ROUGHNESS OF ESTERIFIED EASTERN COTTONWOOD

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The aim of this study was to investigate the effect of esterification via acetic or propionic anhydride on the surface roughness of eastern cottonwood. Eastern cottonwood (*Populous deltoides*) was esterified by using acetic or propionic anhydride without using any solvent or catalyst under different conditions. Two different weight percentage gains (WPGs) were obtained for each of the modifying chemicals. Three main surface roughness parameters, namely average roughness (R_a), mean peak to valley height (R_z) and maximum roughess (R_{max}) were measured by a stylus method before and after esterification. The surface roughness was significantly increased due to the esterifications. The surface roughness of wood increased with increasing WPG.

Keywords: Propionic anhydride; Acetic anhydride; Surface roughness; Esterification

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INTRODUCTION

Different chemical modification methods have been applied to improve some wood properties. Of the chemical modification methods, acetylation has been widely studied. It is well known that acetylation improves some properties of wood and its products (Hill 2006). Propionic anhydride, which is a higher homologue of acetic anhydride, has also been used to modify wood and its products (Suttie et al. 1999; Farahani and Hosseini 2008). The reaction between the anhydrides and wood is a single-site reaction, as depicted in Fig. 1. Each anhydride yields its corresponding acid as a by-product of its reaction with wood. The esterification of wood by the linear chain anhydride results in the substitution of hydroxyl groups with the acyl adducts. In addition, the bonded adducts occupy additional space in the cell wall, over and above that which had been occupied by the proton of the hydroxyl group. Thus, such chemical reactions also result in an increase in dimensions of the reacted wood species, because of swelling of the cell wall.

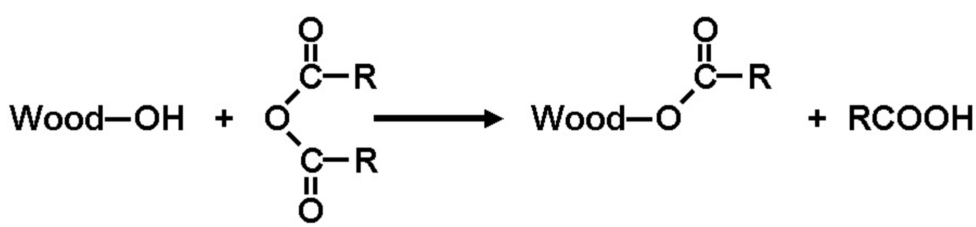

Fig. 1. Anhydride modification scheme, where R = CH_3 (acetic anhydride), and R = C_2H_5 (propionic anhydride)

Despite the fact that some wood properties are improved, esterification may affect some other wood properties, such as bondability, adversely (Hill 2006). Thus, it is important to investigate the properties that have not been studied.

The surface quality of solid wood is important in many of its applications. In addition to this, the surface properties of wood, including surface roughness, are important in producing wood panel products such as laminated veneer lumber (LVL) and plywood. The treatment of wood with some preservatives reduces its surface quality (Madas et al. 1998; Ors et al. 2005, Ayrilmis et al. 2006; Ozdemir et al. 2007; Dundar et al. 2008, Togay et al. 2009). Thus, the use of some preservatives is restricted in producing panel products. The chemical modification by linear chain anhydrides, especially acetic anhydride, has been considered as an alternative for toxic wood preservatives. Surface roughness is among the surface properties of the chemically modified wood that have not been studied. Thus, the aim of this study was to investigate the effect of acetic or propionic anhydride on the surface roughness of wood.

EXPERIMENTAL

Wood

. The wood used was cottonwood (*populous deltoids* 67/51) sapwood. The clone, which originated in Turkey, was planted in the north of Iran in 1981. Two logs cut from two trees were used for this study. The logs were about 100 cm lengths with a diameter about 35cm. The sapwood area of the logs was flat sawed to boards and then season dried. After being dried, the boards, samples with dimension of 50 mm (tangential) x 50mm (longitudinal) x 2mm (radial) were cut from the true flat sawn boards.

Chemicals

Acetic and propionic anhydrides used in this study were supplied from Esfahan petrochemical company and Merck, respectively.

Chemical Modification

Prior to the reaction, the wood samples were carefully sanded to remove loosely adhering fibers. Sanded samples were placed in a soxhlet extractor for solvent extraction using acetone for 16 hours. After extraction, the samples were oven-dried at 105 °C overnight. Following the removal from the oven, the samples were allowed to equilibrate to ambient temperature by placing them in a desiccator over silca gel. After cooling, the samples were weighed using a four-figure balance. The surface roughness of the samples was then measured according to the procedure explained in the next section. Propionylation and acetylation were performed without catalyst by vacuum impregnation of weighed, oven-dry wood samples with propionic or acetic anhydride, respectively. The impregnated samples were then reacted under different treatment conditions (Table 1) in a pressure vessel containing propionic or acetic anhydride. This was followed by solvent extraction and oven drying as explained earlier, before weight determination.

