



Research Article

## Effect of Oak Wood Modification on FTIR Crystallinity Indexes

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**Abstract:** Chemical modification of wood is one of the preservation methods that have been used for a long time to protect wooden materials against pests such as fungi and insects and to extend their service life. During the chemical modification of wood, there is a change in the structure of the wood due to the effects of chemicals and temperature. The cellulose molecule, which constitutes approximately half of wood or lignocellulosic materials, consists of an amorphous and crystalline structure. The crystal structure of cellulose varies depending on the type of plant it is obtained from, the age of the tree and the type of wood. In this study, oak wood was subjected to chemical modification with propionic anhydride and succinic anhydride in order to determine the effect of wood modification on FTIR crystallinity indexes. With propionic anhydride and succinic anhydride, the weight gains of wood were calculated as 4.47% and 38.08%, respectively. Crystallinity indexes were calculated by FTIR spectroscopy before and after the chemical modification of the wood. After the chemical modification process, changes in FTIR crystallinity indexes were observed. According to the FTIR crystallinity index results, the total crystallinity indexes increased.

**Keywords:** wood modification; crystallinity index; propionic anhydride; succinic anhydride; oak wood

## Meşe Odunu Modifikasyonunun FTIR Kristalinite İndekslerine Etkisi

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**Öz:** Odunun kimyasal modifikasyonu ahşap malzemelerin mantar ve böcek gibi zararlılara karşı korunması ve hizmet ömrünün uzatılması için uzun zamandır yapılan koruma yöntemlerinden biridir. Odunun kimyasal modifikasyonu sırasında kimyasal maddeler ve sıcaklık etkisi ile yapısında değişme görülmektedir. Odun veya lignoselülozik malzemelerin yaklaşık yarısını teşkil eden selüloz molekülü amorf ve kristal yapıdan oluşmaktadır. Selülozun kristal yapısı elde edildiği bitkinin türüne, ağacın yaşına ve odunun türüne göre farklılık göstermektedir. Bu çalışmada, odun modifikasyonunun FTIR kristalinite indekslerine etkisinin belirlenmesi amacıyla meşe odunu, propiyonik anhidrit ve süksinik anhidrit ile kimyasal modifikasyon işlemlerine tabi tutulmuştur. Propiyonik anhidrit ve süksinik anhidrit ile odunun ağırlık kazançları sırasıyla %4,47 ve %38,08 olarak hesaplanmıştır. Odunun kimyasal modifikasyonu öncesi ve sonrası FTIR spektroskopisi ile kristalinite indeksleri hesaplanmıştır. Kimyasal modifikasyon işlemi sonrasında FTIR kristalinite indekslerinde değişiklik görülmüştür. FTIR kristalinite indeksi sonuçlarına göre toplam kristalinite indeksleri artmıştır.

**Anahtar Kelimeler:** odun modifikasyonu; kristalinite indeksi; propiyonik anhidrit; süksinik anhidrit; meşe odunu

## 1. Introduction

Cellulose, hemicellulose and lignin are the main components that make up the cell wall of woody plants. Of these components, only cellulose exhibits a crystal structure. Hemicellulose and lignin, the other two main components of wood, exhibit an amorphous structure. The crystallinity of wood has a significant impact on the physical, mechanical and chemical properties of wood-based materials. Lignocellulosic fibers that exhibit high crystallinity have good dimensional stability, high density and strength. In addition, lignocellulosic fibers with high crystallinity exhibit lower shrinkage-expansion ability and lower chemical reactivity [1].

Chemical modification process is an effective method to improve the properties of wood and wood-based composites. Chemical modification process is defined as the reaction that forms covalent bonds between some reactive parts of lignocellulosic substances and chemical substances, with or without a catalyst. Such a reaction leads to changes in the chemical and physical properties of wood. For instance; through the acetylation process, the hydrophilic hydroxyl groups of wood are replaced by hydrophobic acetyl groups. As a result of this reaction, an increase in wood volume is observed due to swelling of the wood cell wall. Moreover, the hygroscopic properties of wood decrease after modification with organic anhydrides [2] - [6].

