers that have been modified.

Acetylation with acetic anhydride has got some disadvantage such as being expensive and requires significant capital investment. In addition, acetic acid is produced as a by-product at the end of the reaction and must be removed from the modified materials. In Turkey, the study of acetylation of wood with acetic anhydride is limited with academic work. There are two main obstacles in the commercialization of acetylation in Turkey. One of them is the cost of acetic anhydride, the other is that acetic anhydride is a restricted chemical. The purchase and the stock of acetic anhydride requires special permission from the Health Ministry because of its use for the synthesis of heroin by the diacetylation of morphine (Ozmen et al., 2010).

In recent studies (Jebrane and Sebe, 2007), maritime pine sapwood was successfully acetylated with vinyl acetate via transesterification reactions. This new technique has some advantages over acetylation of wood with acetic anhydride such as vinyl acetate which is a readily available compound and is cheaper than acetic anhydride, and acetaldehyde is produced as by-product which is none-acidic and has low boiling point (21 °C).

In this paper, the potassium carbonate catalyst transesterification reactions with vinyl acetate (VA) or acetic

*Corresponding author. E-mail: nihatcetin@ksu.edu.tr. Tel: +90 344 223 76 66. Fax: +90 344 221 72 44.

anhydride (AA) and two wood species namely Turkish pine (*Pinus brutia*) and cedar (*Cedrus libani*) sapwood flour were studied. In addition, reactivity of wood components (holocellulose and α -cellulose) with VA or AA was also studied. The chemical modification of wood and wood components was characterised by FTIR studies.

MATERIALS AND METHODS

Preparation of wood flour

Turkish pine (*P. brutia*) and cedar (*C. libani*) sapwood were ground using a hammer mill and sieved to a size of 40 mesh. Following that, the wood flour was extracted with deionised water for 6 h then with toluene : acetone : ethanol mixture [4/1/1, (v/v)], for an additional 6 h using a soxhlet extractor. The extracted wood flour was oven-dried at 105°C for overnight and was transferred to a desiccator containing phosphorus pentoxide, and allowed to cool to room temperature.

Preparation of holocellulose and α -Cellulose

Holocellulose and α -cellulose were produced according to Browning (1967). The products were oven-dried at 50°C overnight. The oven-dried holocellulose and α -cellulose were transferred to a desiccator, and was allowed to cool to room temperature.

Chemicals

AA, VA, dimethyl formamide (DMF) and potassium carbonate (K_2CO_3) were obtained from Merck. All chemicals were used as supplied without further purification.

Modification of wood components with AA or VA

Extractive free wood flour, holocellulose and α -cellulose was transferred to a round bottom flask containing DMF solution with 14 mmol acetic anhydride (AA)/g dry wood. The reaction was carried out with or without a potassium carbonate catalyst (1.1 mmol K_2CO_3 /g dry wood) at 100°C for 3 h.

The vinyl acetate transesterification reaction conditions was derived from earlier publication (Cetin et al., 2010). For transesterification reaction, wood flour, holocellulose or α -cellulose was transferred to a round bottom flask containing 14 mmol vinyl acetate (VA)/g dry wood. Reaction was carried out in DMF solution with a potassium carbonate catalyst (1.1 mmol K_2CO_3 /g dry wood) at 100°C for 3 h.

Each reaction was repeated three times. At the end of the reaction, all the modified samples were extracted with soxhlet extractor with deionised water for 6 h, then with toluene : acetone : ethanol mixture for 6 h. The soxhlet thimble and contents were oven-dried overnight at 105°C (for wood flour) and 50°C (for holocellulose and α -cellulose) in vacuum oven. The samples were transferred to a desiccator containing phosphorus pentoxide until cooled, then weight gain levels were calculated. The weight percentage gain (WPG) was calculated according to the following equations:

$$WPG(\%) = \frac{W_2 - W_1}{W_1} \times 100$$

Where, W_1 = Before treatment sample weight and W_2 = after treatment sample weight.

Infrared spectroscopy

The infrared absorption spectra of the acetylated and unmodified wood flour, α -cellulose and holocellulose were obtained with the KBr (potassium bromide) technique, using a Shimadzu 8400s FT-IR spectrometer, at a resolution of 4 cm^{-1} (40 scans). In each case, 1% (w/w) of the oven dry wood flour was dispersed in a matrix of KBr and was pressed to form pellets.