Table 1. Propionylation and Acetylation Conditions

Reagent	Temperature [°C]	Time [hr]	Concentration	Treatment code
Propionic anhydride	120	4	Neat	A
	100	3	Neat	B
Acetic anhydride	120	4	Neat	A
	100	3	Neat	B

Weight percentage gain (*WPG*) was calculated according to eq.1:

$$WPG\ (\%) = [(W_{mod} - W_{unmod}) / W_{unmod}] \times 100 \quad (1)$$

Surface Roughness

Surface roughness measurements were carried out on each sample before and after the esterifications using a stylus method according to ISO/DIS 4287/1. Prior to the surface roughness measurements, five samples for each level of acetylation and 3 samples for each level of propionylation were conditioned at a temperature of 25 ^{o}C and a relative humidity of 55%. A total of three measurements with the measurement length of 17.5 mm perpendicular to fibre direction were taken from one side (tangential plane) of each sample. The cutoff was 2.5 mm, and the detector tip radius was 16 nm. The three roughness parameters R_a, R_z, and R_{max} were considered to evaluate the surface roughness of the samples. R_a is the arithmetic average of the absolute values, R_z is the average absolute value of the five highest peaks and five lowest valleys, and R_{max} is the greatest peak to valley distance within any one sampling length. The relative roughness (R') was calculated according to equation 2:

$$R' = (R_e/R_o) \quad (2)$$

where, R_e is the surface roughness parameter of wood after esterification and R_o is the corresponding value before esterification.

Statistical Analysis

The equality of the surface roughness parameter means before and after the esterification was tested by a paired t test. Analysis of variance (ANOVA) was used for analysis the relative roughness data.

RESULTS AND DISCUSSION

Esterification of Eastern Cottonwood

For both anhydrides used in this study, two different weight percentage gains were obtained under the two different reaction conditions. WPGs obtained from the reactions are shown in Table 2. The WPGs show that the wood can be propionylated without using any catalyst within the range of temperatures used in this study. Some wood species have been reported not to be propionylated without using any swelling solvent (Hill 2006). Reaction temperature can play a key role in the reaction of wood with propionic anhydride when no catalyst and swelling solvent are used (Li et al. 2001). In this study, a WPG of 18.5% was obtained when the wood was modified with propionic anhydride at a temperature of 120 ^{o}C for the rather short reaction time. Iranian beech was also reported to be propionylated significantly under the same reaction conditions as applied in this research (Farahani and Hosseini 2008).

Table 2. Weight Percentage Gains Obtained from Acetylation and Propionylation Reactions

Reagent	Treatment code	*WPG*
Propionic anhydride	A	18.5
	B	5
Acetic anhydride	A	15.5
	B	8

Surface Roughness of Esterified Wood

The roughness parameters before and after the esterifications are shown in Table 3. As can be observed, all the parameters increased due to esterification via acetic or propionic anhydride. The profile of acetylated or propionylated wood given in Fig. 2 clearly indicate that the surface roughness of acetylated or propionylated cottonwood was higher than that for the untreated wood.

The analysis of the data by paired t test showed that all the differences except for the differences of the R_z and R_{max} before and after the propionylation with the WPG of 5% were significant (Table 3). The *WPG* of 5% was the lowest level of the esterifications studied in this research. The esterifications with higher *WPG*s increased all the parameters significantly.

Table 3. Mean Surface Roughness Parameters Before and After Esterification via Acetic or Propionic Anhydride

		Acetylation		Propionylation	
	WPG (%) / Roughness	8	15.5	5	18.5
Before esterification	R_a	8.64	7.39	9.10	7.03
	R_z	68.87	60.90	68.98	53.71
	R_{max}	89.96	80.61	87.98	67.97
After esterification	R_a	11.39(S)	13.25(S)	11.42(S)	13.69(S)
	R_z	83.56(S)	91.75(S)	77.56(NS)	90.83(S)
	R_{max}	104.90(S)	110.60(S)	98.62(NS)	112.49(S)

S = The difference of the parameter before and after the esterificaton is significant.
NS = The difference of the parameter before and after the esterification is not significant.