FTIR (Fourier Transform Infrared Spectroscopy) is a fast, inexpensive and effective method used to analyze changes in the chemical composition of wood and changes in functional groups during chemical reactions [7] - [9]. Therefore, instrumental analysis methods such as FTIR spectroscopy can be considered as a suitable non-destructive method that can be used to estimate the strength of wood material. The texture, chemical composition and anisotropic structure of wood make it difficult to determine crystallinity [10]. The crystallinity index of cellulose is a widely used parameter to measure the amount of crystalline cellulose present in wood and lignocellulosic materials. The crystallinity index is widely used to prove the structural changes of lignocellulosic materials after physical, chemical etc. treatments. FTIR spectroscopy is the simplest method for determining the crystallinity index of lignocellulosic substances because the resulting spectra always include fractions from both crystalline and amorphous regions in the wood [1].

In this study, oak wood was modified with propionic anhydride and succinic anhydride chemicals in order to determine the effect of chemical wood modification process on the crystallinity indices of wood. Changes in crystallinity indexes of wood after chemical modification were determined using FTIR spectroscopy.

## 2. Experimental

### 2.1. Material

In this study, oak wood was used as a material. Oak wood was first ground in a laboratory type grinder and then sieved with a shaker sieve, and wood flour with a particle size above 40 mesh were used for chemical modification. The chemicals used for chemical modification processes; propionic anhydride ( $C_6H_{10}O_3$ ), succinic anhydride ( $C_4H_4O_3$ ), dimethylformamide ( $C_3H_7NO$ ) and potassium carbonate ( $K_2CO_3$ ) were supplied from Merck KGaA, Darmstadt, Germany and the chemicals used for extraction processes; acetone, toluene and ethanol were supplied from Tekkim Chemical Industry Limited Company.

### 2.2. Method

#### 2.2.1. Soxhlet extraction

In order to remove the extractive substances in the wood structure before the chemical modification process, wood flours were extracted with a 4-1-1 volume ratio of toluene-acetone-ethanol solvent mixture in a Soxhlet extraction apparatus.

#### 2.2.2. Chemical modification

For chemical modification processes, extracted wood flour was subjected to modification with propionic anhydride (PA) and succinic anhydride (SA) chemicals separately. The amount of free hydroxyl (OH) in wood was calculated using Equation 1 determined by Hill and Jones [11].

$$OH (\%) = \frac{N}{H} \times 100 \quad (1)$$

Where;

N: Weight gain after modification/molecular weight ( $\text{CH}_3\text{CH}_2\text{CO}=57.07$  g/mol;  
 $\text{C}_4\text{H}_4\text{O}_3=100.07$  g/mol)

H: Weight of unmodified wood x number of moles of OH groups in 1 g of wood

Chemical modification processes were carried out under DMF and  $\text{K}_2\text{CO}_3$  catalyst for 6 hours in an oil bath set at  $105 \text{ }^\circ\text{C}$ . In order to remove unreacted chemicals remaining in the wood after chemical modification, the modified wood flour was first washed with pure water and then extracted with a mixture of toluene-acetone-ethanol (4-1-1).

### 2.2.3. Chemical characterization and crystallinity calculation by FTIR spectroscopy

FTIR spectroscopy was used to determine the crystallinity index values of wood. Before FTIR analyses, wood flours were dried in an oven at  $103 \pm 2 \text{ }^\circ\text{C}$  until completely dried. Dried wood flour was mixed with KBr (Potassium bromide) at 100 to 1 (KBr/sample) and then made into pellets by a special press. Then, infrared spectra of the pellets were taken in the wavelength range of  $400\text{--}4000 \text{ cm}^{-1}$  with a Shimadzu 8400s FTIR spectrophotometer. The samples were characterized as a result of interpreting the spectra obtained from FTIR analyzes and comparing them with each other. Additionally, FTIR crystallinity indexes were calculated from the intensities of the peaks obtained from the FTIR spectra. For FTIR crystallinity index calculations, the methods used by Teacă [1], Akerholm et al., [12], Hassan et al., [13], Tuong and Le, [14] were taken as reference. Characteristic FTIR bands of various components of wood are illustrated in Table 1.

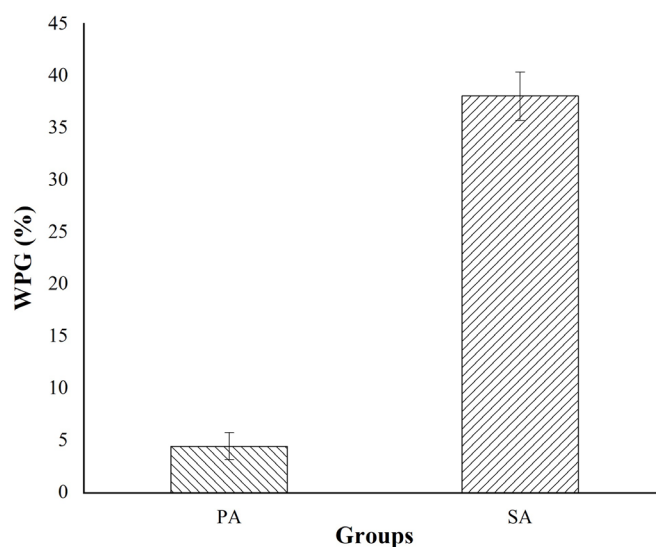
**Table 1.** FTIR wavenumber and corresponding functional groups [15] – [22].