RESULTS AND DISCUSSION

The reaction schemes of the wood flour with acetic anhydride or vinyl acetate are shown in Figure 1. For the determination of the reactivity of wood species, Turkish pine (TP), cedar (CL) and sapwood flour were modified with VA in the presence of potassium acetate as a catalyst. TP and CL wood flour were modified with AA with or without K_2CO_3 catalyst in order to compare them with the new vinyl acetate technique. These reaction conditions were similar to vinyl acetate transesterification reaction. All the modification results are shown in Figures 2 and 3. The best results were obtained with VA modification with the two studied wood species. Maximum of about 20 and 18% weight percentage gain (WPG) values were obtained with Turkish pine (TP) and cedar (CL) wood flour after 3 h reaction at 100°C, respectively. This difference can be attributed to the different chemical composition of these two softwood species (Fengel and Wegener, 1989) and also to their microstructure (Ozmen, 2007). As can be seen from Figures 2 and 3, in the two studied wood samples, acetic anhydride modification without catalyst gave the lowest WPG values (about 4%). When 1.1 mmol K_2CO_3 /g dry wood catalyst was added in the reaction environment, WPG values showed a dreadful increase (TP and CL of about 17%).

In order to determine the reactivity of wood components, holocellulose and α -cellulose were produced from TP and CL wood flour. Holocellulose amount was found as 67 and 70% for TP and CL, respectively. α -Cellulose values of TP and CL were 44 and 46%, respectively. As can be seen from Figures 2 and 3, the wood flour showed greater reactivity than holocellulose and α -cellulose. Higher modification levels were obtained with wood flour than with holocellulose and α -cellulose samples at same reaction times, because the reactive sites of lignin is more accessible than those of holocellulose and α -cellulose (Rowell, 1984; Rowell et al., 1994).

Acetic anhydride (AA) reactions were slower than the vinyl acetate (VA) modification of the wood flour. The effect of removal of lignin is shown in Figures 2 and 3 for the AA and VA modified samples, respectively. It is apparent that holocellulose exhibited a lower degree of substitution than the virgin wood flour. When the sample

