

Synthesis and Properties of Multihydroxy Soybean Oil from Soybean Oil and Polymeric Methylene-Diphenyl-4,4'-Diisocyanate/Multihydroxy Soybean Oil Polyurethane Adhesive to Wood

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ABSTRACT: The reactive multihydroxy soybean oil (MHSBO) was synthesized from epoxidized soybean oil (ESBO). The ESBO was reacted with ethylene glycol to obtain MHSBO having high functionality. This study investigated a feasibility to prepare wood adhesive through the reaction of polymeric methylene-diphenyl-4,4'-diisocyanate (pMDI) with MHSBO. Different polyurethane adhesives were prepared with a variety of equivalent mole ratios (eq. mole ratios) of MHSBO to pMDI. The chemical reactions of adhesives were analyzed using ¹H NMR and Fourier transform infrared (FTIR), and their thermal studies were investigated by DSC and TGA. The MHSBO/pMDI resins (3 : 1 and 2 : 1 eq. mole ratios) showed endothermic peaks, whereas the MHSBO/pMDI resins (1 : 2 and 1 : 3 eq. mole

ratios) showed exothermic peaks. The best adhesion strength was found when plywood was bonded with the adhesive of a eq. mole ratio of 2 : 1 (MHSBO : pMDI). These results indicated that the bond strength was not related to the reactivity obtained from the FTIR spectra. But it was explained that the adhesion strength increased as the residual —NCO groups in the adhesive reacted with the hydroxy groups of wood during the manufacturing of plywood. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 764–769, 2011

Key words: polyurethane; polyol; adhesive; soybean oil; polymeric MDI

INTRODUCTION

Polyurethane resins have been being widely used in versatile application areas due to their rapid and easy processing and to excellent chemical and physical properties. These adhesives have high-functional performance and could be used to bind high-moisture content woods.^{1–4} And these adhesives also show superior adhesion performance between wood and nonwood materials. Therefore, this adhesive is being used for structural applications of wood-based composites. Especially, isocyanate-based polyurethane resins were regarded as nonformaldehyde releasing resin.^{5–7} But, high cost is a limiting factor of using isocyanate-based polyurethane resins. Particularly, the high price of polyol is a dominant parameter in their uses. Therefore, an alternative of

replacing polyol is to use cooking oil from vegetable resources that is natural organic compound.⁵ The mechanical properties and morphological structure of polyurethane depend mainly on the polyol structure, molar mass, and its functionality on the nature of the polyisocyanates. Recently, some works on synthesizing polyol with reactive groups have appeared in the literature.^{8,9}

Other efforts have been made to improve adhesion by using modified polyols, as demonstrated in a number of papers.^{8,9} Somani et al.¹⁰ used cater oil to produce a PU resin for wood. Kansara et al.¹⁰ refined vegetable oil into glycerol and fatty acids and then reacted it with isocyanate to evaluate its bond strength of PB. Petrovic et al.¹¹ mixed soybean oil with Br—, Cl—, CH₃O—, and H— to create polyols and used them to produce a PU resin. Pechar et al.⁹ reported PU foam from palm polyol obtained from kernel oil and glycol. Wilkes et al.⁹ used soy-based polyol, which was prepared via oxirane ring-opening reaction of epoxidized soy bean oil with methanol to make PU foam.

This research was conducted to evaluate the possibility of using MHSBO/pMDI resin, obtained from

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soybean oil, as a wood adhesive. MHSBO was reacted with pMDI resin at different eq. mole ratios to prepare adhesives. This study tried to compare adhesive performance and to find optimum eq. mole ratios of MHSBO and pMDI using Fourier transform infrared (FTIR) spectroscopy, DSC, and TGA. These adhesives were used to investigate adhesive properties and bond performance in wood application.

EXPERIMENTAL

Materials

HBF₄ (tetrafluoroboric acid) and epoxidized soybean oil (ESBO) were purchased from Aldrich Chemical Co. and Scientific Polymer Products, respectively. Common reagents such as anhydrous sodium sulfate, ethylene glycol, isopropanol, ammonia (30%), and ESBO were used without further purification. The pMDI with molecular weights ranging from 300 to 400, a viscosity of 192 mPa s (at 23°C), a functionality of 2.7, and an equivalence of 133.3, was a gift from a local urethane foam board manufacturer (BASF Co).