Wavenumber ( $\text{cm}^{-1}$ )	Functional groups
895	Anomeric stretching in $\beta$ -glycosidic bonds
1054	C-C and C-O stretching
1269	C-O stretching in lignin and hemicellulose
1317	$\text{CH}_2$ wagging (crystalline cellulose I)
1336	O-H stretching (amorphous cellulose)
1366	C-H stretching in cellulose and hemicelluloses
1375	C-H stretching in cellulose
1421	O-H in aromatic structure; C-H stretching in $\text{CH}_2$ of cellulose
1463	Asymmetric $\text{CH}_2$ stretching in lignin
1510	C-C stretching of aromatic ring
1595	C-C stretching of the aromatic ring
1642	O-H stretching due to water absorption
1730	C=O stretching in unconjugated ketone, aldehyde and carbonyl
2900	C-H stretching in methyl and methylene groups
3400	O-H stretching in hydroxyl groups

## 3. Results and Discussion

### 3.1. Weight Gain After Chemical Modification

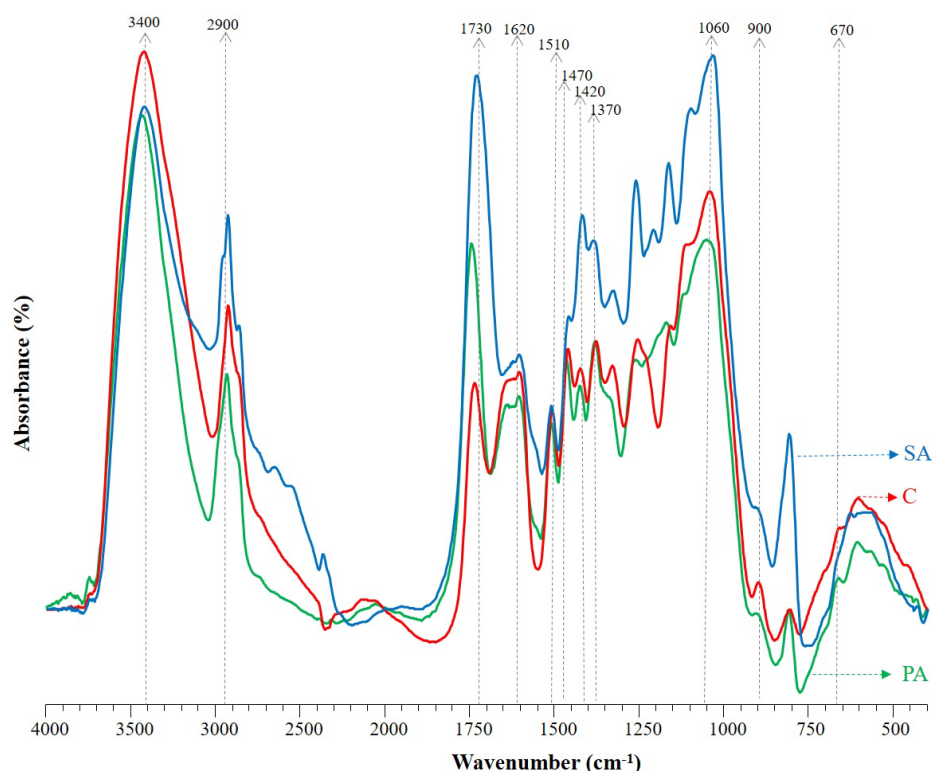
Percentage weight gain (WPG) values after chemical modification of oak wood with propionic anhydride (PA) and succinic anhydride (SA) are given in Figure 1. When the weight gains after chemical modification under the same conditions were examined, an increase in wood weight of 4.47% was observed after chemical modification with propionic anhydride and 38.08% after chemical modification with succinic anhydride.