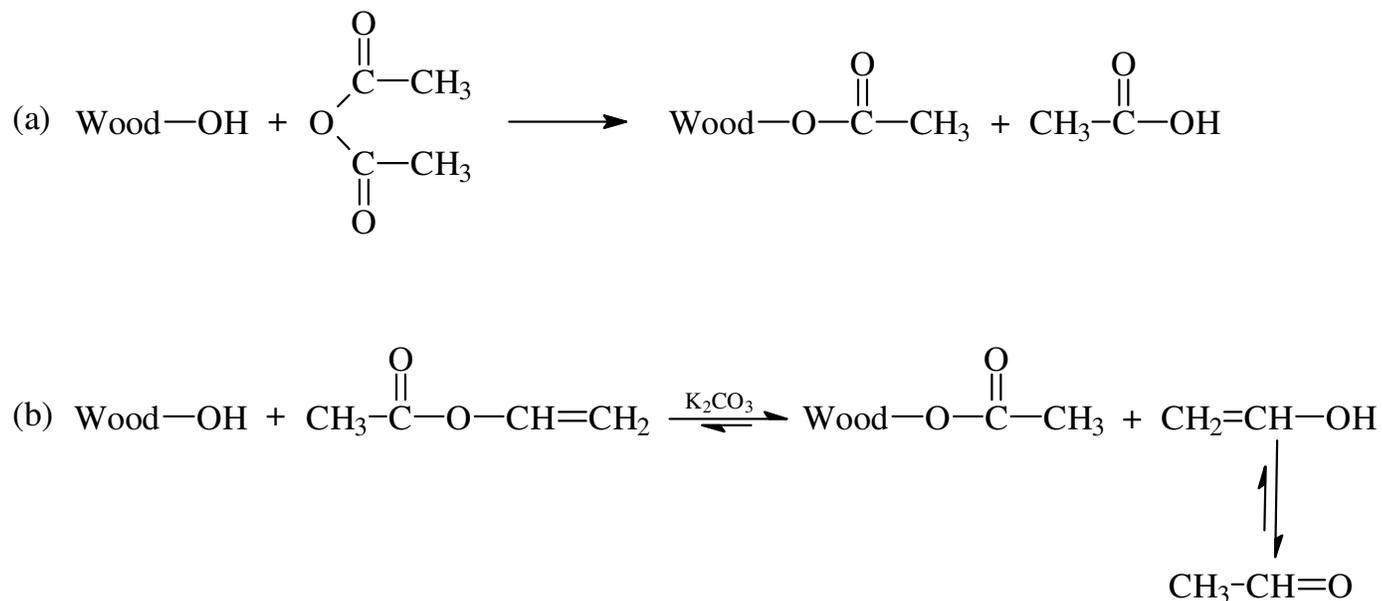


Figure 1. The reaction schemes between acetic anhydride (AA) (a) or vinyl acetate (VA) (b) and wood flour.

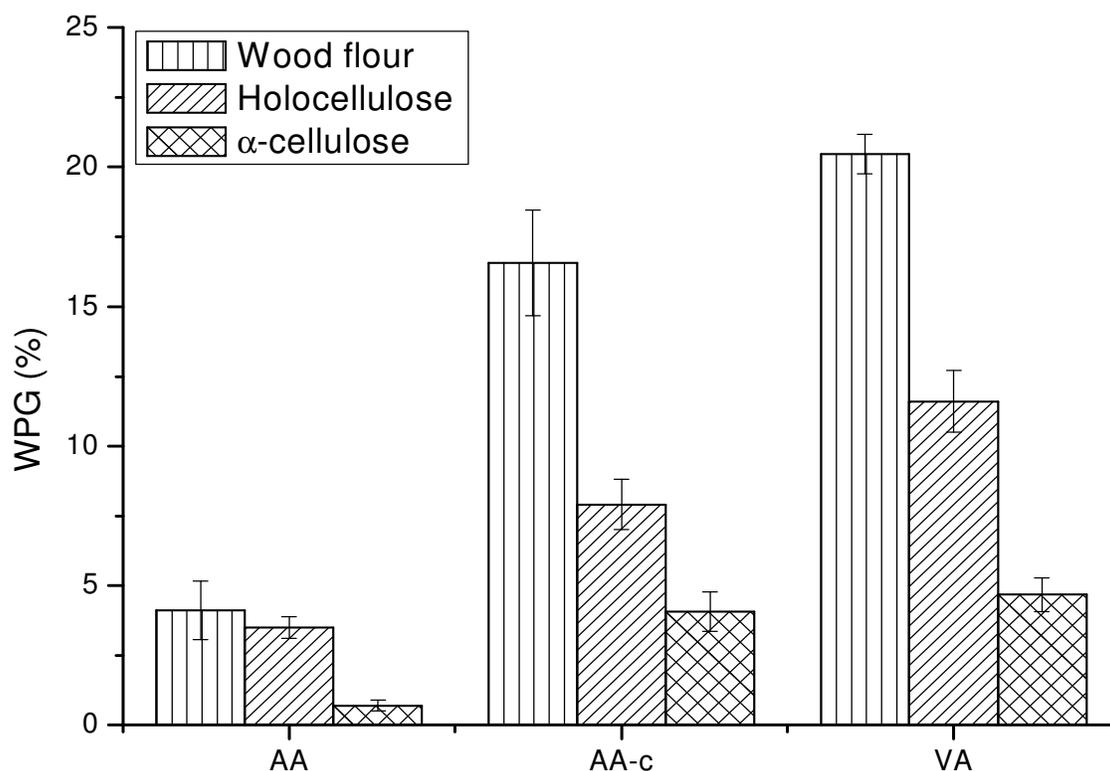


Figure 2. WPG (%) values of Turkish pine (TP) wood flour, holocellulose and α -cellulose modified with acetic anhydride(AA), acetic anhydride with catalyst (AA-c) and vinyl acetate (VA) for 3 h at 100°C.

was delignified, WPG levels of the sample were markedly reduced from about 17 to 8% and 20 to 12% for the modification with AA and VA, respectively. This result

presumably reflects the lower reactive OH content resulting from the lignin removal.