Synthesis of mutihydroxy soybean oil

ESBO (200 g) was slowly added to a stirred mixture of ethylene glycol (200 mL), water (20 mL), isopropanol (500 mL), and 8 g of 48% HBF₄ (aq). After reaching a constant temperature of 50°C for 1 h, ammonia (30% in water) was being added drop-wise to quench the reaction, until the mixture attained a neutral pH. The mixture was extracted three times with a mixture solution of water and hexane (5 : 5). The hexane layer was then placed under vacuum to remove the solvents and to get viscous yellow liquid with a mass of 150 g, 75% yield; ¹H NMR (CDCl₃) δ 0.89 (t, -CH₃), δ 1.16–1.61 (m, CH₂), δ 2.32 (t, CH₂-COO-), δ 3.68 (m, -OH), δ 4.12 (m, COO-CH₂), δ 4.34 (m, COO-CH), δ 5.31–5.53 (CH=CH, residue), δ 7.18 (s, CDCl₃), δ 7.25 (m, toluene). FTIR (KBr, ν_{max} cm⁻¹); 3500–3200 (-OH), 2930 (O-CH₂, sp³), and 1745 (C=O).

Plywood preparation

To determine the most effective mixing ratio in the production of adhesive with MHSBO and pMDI, each mixture was used to fabricate plywood and evaluated the bonding performance. Radiata Pine (*Pinus radiata* D. Don., Specific Gravity 0.48) with a moisture content of 1–2% was used for the production of plywood with thicknesses of 1.5 mm for the face and 2.5 mm for the core. Each veneer, obtained by rotary-cut, was cut into 250 mm × 250 mm pieces to construct a three-plywood with veneers of 1.5 mm

for face, 2.5 mm for core, and 1.5 mm for face. The grain direction of the face and core veneers is perpendicular, and the face veneers are parallel. Each adhesive mixture was applied on one side of the veneer with 150 g/m² and thermal-pressed at 20 s/mm with 10 kgf at 150°C. The samples were prepared with 3 : 1, 2 : 1, 1 : 1, 1 : 2, and 1 : 3 eq. mole ratios of MHSBO to pMDI. The final plywood's bond strength was measured with respect to a standard. As the control 1, polyol/pMDI (polyol : polyoxyalkyleneglycol, *M_w* 2,000, functionality 2, SungChang Co.) adhesive was prepared by mixing in a mole ratio of 1 : 4. The mixed adhesive had solid content of 53.8%, pH of 9.1, and viscosity of 150 mPa s at 25°C. Phenol/formaldehyde (PF, SungChang Co.) resin adhesive was also used as a control 2, which is a commercial product with solid content of 43%, pH of 10.92, and viscosity of 284 mPa s at 25°C. PF was used 40 s/mm because of the characteristic of slow reaction rate. This work was followed KS F 3101 (2006), which is Korea Standard for ordinary plywood.