**Figure 1.** WPGs after chemical modification

### 3.2. FTIR Analysis Results

FTIR spectra of wood before and after chemical modification are given in Figure 2. After chemical modification, an increase in some peak intensities was observed as a result of the replacement of free OH groups in the structure of cellulose, hemicellulose and lignin with propyl and succinyl groups.



**Figure 2.** FTIR spectra (PA propionic anhydride modified wood, SA succinic anhydride modified wood, C unmodified wood)

The absorbance intensity in all spectra of wood flour shifted towards wavelength values lower than  $3400\text{ cm}^{-1}$  after chemical modification. This shift is an indication that the OH group content decreased during the reaction between oak wood and PA and SA. In addition, after chemical modification, the band starting from  $1730\text{ cm}^{-1}$ , attributed to carbonyl (C=O) groups, shifted to lower wavelength values ( $1720\text{ cm}^{-1}$ ) and a significant increase in peak intensities was recorded. The peak at  $1730\text{ cm}^{-1}$  is specific to the holocellulose component

(cellulose and hemicellulose) in the structure of wood. Carboxylic acid groups are more prominent after chemical modification [1].

The broad peak around  $3354\text{ cm}^{-1}$  is associated with mixed OH stretching vibration, mainly originating from cellulose and hemicellulose. Waggings from  $2900\text{ cm}^{-1}$  characterize C-H stretching in methyl and methylene groups. The signal from  $1729\text{ cm}^{-1}$  corresponds to the carbonyl stretching vibration in unconjugated ketones and free aldehyde found in lignin and hemicelluloses. The peak around  $1630\text{ cm}^{-1}$  is the characteristic absorption of the conjugated C=O group of lignin in wood samples [23]. The absorbance values at  $1420\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$  are sensitive to the amount of crystalline versus amorphous structure in lignocellulosic materials, meaning that the broadening of these bands reflects a more disordered structure [24], [25].

The change in the C-H peaks of chemically modified wood samples and the decrease in the intensity of the OH group peak around  $3400\text{ cm}^{-1}$  was associated with the decrease in the OH group after chemical modification. The total crystallinity index is defined as the absorbance ratio of  $1370/2900$ ; where the band at  $1370\text{ cm}^{-1}$  is attributed to C-H deformation and the band at  $2900\text{ cm}^{-1}$  is attributed to C-H and CH stretching [1], [24], [26].

A slight increase in the total crystallinity index ( $1370/2900$ ) was noted after the chemical modification of the wood samples. The total crystallinity index was calculated as 1.026 in the unmodified sample, 1.037 in the PA modified sample and 1.154 in the SA modified sample.

**Table 2** Structural indexes calculated from FTIR spectra.

Groups	1370/2900	1720/2900	3400/2900	1470/897	1370/1670	1370/1512	2900/3400	2900/1060
PA	1.037	1.009	0.778	0.833	0.891	1.008	1.285	1.096
SA	1.154	0.945	0.884	0.860	0.800	0.889	1.130	1.053
Unmodified	1.026	1.143	0.764	0.860	0.913	0.956	1.308	1.181

The  $1370/1512$  absorbance ratio is the ratio of the peak intensity at  $1375\text{ cm}^{-1}$  resulting from cellulose and the peak intensity at  $1512\text{ cm}^{-1}$ , which is characteristic of lignin, and this ratio can be used as the crystallinity index of wood [27]. This ratio ( $1375/1512$ ) was found to be lower after chemical modification with succinic anhydride than in the unmodified and propionic anhydride-modified groups. Another relative cellulose crystallinity can be estimated by the ratio between the intensities of the peaks at  $1474\text{ cm}^{-1}$  and  $897\text{ cm}^{-1}$ , respectively, which are assigned to the deformation of CH in lignin and CH in the glucose ring of cellulose [14]. It was observed that this ratio ( $1470/897$ ) was 0.833 in the propionic anhydride-modified and similar (0.860) in the unmodified and succinic anhydride-modified groups.

#### 4. Conclusions

Structural changes occurred in the wood after chemical modification processes using propionic anhydride and succinic anhydride.

A significant increase in WPG was observed in the modification process with succinic anhydride compared to unmodified wood and propionic anhydride-modified wood samples.

According to the spectral changes proven by FTIR spectroscopy, changes in the chemical structure of wood have been proven as a result of its reactions with propionic anhydride and succinic anhydride.

After chemical modification processes, some peak intensities in the FTIR spectra increased due to the increase in the C=O group while some decreased due to the decrease in the OH group.

There was a slight increase in the total crystallinity index calculated from FTIR spectroscopy after chemical modification.

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