α -Cellulose was reacted with AA and about 0.7%

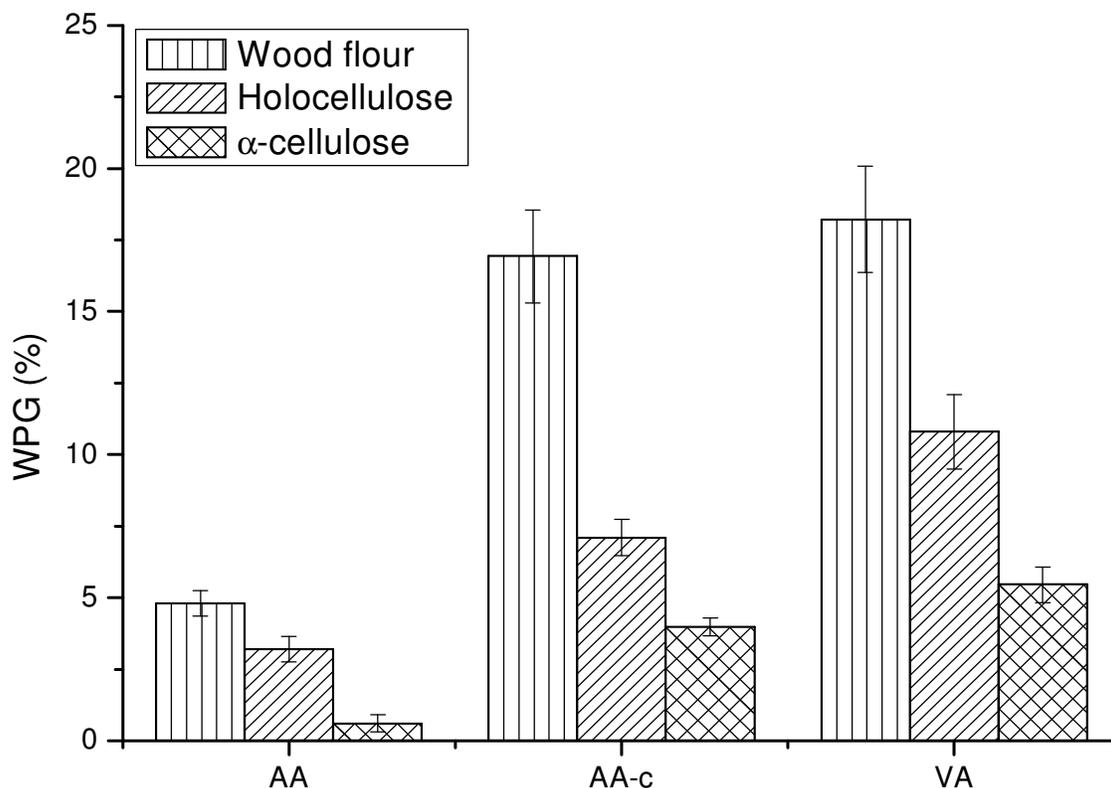


Figure 3. WPG (%) values of cedar (CL) wood flour, holocellulose and α -cellulose modified with acetic anhydride (AA), acetic anhydride with catalyst (AA-c) and vinyl acetate (VA) for 3 h at 100°C

weight gain was obtained. α -Cellulose was found to be completely unreactive to acetic anhydrides without catalyst (Figures 2 and 3). When K_2CO_3 was used as the catalyst, the cell-AAc and cell VA samples showed about 4% WPG. In an earlier work, the reactivity of wood and wood components with acetic anhydride was studied (Ozmen and Cetin, 2002). The reactivity of other components was summarised as: lignin > hemicellulose >> cellulose. The whole wood reacted faster than the holocellulose or cellulose. It was reported that cellulose was not reactive to AA and no weight percentage gain was obtained. But in this study, when K_2CO_3 was used as the catalyst, α -cellulose samples were successfully acetylated with VA or AA (Figure 6).