Measurements

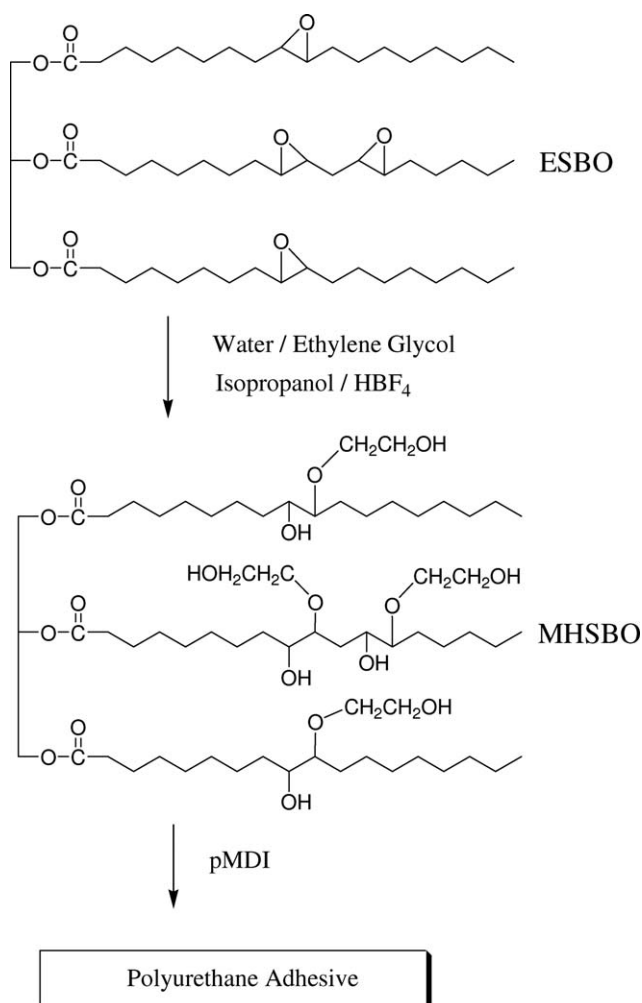
FTIR spectroscopy was used to confirm the presence of the functional groups on the polymers. FTIR spectra were recorded as KBr pellets using a MIDAC FTIR spectrometer at a resolution set at 4 cm⁻¹ with a spectral range of 400–4000 cm⁻¹; ¹H NMR spectra in CDCl₃ (Chloroform-d) on a Bruker DRX (400 MHz) spectrometer using TMS as internal standard. Differential scanning calorimetry (DSC) was conducted using a Perkin-Elmer DSC7, calibrated with indium, in a temperature range of 30–350°C under nitrogen atmosphere at a heating rate of 10°C/min. The second-run DSC studies were performed with following procedure: initial heating up to 250°C, quenching, and heating up to 300°C; thermogravimetric analysis (TGA) in Perkin-Elmer TGA7 at a heating rate of 10°C/min under a gas flow rate of 50 mL/min was reported both maximum and onset degradation temperature. The measurement of tensile strength of plywoods was performed in three different conditions, such as dry, wet, and cyclic boil condition in a universal test machine (H 50K-Ss, HOUNSFIELD, UK) at a strain rate of 2 mm/min. Tensile shear adhesive test was carried out by KS F 3101 B type, which is useful for the lower than 1.6 mm thickness of the face veneers. Samples of dry test were measured without any additional conditions. Samples of wet test were soaked in water at 60°C for 3 h, washed with normal water, and tested under wet condition. Samples of cyclic boil test were prepared by keeping them soaking in boiled water for 4 h, then drying at 60°C for 24 h, again treating in boiled water for 4 h, and washing with normal water and then tested under wet condition.

RESULTS AND DISCUSSION

Synthesis of MHSBO

The introduction of multihydroxy groups into vegetable oil provides a highly reactive precursor for reaction with pMDI. MHSBO was obtained by ring opening reaction of ESBO with ethylene glycol as shown in Scheme 1. This compound is stable materials that can be stored for extended periods of time. This reaction is an especially attractive route for the preparation of MHSBO from ESBO bearing reactive functional groups for several reasons, such as MHSBO bearing ester groups are stable and readily available, the reaction with pMDI leads directly to the formation of thermally and hydrolytically stable urethane bonds, the formed urethane adhesives provide flexible structure with the help of aliphatic long chains and typically proceed to high conversions without the formation of by-products.

Figure 1 depicts the ^1H NMR spectra of soy bean oil, ESBO, and MHSBO. The peaks of CH—O of ester group and the protons of double bonds of soybean oil were characteristically appeared at δ 5.27–5.45 and δ



Scheme 1 Synthesis of MHSBO and polyurethanes.

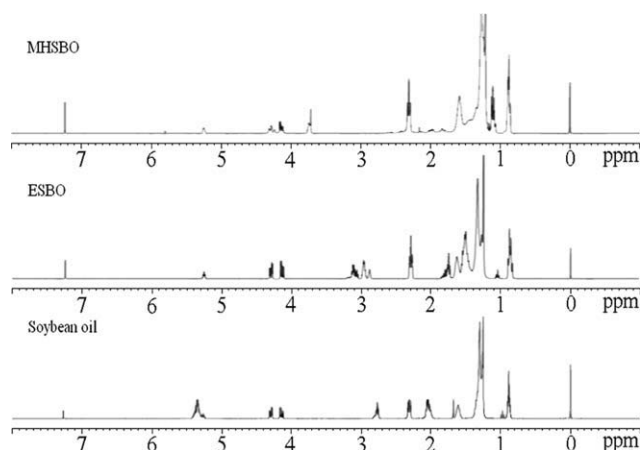


Figure 1 ^1H NMR spectra of soy bean oil, ESBO, and MHSBO.

