Chemical Modification of Japanese Cedar with 2-Methacryloyloxyethyl Isocyanate*1

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2-메타크릴로일옥시메틸 이소시아네이트에 의한 삼나무재의 화학처리*1
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ABSTRACT

This study was carried out to introduce functional groups onto wood by reacting with 2-methacryloyloxyethyl isocyanate (MOI). The effects of the catalyst and the reaction conditions (temperature and time) on the treatment were investigated. The evidence of bonding between wood and MOI were examined by infrared (IR) spectroscopy. The change in surface characteristics of MOI treated wood was examined by water contact angle measurement and X-ray photoelectron spectroscopy (XPS). Wood reacted quickly with MOI in the presence of di-n-butyltin dilaurate catalyst. Especially, the increase in weight percent gain (WPG) with increasing in reaction time was remarkable at the reaction temperature of over 50°C. The IR spectrum of wood reacted with MOI showed a strong urethane absorption (1715 cm⁻¹), but no isocyanate (2235 cm⁻¹) absorption. It also showed a sharp olefinic C=C double bond absorption at 1635 cm⁻¹. This means that an introduced methacrylate group becomes the starting point of further graft copolymerization with another vinyl monomers. The wood modified with MOI showed a gradual increase in contact angle with increasing in WPG, which means that the hydrophilic wood surface become quite hydrophobic. Also, it was cleared that most parts of the wood surface were modified with MOI by XPS analysis.

Keywords: chemical modification of Japanese cedar, isocyanate, IR spectroscopy, contact angle, XPS

- 요 약 -

목재는 2-메타크릴로일옥시메틸 이소시아네이트(MOI)와 50~60°C에서 촉매 존재하에서 매우 쉽게 반응하였다. 적외선 분광분석을 통하여, 목재가 MOI와 스핀홀합(1715cm⁻¹)을 형성하였고 또한, 컬러핀구조의 탄소간 이중결합 (1635cm⁻¹)이 존재하고 있음을 밝혀졌다. 도입된 메타크릴산기는 다른 비닐모노머와의 그래프트공중합시 반응시키므로 작용하기도 한다. 또한 MOI 처리목재는, MOI와의 반응에 의해 전수성이던 목재의 표면이 소수화되어 접촉각이 증대되는 결과를 낳았다. X선광전자분광분석(XPS)의 결과, 목재의 표면부위의 대부분은 MOI에 의해 개질되었음을 밝혔다.

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INTRODUCTION

Chemical modification have been investigated extensively to improve the disadvantages of wood. Two methods of wood modification are under investigation: cross-linking of wood with cross-linking chemicals such as formaldehyde, and reaction of wood with reactive organic compounds including isocyanates, anhydrides, and epoxides. Isocyanates have been used as chemical reagents for modification of wood, because they react quickly with hydroxyl group of cell wall substances, yielding stable urethane bond, which is very stable to acid and base hydrolysis.

There are many researches on modification of wood using isocyanate. Clermont and Bender (1957) and Baird (1969) reacted woods with several isocyanates at vapor phase, and reported enhanced antiswelling efficiencies (ASE) of treated wood. White cedar reacted with diisocyanate with a pyridine catalyst, showed increased compressive strength and bending modulus, and 50% of ASE at 22% weight percent gain (WPG) (Wakita et al., 1977). Southern pine blocks reacted with methyl isocyanate at 120°C and 150 psi, without catalyst, showed high ASE (60 to 70%) at levels of 16 to 28% WPG (Rowell and Ellis, 1979). Treated wood above 35% WPG showed splitting, occurred in the tracheid walls, which resulted in the reduction of ASE. Treated wood of 20 to 25% WPG was found to be resistant to attack by *Gleophyllum trabeum*. Chen (1992) reacted loblolly pine with 1,6-diisocyanatohexane. At 28.5% WPG, the reacted wood had no weight loss by *Gleophyllum trabeum*. At 20.9 and 23.8% WPGs, the reacted wood had ASEs of 58 and 61%, respectively.