The proof of the reaction with anhydrides can be obtained by using FTIR spectra. Figure 4 shows the FTIR spectra of the unmodified (C), acetic anhydride modified (AA), acetic anhydride modified with catalyst (AAc) and vinyl acetate modified (VA) cedar sapwood flour. As shown in Figure 4, no spectral difference was noted between the two acetylation methods. The acetylated samples (AA-c and VA) were easily identified in the FTIR spectra, and the emergence of a carbonyl stretching vibration at 1745 cm^{-1} ($\nu_{C=O}$) in the spectra confirmed the formation of ester bonds after reactions with AA-c and VA. In addition, the intensity of the band at 1242 cm^{-1}

also increased and was associated to the C-O stretching vibration (ν_{C-O}) of the acetyl moieties. The in plane bending (δ_{C-H}) and out of plane bending (γ_{C-H}) vibrations of the methyl groups introduced were also observed at 1375 and 900 cm^{-1} , respectively (Cetin et al., 2010). The intensity of the band at 605 cm^{-1} also increased and was associated with some vibrations of the grafted methyl groups.

Figure 5 shows the FTIR spectra of the untreated (H), AA modified (H-AA), AA modified with catalyst (H-AAc) and VA modified (H-VA) cedar holocellulose samples. When the FTIR spectra of virgin wood flour (Figure 4C) was compared with the unmodified holocellulose spectra (Figure 5H), there was no significant difference observed (except the disappearance of the peak at 1510 cm^{-1} due to removal of the lignin). AA and VA modified holocellulose samples showed C=O absorptions in the region of 1740 cm^{-1} .

Figure 6 shows the FTIR spectra of α -cellulose (cell), AA modified (cell-AA), AA modified with catalyst (cell-AAc) and VA modified (cell-VA) α -celluloses. When the spectra of unmodified α -cellulose (Figure 6, cell) was compared with the spectra of the unmodified holocellulose (Figure 5H), the most significant difference was the disappearance of the weak C=O peak in the region of 1740 cm^{-1} , which is attributable to the loss of hemicellulose.

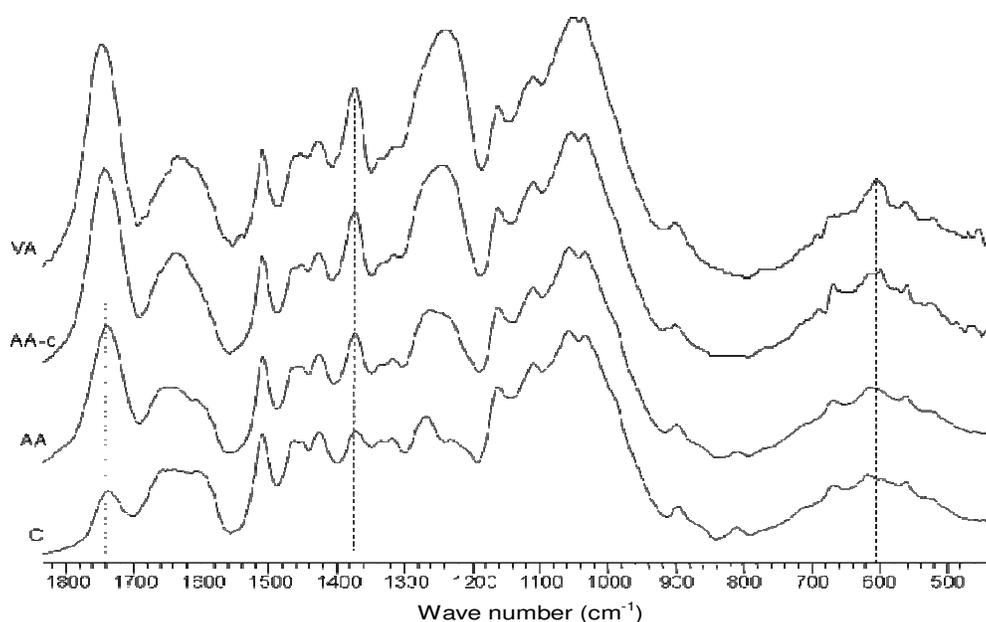


Figure 4. The 450 to 1900 cm^{-1} region of the infrared spectra for acetic anhydride modified (AA = 4.8% WPG), acetic anhydride modified with catalyst (AA-c = 16.9% WPG), vinyl acetate modified (VA = 18.2% WPG) and unmodified (C) cedar wood flour