5.25, respectively. In ^1H NMR spectra of MHSBO and ESBO, the bands for the protons of double bond disappeared, whereas the peaks of CH—O of ester group still appeared at δ 5.25. The hydroxy peaks were assigned at δ 3.72, and the bands of epoxy CH groups of ESBO within δ 2.86–3.13 disappeared. The bands at δ 4.1–4.34 ppm corresponding to the protons of CH_2 —O of ester groups appeared as same as those of ESBO. The ^1H NMR spectrum is complicated by the peaks in the area of aliphatic groups as expected. Figure 2 shows FTIR spectra and presents characteristic peaks for the ESBO and MHSBO. The absorption bands of epoxidized vegetable oil appeared within 1720 – 1700 cm^{-1} for $\text{C}=\text{O}$, at 1150 cm^{-1} for epoxy, and within 3000 – 2800 cm^{-1} for —CH— (sp^3 mixture), and the CH stretching absorption band, at 3070 cm^{-1} (sp^2 mixture) of $\text{C}=\text{C}$ bonds disappeared. The hydroxy absorption band of MHSBO appeared broadly within 3500 – 3200 cm^{-1} and disappeared epoxy band at 1150 cm^{-1} .

FTIR spectra of UF-CWO/pMDI prepolymer resin

To examine the chemical reaction between MHSBO and pMDI, different amounts of the MHSBO/pMDI

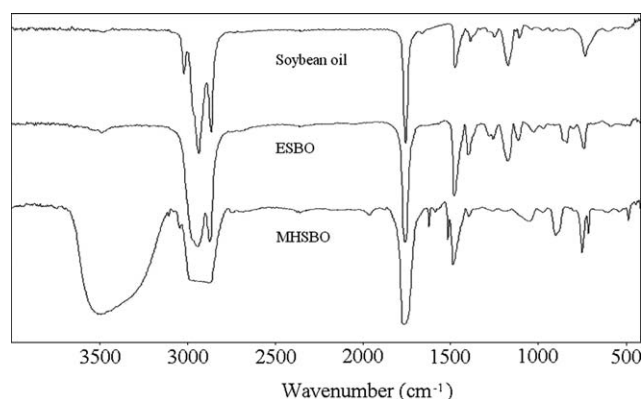


Figure 2 FTIR spectra of soy bean oil, ESBO, and MHSBO.

TABLE I
Tensile Strengths of MHSBO/pMDI Resins, Control 1, and Control 2: Dry Test, Wet Test, and Boiling Wet Test

Resin type	Tensile strength (kgf/cm ²)		
	Dry test	Wet test	Cyclic boil test
3 : 1	34.8	16.8	15.5
2 : 1	36.5	21.3	21.4
1.5 : 1	38.9	27.5	25.6
1 : 1	38.3	28.1	24.1
1 : 2	42.3	31.0	28.7
1 : 3	26.2	26.3	21.8
Control 1	29.2	17.7	18.0
Control 2	30.8	14.2	17.3

(3 : 1, 2 : 1, 1 : 1, 1 : 2, and 1 : 3 eq. mole ratios) were mixed and then used for Fourier transform infrared (FTIR) scans. The mole ratios were calculated based on the equivalent mole ratio of the hydroxy and isocyanate groups in MHSBO/pMDI (Table I). One mole of MHSBO is eight equivalent moles, because MHSBO has 8 hydroxy groups, and 1 mol of pMDI has 2.7 equivalent moles of isocyanate. Figure 3 shows different intensities of absorption bands of hydroxy and -NCO groups, which are generally presented at 3500 and 2250 cm^{-1} , respectively. The hydroxy and -NCO groups of MHSBO were characterized within 3200–3600 cm^{-1} and at 2150 cm^{-1} , respectively. As pMDI contents increased, the peak intensity of hydroxy groups decreased and that of -NCO groups increased. An N-H absorption band of urethane bond, which is characteristic of primary amine, appeared in MHSBO/pMDI (1 : 1, 1 : 2, and 1 : 3 mol ratios) resin. The ester carbonyl peak of MHSBO/pMDI resins was found at 1760 cm^{-1} , whereas urethane carbonyl peaks appeared strongly at 1870 cm^{-1} as the contents of pMDI increased. The absorption bands at 1,500 cm^{-1} assigned to the mixture of C=N and carbonyl stretching of urethane and amide. The bands within 750–1150 cm^{-1} due to the C-H absorption band of $\text{-CH}_2\text{-}$ and -CH_3 , C-O , and C-N absorption bands were presented. The adequate amount of hydroxy groups could play a role in controlling reactivity and properties of MHSBO/pMDI resin depending on various ratio conditions.

