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Acylation of Hinoki Wood by Maleic Anhydride and the Dynamic Properties

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無水マレイン酸によるヒノキ材のアシル化とその動的物性

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SYNOPSIS

Acylation of hinoki wood (*Chamaecyparis obtusa* Sieb. et Zucc.) with specific gravity of 0.42 was made by mareic anhydride without catalist and solvent. The reaction condition was 80-160℃ for 2h in liquid phase. The mechanical properties of the acylated wood material were measured by flexural vibration method and the antiswelling efficiencies were also obtained. The lowering of the mechanical properties is inevitable due to the decreasing of the cohesive force of the wood substance by the reaction with maleic anhydride. However, the material has both practical dimensional stability and sufficient hygroscopicity.

INTRODUCTION

Acetylation is known as the most popular chemical modification of wood, and acetic anhydride is usually used in the reaction[1]. As a consequence of the reaction, acetylated wood and byprocuct, acetic acid yield. We have to consider the exsistence of the byproduct in the process of the reaction. In the liquid phase reaction the concentration of acetic anhydride is reduced by the production of the acetic acid. Furthermore, this makes the reuse of the reactant difficult without refinement.

In the vapor phase reaction the pressure of the reactant will also be redused and the rate of the reaction may be supressed as the reaction is advanced.

On the other hand, the acylation of wood by dibasic anhydride does not accompany any byproduct[2]. Especially, maleic anhydride and phthalic anhdride are usuful for the reactants[3]. The reaction will be accomplished without catalist by raising the reaction temperature.

In this report the modified wood will be prepared without catalist and solvent in the liquid phase and the dynamic mechanical properties will be measured to evaluate the performance in practical use.

EXPERIMENT

We used hinoki wood (*Chamaecyparis obtusa* Sieb. et Zucc.) with specific gravity

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of 0.42 as the specimen for the reaction and dynamic measurement. The shape of the specimen is a bar with rectangular cross section and the dimensions is 120mm (L) × 3mm (T) × 10mm (R) for flexural vibrational measurement. The specimens were dried in a vacuum dry oven at 50℃ for 24h. The weight and dimensions of the specimen under the completely dried condition were measured, and then they were put in the room with a constant temperature and humidity (20℃, 60% R. H.) for a long time enough to reach a constant moisture content. The dynamic Young's moduli (E') and the internal frictions ($\tan\delta$) of the specimens were obtained by the resonance frequencies and the resonance curves of the fundamantal mode for the flexural vibration with both edges free. After the measurement they were dried again for the following reaction.

The liquid phase acylation by an excess amount of maleic anhydride was made the separable flask which was kept at a constant reaction temperature (80−160℃) in the oil bath. A specimen was put into the flask and left for 2 h. The specimen was picked out from the flask and put into acetone to finish the reaction. Extraction with a Soxhlet apparatus was made by acetone for 12 h to remove the residual reagent in the specimen. After the substitution with water the specimen was dried completely and the weight was measured to obtain the weight percent gain (WPG) due to the reaction. It was put in the constant temperature−humidity room and the vibrational measurement was made. Dimensional change due to the water absorption was also observed to obtain the antiswelling efficiency (ASE)[4].

RESULTS AND DISCUSSION

Reaction formula of wood with maleic anhydride is

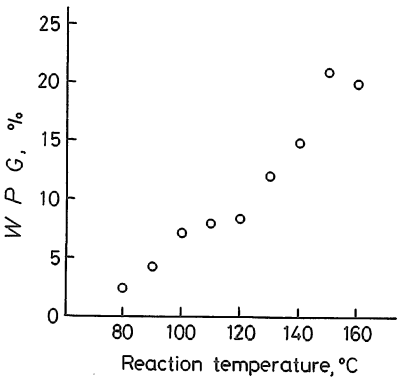


Fig. 1. Relationship between weight percent gain due to the acylation by maleic anhydride and reaction temperature for the reaction time of 2 h.

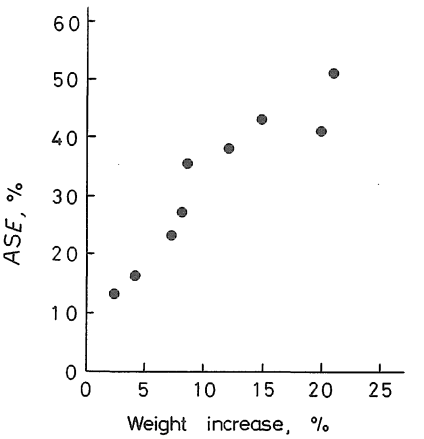
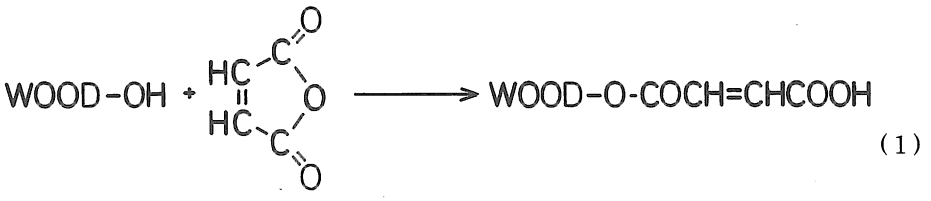
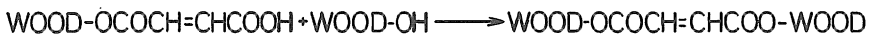