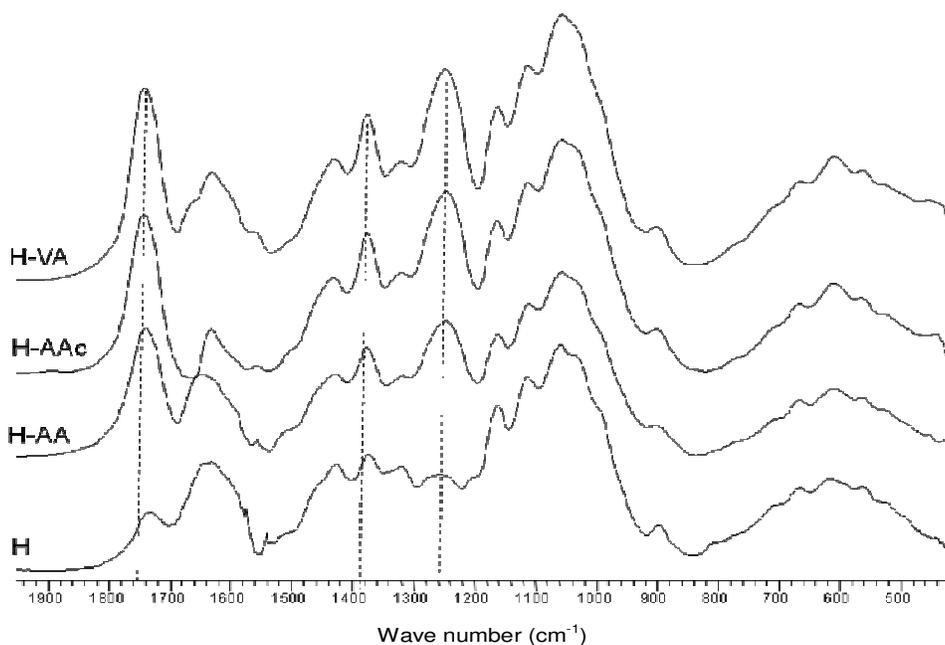


Figure 5. The 450 to 1900 cm^{-1} region of the infrared spectra for acetic anhydride modified (H-AA = 3.2% WPG), acetic anhydride modified with catalyst (H-AA-c = 7.1% WPG), vinyl acetate modified (H-VA = 10.8% WPG) and unmodified (H) cedar holocellulose.

celluloses. AA modified samples showed a small peak at the region of 1740 cm^{-1} due to the C=O peak (Figure 6 cell-AA). This peak was weak, due to the low level of substitution. When K_2CO_3 was used as catalyst, cell-AAc

and cell VA samples showed similar characteristic vibration peaks in the FTIR spectra (Figure 6 cell-AAc and cell-VA). These peaks were the carbonyl stretching vibration at 1740 cm^{-1} , the methyl in-plane bending at