Thermal behaviors of MHSBO/pMDI resin

The thermal behavior of the polymers was investigated by DSC preparing the samples at room temperature and measuring at the ambient temperature from 25 to 300°C. Figure 4 shows DSC thermograms of MHSBO/pMDI resin with different MHSBO/pMDI contents to compare their curing behaviors. Thermal behaviors showed exothermic reaction at the range of 160–200°C as pMDI content increased.

The MHSBO/pMDI resins (3 : 1 and 2 : 1 eq. mole ratios) showed relatively broad exothermic peaks at higher temperature, whereas the MHSBO/pMDI resins (1 : 2 and 1 : 3 eq. mole ratios) showed exothermic peaks at lower temperature. The different thermal behaviors would make a prediction of the pMDI content as the higher content of NCO provides the faster reaction. At an elevated temperature, the -NCO groups reacted strongly with hydroxy groups to form crosslinked polymer. The second-run DSC studies were presented in Figure 5. MHSBO/pMDI resins were fairly so strong cross-linked polymers that they did not show any thermal behaviors.

Thermo-oxidative stability of MHSBO/pMDI resins was studied using TGA with results shown in Figure 6. Most of the polymers showed good thermal stability at high temperature under nitrogen atmosphere. The initial weight loss around 270–330°C is attributed to functional groups such as NCO and hydroxy release from the crosslinked polymer. The second weight loss over 350°C was assigned to the breakaway of urethane groups, which are linkages of polymer chains. The third weight loss over 400°C was assigned to the degradation of the polymer main

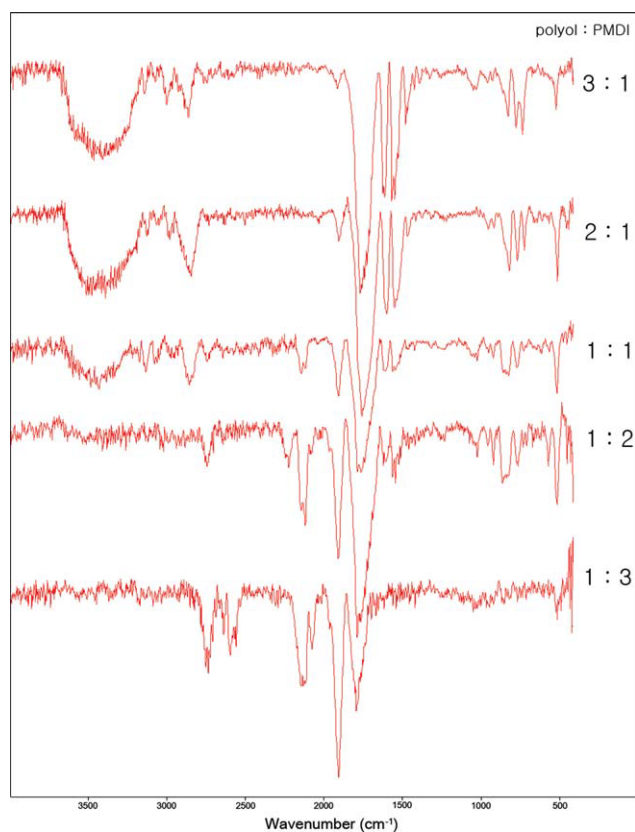


Figure 3 FTIR spectra of MHSBO/pMDI resins as function of different mixing ratio (3 : 1, 2 : 1, 1 : 1, 1 : 2, and 1 : 3 mol ratios). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

