

## **A NEW APPROACH FOR ACETYLATION OF WOOD:**

### **VINYL ACETATE**

**Nilgöl ÖZMEN, Nihat Sami ÇETİN, Emre BİRİNCİ and Nasır  
NARLIOĞLU**

KSU, Faculty of Forestry, Department of Forest Industry  
Engineering, Kahramanmaraş

#### **Abstract**

The chemical modification of wood has been the subject of research for many decades. The most favoured modification reaction involves the acetylation of wood with acetic anhydride. 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 that chemical modification also provides biological resistance. With acetylation, it is possible to extent at least twice or three times service life of wood as compared to control one. Acetylation of wood with acetic anhydride is not subject only academic studies, it is also became commercial process since 2003.

In Turkey, the study of acetylation of wood with acetic anhydride is limited with academic work. There are two main obstacles commercialization of acetylation in Turkey. One of them is the cost of acetic anhydride, the other is that acetic anhydride is the restricted chemical. The purchase and the stock of acetic anhydride are requiring special permission from Health Ministry because of its use for the synthesis of heroin by the diacetylation of morphine.

The purpose of this study is to show the new methods for acetylation of wood. Scots pine (*Pinus sylvestris*) sapwood was successfully acetylated by the new transesterification reaction with vinyl acetate. Under identical conditions, Scots pine sapwood was also modified with acetic anhydride to compare with the new technique. The results of acetylated wood with acetic anhydride and vinyl acetate were compared, and characterized by Infrared (FTIR) and <sup>13</sup>C CP MAS NMR analysis.

**Keywords:** Acetylation, Acetic anhydride, Vinyl acetate, Scots pine, Chemical modification.

## 1. Introduction

Wood is renewable resources and has many utilisation areas. Unfortunately, some of the wood properties such as dimensional instability, biodegradability, flammability etc. limit the utilisation areas (Fengel and Weneger 1989).

Chemical modification can be defined as a chemical reaction between reactive parts of wood cell wall polymers (hydroxyl groups generally) and a chemical reagent, with or without catalyst, to form a covalent bond between these two. All of the methods investigated to date have involved the chemical reaction of a reagent with the cell wall polymer hydroxyl groups. The chemical modification of wood with various reagents including anhydrides (such as acetic, succinic, maleic, propionic, butyric, hexanoic, crotonic and methacrylic anhydrides), isocyanates, formaldehyde, acetaldehyde, epoxides (such as ethylene or propylene oxide, glycidyl methacrylate, allyl glycidyl ether etc.) has been the subject of research for many decades (Stamm and Tarkow, 1947,

Banks and Lawther, 1994, Kumar, 1994, Hon, 1996, Rowell, 1983, 1991, 2006, Cetin and Ozmen, 2001, Hill, 2006).

While there has been a lot of research conducted with various chemical reaction systems; many of them focused on the acetylation of wood with acetic anhydride. In spite of the vast amount of research on the acetylation of both bulk wood and wood particles (for composites), commercialisation has been limited. There are reports of a commercial acetylation plant for solid wood in Japan but few details are available (Rowell, 2006).

Acetylation became commercial product recently. In Netherlands, Titan Wood is the first company to produce acetylated wood in commercial scale (its name is Accoya wood). Their production capacity is about 24.000 m<sup>3</sup> per annum. It was expected that in near future, acetylated wood will replace the more toxic preservative treatments in many application (Kattenbroek, 2005).

In Turkey, there is no commercial application of acetylation wood with acetic anhydride. Also wood acetylation with acetic anhydride is limited since this chemical is used for the synthesis of heroin by the diacetylation of morphine. Because acetic anhydride is restricted in Turkey, it requires special permission from Turkish Health Ministry, General Directorate of Pharmacology and Pharmacologist.

Acetylation with acetic anhydride has got some disadvantage such as being expensive and requires significant capital investment. In addition, acetic acid is produced as by-product the end of the reaction and must be removed from modified materials.

Maritime pine sapwood has recently been successfully acetylated with a new transesterification reaction using vinyl acetate and a potassium carbonate catalyst (Jebrane and Sebe,

2007). The main advantages of this new technique are that vinyl acetate is cheaper than acetic anhydride and that acetaldehyde is produced as a by product. Acetaldehyde is a non-acidic, low boiling point (bp= 21°C) compound that is easily removed from modified wood after reaction.

In this study, Pine sapwood (*Pinus sylvestris*) samples were acetylated using vinyl acetate and acetic anhydride. Modified samples were characterised by weight percent gain (WPG) calculations. FTIR and <sup>13</sup>C CP-MAS NMR spectroscopy on both acetylation methods of the modification of wood was also determined.

## **2. Studies having been done**

### **2.1. Material**

Acetic anhydride, vinyl acetate, potassium carbonate and dimethyl formamide were purchased from Merck. All chemicals were used as received without further purification. Deionized water was used in all experiments.