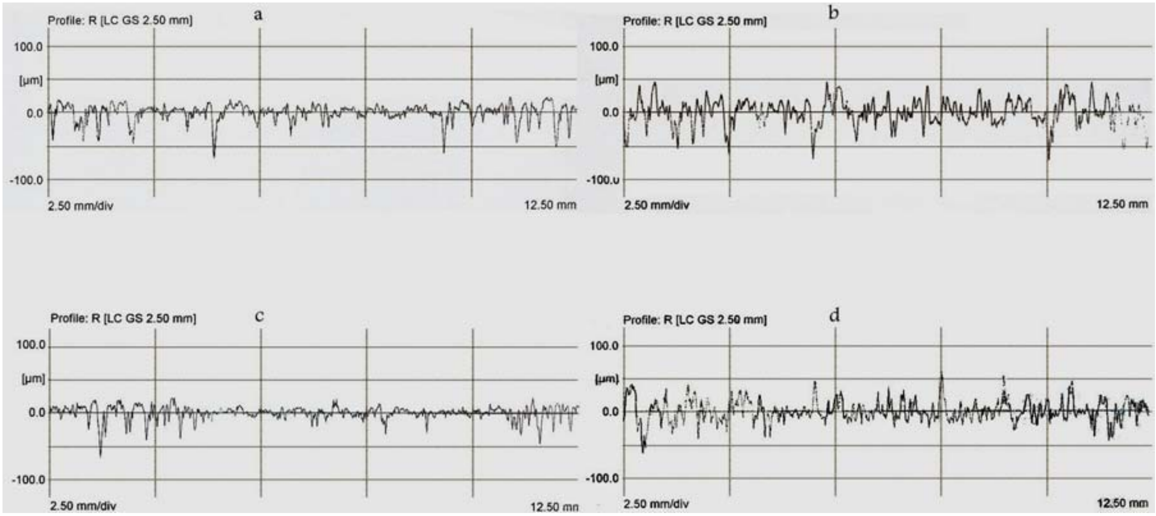

Fig. 2. Surface roughness profiles of Eastern cottonwood before and after esterification: (a) before acetylation, (b) after acetylation, (c) before propionylation, and (d) after propionylation

The relative surface roughness parameters are given in Table 4. As can be observed, the parameters increased with increasing the WPGs, irrespective of the anhydride. For example, R'_a of 1.95 was obtained when WPG increased up to 18.5%. The R' value of close to 2 is an indication of noticeable change on the wood roughness (Kamdem and Grelier 2002).

Table 4. Relative Surface Roughness Parameters of Acetylated or Propionylated Wood

Anhydride *(NS)	*WPG* **(S)	R'_a	R'_z	R'_{max}
Acetylated	8	1.36	1.22	1.17
	15. 5	1.81	1.51	1.37
Propionylated	5	1.24	1.12	1.1
	18.5	1.95	1.69	1.65

*NS= not significant
**S= significant

Table 5. Analysis Variance for R'_a, R'_z, and R'_{max} Relative Roughness Parameter

Relative roughness parameter	Source	DF	Seq SS	Aduj SS	Aduj MS	F value	P value
R'_a	Anhydride	1	0.02352	0.00109	0.00109	0.03	0.866
	WPG(Anhydride)	2	1.42316	1.42316	0.71158	19.28	0
R'_z	Anhydride	1	0.00417	0.00685	0.00685	0.22	0.643
	WPG(Anhydride)	2	0.8003	0.8003	0.40015	13.08	0.001
R'_{max}	Anhydride	1	0.01923	0.07361	0.07361	1.45	0.248
	WPG(Anhydride)	2	0.60833	0.60833	0.30416	6.01	0.013

DF = Degrees of Freedom; Seq SS= Sequential Sums of Squares;
Aduj SS = Adjusted Sums of Squares; Aduj MS = Adjusted Means Squares

The statistical analysis of the relative roughness data by ANOVA showed that there was no significant difference attributable to the treatment with acetic vs. propionic anhydrides, but there was at least one significant different between the WPGs (Tables 4 and 5). These may suggest that the substitution of cell wall hydroxyl groups with the acyl adducts does not play a key role in the roughness increase, because the degree of the substitution for acetylation at a given WPG was higher than that for propionylation. Of course, this suggestion can be further examined by studying the roughness of wood modified with longer linear chain anhydrides such as hexanoic anhydride compared with acetic anhydride.

As has been mentioned, wood is bulked when it is esterified by a linear anhydride. Wood bulking increases the surface roughness (Togay et al. 2009). Thus, wood bulking due to esterification could be an important reason for the increased surface roughness.

CONCLUSIONS

1. Eastern cottonwood (*Populous deltoides*) can be propionylated without using any catalyst or solvent at common temperatures used for the acetylation of wood.
2. Chemical modification via acetic or propionic anhydride increases the surface roughness of wood significantly. The increase in the surface roughness was attributed to the bulking of wood due to modification.
3. Modification of wood via acetic or propionic anhydride reduces its surface quality, so that the surface quality decreased with increasing WPG. As was mentioned, the surface quality of wood is important in many of its applications. Therefore, for the applications, WPGs should be considered to provide sufficient improvement in the desired property of wood while providing minimal negative effect on its surface quality. In addition, the effect of sanding on the surface quality of anhydride modified wood can be investigated.

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