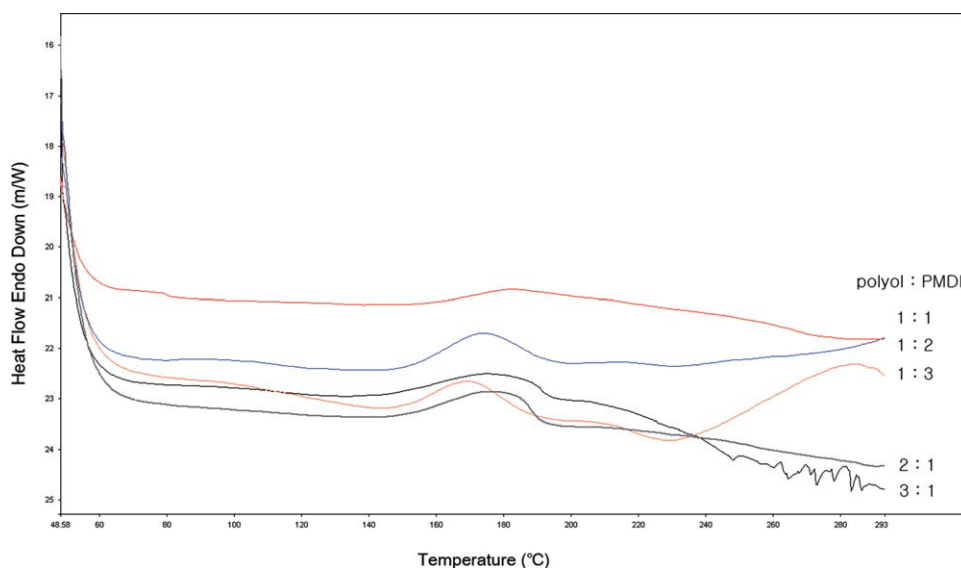


Figure 4 DSC curves of MHSBO/pMDI resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chain. The initial mass loss of the MHSBO/pMDI (1 : 3 mol ratios) resin was observed lower than those of others because of high content of unreacted —NCO residue groups, while the initial mass loss of the MHSBO/pMDI (3 : 1 eq. mole ratios) resin was observed higher than those of others.

Adhesive bond strength

As shown in Figure 7, the bond strength was the best for the eq. mole ratios of 1 : 2 of MHSBO/pMDI resin. This result made us believe that a slightly excess of —NCO groups in the MHSBO/pMDI resin of 1 : 2 eq. mole ratio was attributed to improve bond strength rather than that of 1 : 1 eq. mole ratio and

other conditions. Sonnenschein reported that the generation of polyurea compounds by the reaction of —NCO group with —OH group contributes to improve bond strength.¹² In addition, Simon et al.¹³ reported that there is a trend of increasing the bond strength with increasing the quantity of the pMDI. And the performance of adhesives prepared was superior to that of the control 1 and 2 in dry test. The results of wet state test of plywood bonded with different equivalent mole ratios of pMDI resin were similar behaviors as in dry condition. The bond strength in wet test was increased up to the eq. mole ratio of 1 : 2 and then decreased. The adhesive with the eq. mole ratios of 2 : 1 showed the best adhesion strength in wet test. The tensile shear strength of

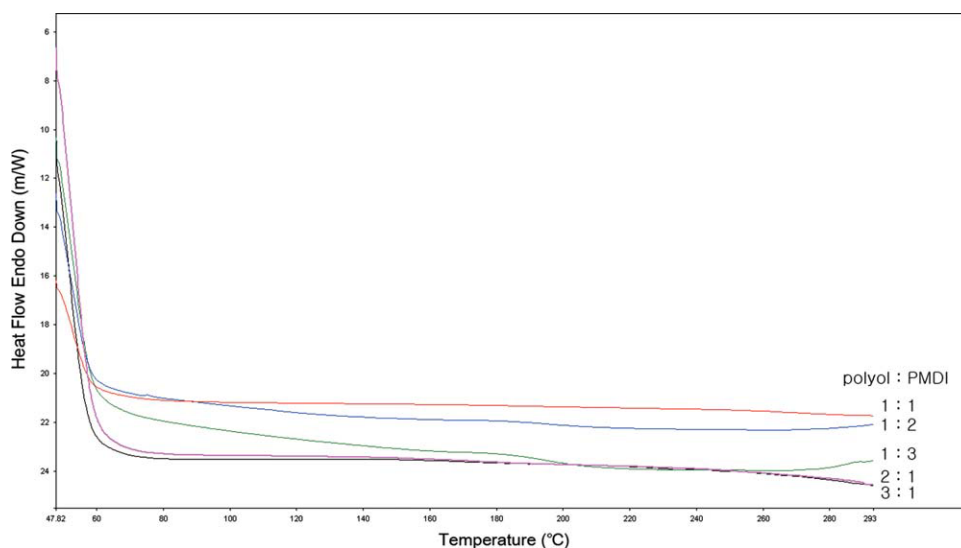


Figure 5 Two-run DSC curves of MHSBO/pMDI resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