Scots pine (*Pinus sylvestris*) sapwood was ground using a hammer mill and sieved to a size of 40 mesh. Following that, the wood flour was extracted with the standard solution (4/1/1, vol./vol., toluene:acetone:ethanol) using a Soxhlet extractor for 6 hours. Extracted wood flour was oven-dried at 103°C overnight. Oven-dried wood flour was transferred to a desiccator, and allowed to cool to room temperature.

## **2.2. Method**

### **2.2.1. Acetylation of Wood Flour**

Extractive free Scots pine sapwood flour was transferred to a round bottom flask containing DMF solution with acetic anhydride (AA) or vinyl acetate. All reactions were performed at 100°C. Reaction conditions were derived from earlier publication (Jebrane and Sebe, 2007). For each reactions 1g wood flour were used and each set of conditions were repeated at three times. At the end of the reaction, all modified samples were Soxhlet extracted with deionised water for 6 hours then with toluene:acetone:ethanol mixture (4/1/1, vol./vol.) for 6 hours. This was done to remove excess unreacted chemicals and by products. The Soxhlet thimble and contents were oven-dried overnight at 103°C transferred to a desiccator containing phosphorus pentoxide until cool, then weight gain levels were calculated.

The weight percentage gain (WPG) was calculated according to following equations.

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

$W_1$  = Before treatment sample weight

$W_2$  = After treatment sample weight

### **2.2.2 Infrared spectroscopy**

Infrared absorption spectra of acetylated and unmodified wood flour were obtained with the KBr (potassium bromide) technique, using a Shimatzu 8400s FT-IR spectrometer, at a resolution of 4 cm<sup>-1</sup> (40 scans). In each case, 1% w/w of oven dry

wood flour was dispersed in a matrix of KBr and pressed to form pellets.

### **2.2.3 $^{13}\text{C}$ and NMR CP-MAS analysis**

Solid state  $^{13}\text{C}$  CP-MAS (Cross Polarisation-Magic Angle Spinning) NMR spectra of Scots pine wood flour were performed at room temperature on a Bruker DPX-400 NMR spectrometer (Bruker), using MAS rates of 4 and 8 kHz, a frequency of 100.61 MHz for  $^{13}\text{C}$  NMR.

## **3. Conclusion**

In this study, the catalysed acetylation of Scots pine with acetic anhydride (AA) or vinyl acetate (VA) was investigated with using potassium carbonate catalyst. The acetylation of wood has been confirmed by WPG calculations, FTIR spectroscopy and  $^{13}\text{C}$  CP-MAS NMR analysis. In comparison between AA and VA modification results, the AA modification gave higher WPG values than VA modification at the same reaction conditions.

## **4. Discussion**

The reaction mechanism between wood hydroxyl groups and AA or VA is shown in Figure 1. As seen from Figure 2, that approximately 24% and 20% WPG levels were ultimately achieved for 6 hours reaction with acetic anhydride and vinyl acetate, respectively.

The proof of the reaction between acetic anhydride or vinyl acetate and Scots pine was obtained by analysing the samples with FTIR spectroscopy (Figure 3). No spectral difference was



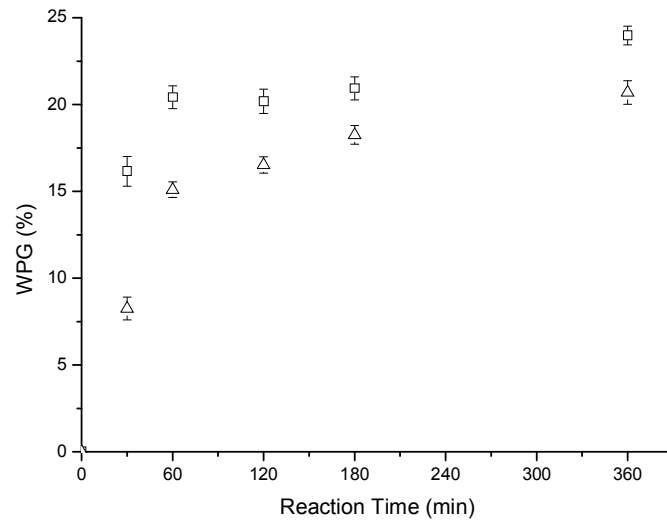


Figure 2. Reaction of Scots pine with acetic anhydride (square) or vinyl acetate (triangle) at 100°C up to 6 hours.