Chemical characteristics of modified wood has been studied by instrumental analysis. Infrared (IR) data has been used as evidence that a chemical has reacted in the cell wall and that it has bonded with the cell wall polymers. The proof of bonding between the isocyanate groups and the wood cell wall hydroxyl groups was shown in the IR spectra of isocyanate modified wood (Rowell, 1980; Chen, 1992). Several X-ray photoelectron spectroscopy (XPS) studies of wood and fiber have been reported (Dorris and Gray, 1978a, b; Young et al., 1982; Hon, 1984; Torr et al., 1996; Dawson, 1997). XPS has proved to be a powerful method for the surface analysis of wood.

This study was carried out to introduce functional groups onto wood by reacting with 2-methacryloyloxyethyl isocyanate (MOI). The effects of the catalyst and the reaction conditions (temperature and time) on the treatment were investigated. The evidence of bonding between wood and MOI were examined by Fourier transform infrared spectroscopy. The change in surface characteristics of MOI treated wood was examined by water contact angle measurement and X-ray photoelectron spectroscopy (XPS).

Materials and Methods

Chemical modification of wood with isocyanate

The sliced veneers of Japanese cedar (*Cryptomeria japonica*), 0.2 by 30 by 40 mm in tangential, radial, and longitudinal directions, were prepared. All specimens were extracted with methanol/benzene and then oven dried. 2-methacryloyloxyethyl isocyanate (MOI) was selected as a modifying agent and used without purification. Ten oven-dried veneers were reacted in a three-neck separable flask with MOI/dimethyl sulfoxide (DMSO) solution (10% v/v). A catalyst and inhibitor used was 0.2% (w/w) di-n-butyltin dilaurate (DBTDL) and 0.2% (w/w) 2,6-di-tert-butyl-4-methylphenol (DBMP), respectively. DMSO, DBTDL, and DBMP were pure grade and used without purification. Target WPGs of 10 to 40% were controlled by reaction temperature (30-60°C) and time (1-5 hours). The chemically modified samples were soaked in acetone for 24 hours and then washed. The washed samples were
dried at 50°C in a vacuum oven for 24 hours.

Measurement of contact angle
Static contact angles toward water were measured at 25°C and 65% RH with the sessile drop method, using a small droplet(4μl) of water and averaged for 6 readings on different locations of sample surface. Deionized water was used for the measurements.

Fourier transform infrared spectroscopy
A Perkin-Elmer Spectrum 2000 was employed for recording the spectra using the KBr pellet technique. The resolution of the spectrometer is 1 cm⁻¹ and the spectra were taken with 16 scans and a KBr pellet as background. KBr pellets were prepared with a sample concentration of 1%.

X-ray photoelectron spectroscopy
A spectrometer Shimadzu ESCA-850 was employed to carry out the XPS measurements of the treated woods using MgKα x-ray source at 7 kV. The samples were analyzed for the C1s, O1s, and N1s peaks. The ratio of oxygen atoms to carbon atoms and the ratio of nitrogen atoms to carbon atoms were calculated by peak area ratios.

Results and Discussion

Reaction behavior
The effects of reaction conditions and of catalyst on the reaction were investigated.

As shown in Fig. 1, the wood reacted quickly with MOI in the presence of catalyst. Generally, the WPG increased with the increase in the reaction temperature and time. Especially, the increase in WPG with increasing in reaction time was remarkable at the reaction over 50°C. On the other hand, the reaction of wood with MOI without catalyst showed much lower WPG compared with that with catalyst.

Proof of bonding between wood and MOI
Bonding between wood and MOI was evidenced by the characteristic infrared absorptions of the modified wood as shown in Fig. 2.

The infrared spectrum for unmodified wood in the region of 1730 cm⁻¹ showed a weak carbonyl stretching vibration compared with a strong absorption near 1630 cm⁻¹. The absorption at 1730 cm⁻¹ is attributed to C=O stretching vibration of acetyl and carboxyl groups of hemicelluloses, and broad absorption near 1630 cm⁻¹ is attributed to H-O-H deformation vibration(1628 cm⁻¹) of strongly adsorbed water and C=O stretching vibration(1653 cm⁻¹) of lignin and aromatic skeletal vibration(1608 cm⁻¹) of lignin. The absorption at 2900 cm⁻¹ is attributed to C-H stretching vibration of methylene groups.