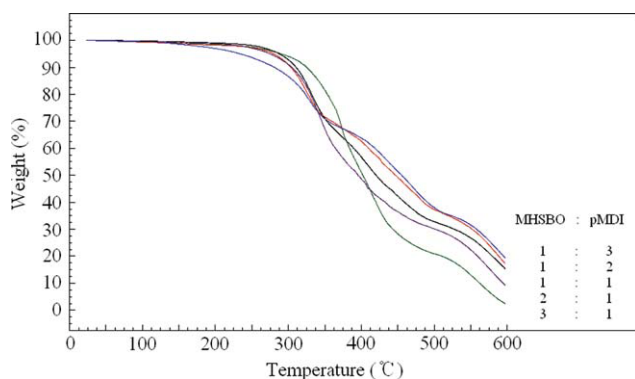


Figure 6 TGA curves of MHSBO/pMDI resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

plywood after the accelerated weathering treatment was tested. The result showed bond strength greater than the required one of the Korea Standard (7 kgf/cm² for board-leaved trees and 6 kgf/cm² for needle-leaved trees) at the eq. mole ratio of 1 : 2. This might be attributed to the reaction between the residual —NCO group and water in wet test condition. Park et al.¹⁴ reported that urea bond arising from the reaction of —NCO group with water affected the chemical behavior of polyurethane film using FTIR spectroscopy. These results could be attributed to a greater number of —NCO groups in the MHSBO/pMDI resin, which created more bonds between the unreacted —NCO group and the hydroxy group of cellulose in plywood and changed it into urea bonds, biuret bonds, or urethane bonds under the heat of hot-pressing, thereby enhancing its bonding properties.^{15,16} Modified MHSBO has characteristics of effective reactivity and wet stability, and the MHSBO/pMDI resin was showed as an excellent candidate of adhesive applications.

CONCLUSIONS

This study was an attempt to investigate a feasibility of developing wood adhesives using MHSBO, modified from vegetable oil, and pMDI. Adhesive resins depending on different eq. mole ratios of MHSBO and pMDI were chosen to find an optimum condition using bonding strength and chemical structure analysis with FTIR spectroscopy and to investigate thermal curing behavior using DSC and TGA. The MHSBO/pMDI resins (3 : 1 and 2 : 1 eq. mole ratios) showed relatively sharp endothermic peaks, whereas the MHSBO/pMDI resins (1 : 2 and 1 : 3 eq. mole ratios) showed broad exothermic peaks. After heating up to 250°C MHSBO/pMDI resins (3 : 1 and 2 : 1 eq. mole ratios) showed glass

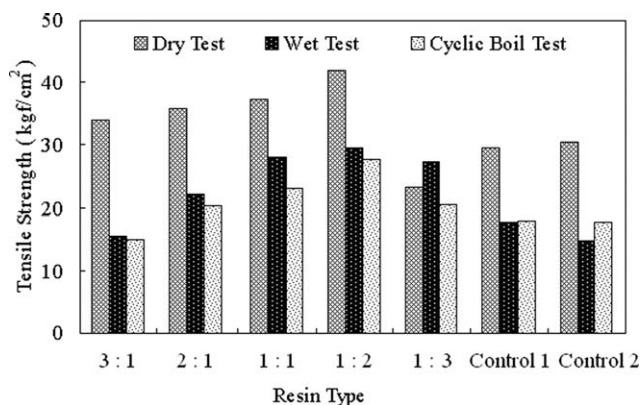


Figure 7 Tensile strengths of MHSBO/pMDI resins, control 1 and control 2.

transition temperature, which means amorphous region would be existed in polymer networks. Bond strength was the best at the eq. mole ratios of 1 : 2 of MHSBO/pMDI resins. These results indicated that the bonding strength was not related to eq. mole ratio of 1 : 1. Rather, the bonding strength increased as the residual —NCO of adhesives reacted upon with the —OH groups of cellulose in plywood.

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