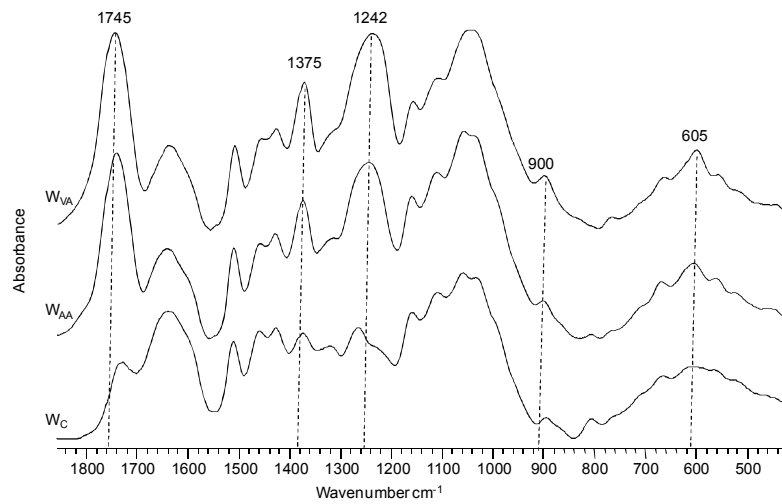


Figure 3. FTIR spectra of untreated ( $W_C$ ), acetic anhydride modified (24% WPG) ( $W_{AA}$ ), vinyl acetate modified (20% WPG) ( $W_{VA}$ ) Scots pine flour

The FTIR observation was confirmed by the  $^{13}\text{C}$  NMR spectrum of the samples. The  $^{13}\text{C}$  NMR spectra of unmodified Scots pine are shown in Figure 4 (W). As can be seen in Figure 8, the dominant pattern of the  $^{13}\text{C}$  NMR spectra is that of the carbohydrates, namely  $\text{C}_1$  (107 ppm),  $\text{C}_4$  crystalline (91 ppm),  $\text{C}_4$  amorphous (86 ppm),  $\text{C}_2$  (77 ppm),  $\text{C}_3/\text{C}_5$  (75 ppm),  $\text{C}_6$  crystalline (68 ppm),  $\text{C}_6$  amorphous (65 ppm) (Boonstra et al., 1996, Çetin et al., 2005). The signal at 59 ppm indicates the lignin methoxy groups. The aromatic groups of the lignin appear at 150 ppm as wide band.

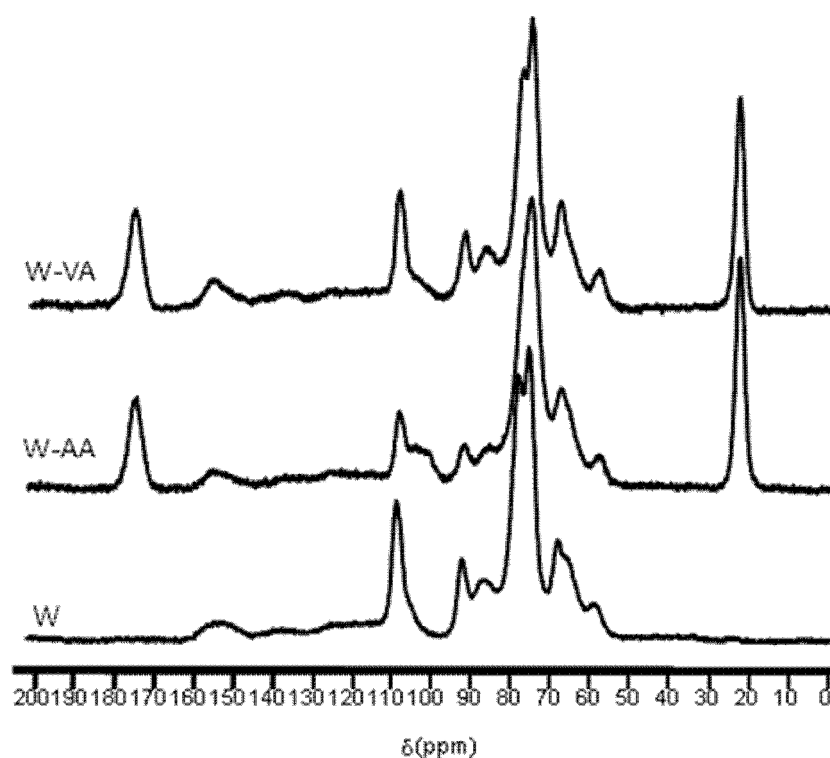


Figure 4.  $^{13}\text{C}$  CP-MAS NMR spectra of unmodified (W), acetic anhydride modified (W-AA), vinyl acetate modified (W-VA) Scots pine flour

After acetylation of Scots pine wood with acetic anhydride or vinyl acetate, the methyl band of the acetyl group at 21 ppm and the carboxylic group at 171 ppm show the acetyl groups on the wood components. There was no difference between the VA or AA modified wood spectra.

## **5. Proposals**

In this study, classical acetylation of wood with acetic anhydride was compared with the acetylation method using vinyl acetate. In comparison between AA and VA modification results, the AA modification gave higher WPG values than VA modification at the same reaction conditions.

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