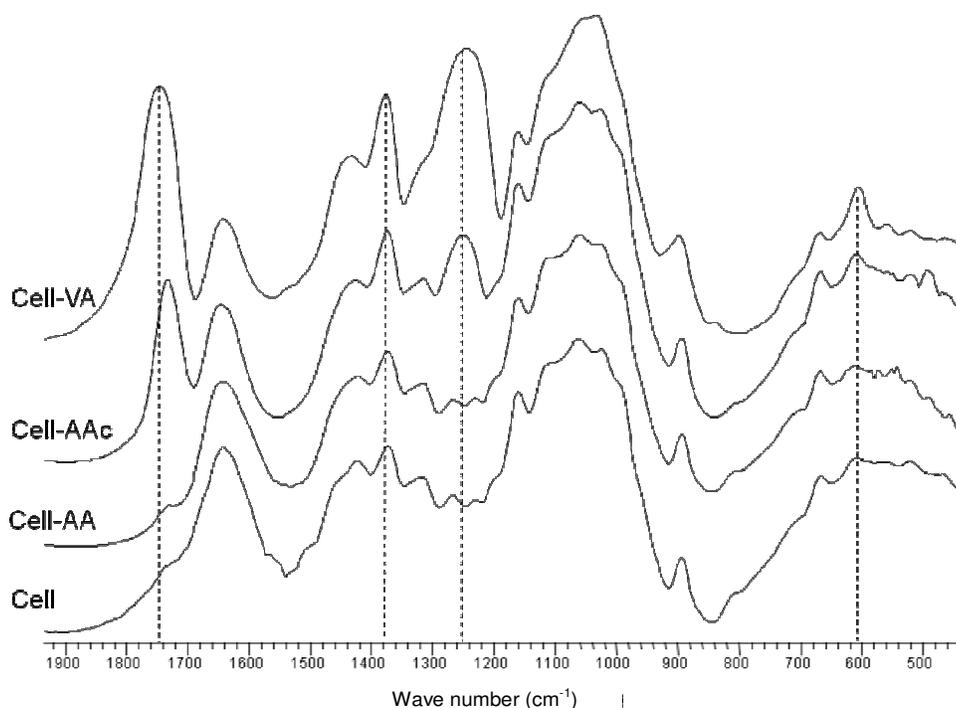


Figure 6. The 450 to 1900 cm^{-1} region of the infrared spectra for acetic anhydride modified (cell-AA = 0.7% WPG), acetic anhydride modified with catalyst (cell-AA-c = 3.9% WPG), vinyl acetate modified (cell-VA = 5.5% WPG) and unmodified (cell) cedar α -cellulose

1735 cm^{-1} and the C-O stretching at 1235 cm^{-1} .

Conclusions

The order of reactivity was found to be virgin wood flour > holocellulose >> α -cellulose. The VA modification gave higher WPG values than the acetic anhydride. FTIR studies showed that the esterification between AA or VA and α -cellulose occurred in the presence of a catalyst.

REFERENCES

- Banks WB, Lawther ML (1994). Cellulosic Polymers Blends and Composites. Hanser, Munich, Germany.
- Browning BL (1967). Methods of Wood Chemistry. Interscience Publishers, London, UK.
- Cetin NS (2000). Surface activation of lignocellulosics by chemical modification. PhD Thesis. University of Wales Bangor, UK.
- Cetin NS, Ozmen N, Birinci E (2010). Acetylation of wood with various catalysts. J. Wood Chem. Techn. In press.
- Fengel D, Wegener G (1989). Wood: Chemistry, Ultrastructure, Reactions. Water de Gruyter, Berlin, Germany.
- Hill CAS (2006). Wood Modification: Chemical, Thermal and Other Processes, John Wiley & Sons, Chichester, UK.
- Hill CAS, Jones D (1996). The dimensional stabilisation of Corsican pine sapwood by reaction with carboxylic acid anhydrides. The effect of chain length. Holzforschung, 50: 457-462.
- Jebrane M, Sebe G (1997). A novel simple route to wood acetylation by transesterification with vinyl acetate. Holzforschung, 61: 143-147.
- Kumar S (1994). Chemical modification of wood. Wood Fibre Sci. 26: 270-280.
- Obataya E, Minato K (2009). Potassium acetate-catalyzed acetylation of wood: extraordinarily rapid acetylation at 120°C. Wood Sci. Technol. 42: 567-577.
- Ozmen N (2007). Dimensional stabilisation of fast growing forest species by acetylation. J. Appl. Sci. 7: 710-714.
- Ozmen N, Cetin NS (2002). Anhydride modification of wood components and FTIR studies. Proceeding of The Fourth GAP Engineering Congress, Sanliurfa, Turkey. pp. 1697-1702.
- Ozmen N, Cetin NS, Birinci, E, Narlioglu N (2010). A new approach for acetylation of wood: Vinyl acetate. The 1st International Symposium on Environment and Forestry, Trabzon, Turkey. pp. 1540-1551.
- Rowell RM (1983). Chemical modification of wood. Forest Prod. Abst. 6: 363-382.
- Rowell RM (1984). The Chemistry of Solid Wood. American Chemical Society, Washington, USA.
- Rowell RM (1991). Chemical modification of wood. In Wood and Cellulosic Chemistry. Marcel Dekker, New York, USA.
- Rowell RM (2006). Acetylation. For. Prod. J. 56: 4-12.
- Rowell RM, Simonson R, Hess S, Plackett DV, Cronshaw D, Dunningham E (1994). Acetyl distribution in acetylated whole wood and reactivity of isolated wood cell-wall components to acetic anhydride. Wood Fibre Sci. 26: 11-18.
- Stamm AJ, Tarkow H (1947). Dimensional stabilisation of wood. J. Phys. Colloid. Sci. 51: 493-505.