Fig. 2. Relationship between antiswelling efficiency and weight increase due to the acylation by maleic anhydride.



(1)

and the further reaction is described by the following expression.



(2)

This reaction is the formation of cross linkage in the wood polymer substance. It is expected that the mechanical property and dimensional stability of wood will be enhanced as a result of the cross linkage.

Relationship between *WPG* and reaction temperature is shown in Fig. 1 for the reaction time of 2h. Constant increase in the *WPG* is observed against the raising reaction temperature up to 150℃. It can be said that raising reaction temperature is effective to attain higher reaction rate or greater *WPG*, but above 150℃ coloration of the specimen is observed which may be attributed to the degradation of wood substance due to the high temperature in the presence of maleic anhydride as acid[3].

Fig. 2 shows the relationship between *ASE* and *WPG* for acylation with maleic anhydride. In the lower *WPG* resion the *ASE* value increases according to the raising *WPG*, In the higher *WPG* resion, however, the *ASE* value is at most 50% for the *WPG* of more than 20%. On the other hand, acetylation of wood attains the *ASE* value of more than 70% for that *WPG* value[5]. This comes from hydrophilicity of cardoxyl group which is produced as a result of the acylation. It is expected that the acylated wood possesses both hygroscopicity and pretty good dimensional stability

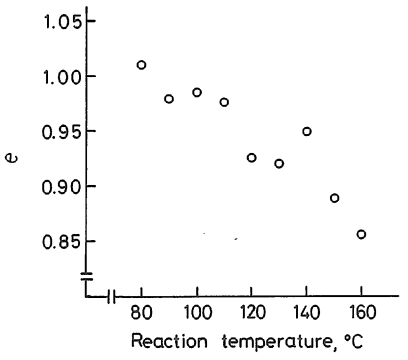


Fig. 3. Relative value of specific modulus against reaction temperature due to the acylation by maleic anhydride for 2 h.

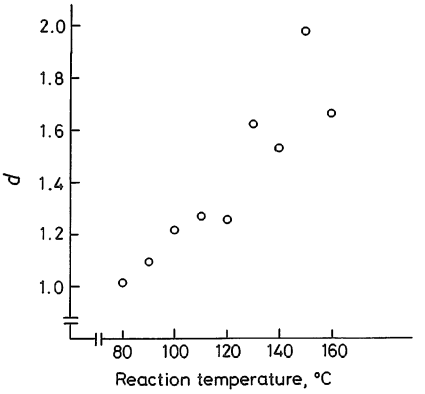


Fig. 4. Relative value of internal friction against reaction temperature due to the acylation by maleic anhydride for 2 h.

agaist absorbing moisture, and the material can adsorbe or desorbe the moisture in a room so as to avoid a drastic change of humidity when it is used for interior material.

To evaluate the change of the dynamic mechanical properties due to the chemical treatment relative values to ones before the treatment are adopted, namely

$e=(E'/\gamma)/(Eo'/\gamma o)$

$d=\tan\delta/\tan\delta$ o

where $/E'/\gamma$ and $Eo'/\gamma o$ are specific dynamic moduli after and before the acylation, and $\tan\delta$ and $\tan\delta$ o are the internal frictions after and before acylation.

Fig. 3 shows the relative value of specific modulus agaist the reaction temperature. The higher reaction temperature is set, the lower e value becomes. This may be mainly caused by the lowering of the cohesive force of the wood substance due to the acylation[6]. At higher reaction temperatures the cellulose crystalline may irreversiblly change[7] and this is considered to reduce the mechanical properties of the treated wood.

Fig. 4 shows the relationship between the relative value of internal friction and reaction temperature The value of d internal friction and reaction tempeature raising. It is reported that a negative corelationship exsists between the logalism of internal friction and the logalism of dynamic modulus[8]. In the present case the trend is also observed.

The lowering of the mechanical properties is inevitable due to the decreasing of the cohesive force of the wood substance in the case that wood is treated in the reaction system including maleic anhydride. The formation of the cross linkage due to the diester which is expected to enhance the mechanical properties can not be confirmed. However, the material has both practical dimensional stability and sufficient hygroscopicity.

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