The infrared spectrum of wood reacted with MOI showed a strong urethane(carbamate)

Fig. 2. Infrared spectra of Japanese cedar modified with MOI.
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absorption(1715 cm$^{-1}$) but no isocyanate(2235 cm$^{-1}$) absorption. This indicates that the only urethane bonding between wood and MOI takes place and no unreacted isocyanate groups remain in the samples. It also showed a sharp olefinic C=C double bond absorption at 1635 cm$^{-1}$, which reveals that introduced methacrylate groups are not polymerized. The infrared absorption at 1715 cm$^{-1}$ in modified wood is attributed to carbonyl stretching vibration of urethane. The intensity of this absorption became very strong when the WPG in the modified wood increased from 13.7% to 37.1%. There was also an increase in the absorption bands as the WPG increased: C=C stretching at 1635 cm$^{-1}$, N–H deformation at 1538 cm$^{-1}$, C–N stretching at 1299 cm$^{-1}$, and N–H deformation at 773 cm$^{-1}$.

The relative absorbance of the carbonyl peak of sample at 1715 cm$^{-1}$ against the methylene peak at 2900 cm$^{-1}$ was investigated (Fig. 3). The absorbance ratio increased with the increase in WPG. This result suggests that high linear relationship between urethane absorption and WPG exists.

The wood and MOI reacts quickly each other and forms urethane bonds[Eq. (1)]. In addition, an introduced methacrylate group becomes the starting point of further graft copolymerization with another vinyl monomers.

\[ \text{CH}_3 \]
\[ \text{H}_2\text{C}-\text{C}={\text{O}}-\text{CH}_2-\text{CH}_2\text{N}=\text{C}=\text{O} \]
\[ \text{O} \]
\[ \text{CH}_3 \]
\[ \rightarrow \text{Wood-O-C-NH-CH}_2-\text{CH}_2-\text{O-C-C}=\text{CH}_2 \ldots \ldots \ldots (1) \]

Surface properties of isocyanate modified wood

Further evidence supporting the occurrence of reaction between wood and MOI can be obtained by studying the change of surface characteristics after reaction, since some of the surface properties should be detectably changed if the reaction really takes place. One of the easiest means of examining the surface property change is to measure the water contact angle of the material concerned(Fig. 4).

As expected, the contact angle method was accurate enough to confirm the reaction between wood and MOI. Moreover, it was known that the hydrophilic wood surface became quite hydrophobic upon reacting with MOI. The wood modified with MOI showed a gradual increase in contact angle with increasing in WPG and a levelling-off values over WPG of 25%.

The chemical analysis of wood surface was carried out by XPS. The result of XPS on the wood surface is given in Fig. 5. As can be seen in this figure, the C$_1$s spectrum of unmodified wood is made up of three components with

Fig. 3. Adsorption ratios of the carbonyl peak at 1715 cm$^{-1}$ to the methylene peak at 2900 cm$^{-1}$ for the Japanese cedar modified with MOI.

Fig. 4. Contact angles of Japanese cedar modified with MOI.
assignments of C1 peak as carbon bonded only to carbon and hydrogen, C2 peak as C=O bonds, and C3 peak as C=O or O-C=O bonds (Young et al. 1982, Hon 1984). On the other hand, the XPS pattern of isocyanate modified wood surface showed intensified C1 and C3 peaks of C1s, which resulted from the structure of reacted isocyanate.

The XPS pattern of isocyanate modified wood showed clear N1s peak assigned to urethane bond, and new oxygen shoulder assigned to C=O bond of urethane (Clark and Harrison 1981), contrary to the untreated wood showing only single oxygen peak assigned as C=O bond.

The elemental analyses were carried out by XPS on the surfaces of modified woods, and the results of those are given in Fig. 6. It is clear that the ratios of the nitrogen atoms to carbon atoms(N/C) ratio of modified wood becomes higher and the ratio of oxygen atoms to carbon atoms(O/C) of modified wood becomes lower by addition of MOI. The theoretically calculated maximum value of N/C ratio of cellulose (degree of substitution = 3) modified with MOI is 0.111. However, the wood surfaces modified with MOI showed the high values of N/C ratios over 0.08 as shown in Fig. 6. This reaveals that most parts of the wood surface were modified with MOI. This is another evidence of highly water-repellent property of modified surface as shown in Fig. 4.

LITERATURE CITED

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