

Synthesis of Polyurethane Resins and Its Improvement on Dimensional Stability and Finishing Performances of Medium- and Small-Diameter Softwoods

Kun-Tsung Lu, Shih-Ling Lin

Department of Forestry, National Chung Hsing University, Taichung 402, Taiwan

Received 12 April 2007; accepted 18 July 2007

DOI 10.1002/app.27169

Published online 4 February 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This study analyzed the effects of polyurethane (PU) resin treatments on surface homogeneity, dimensional stability, and finishing performances of medium- and small-diameter softwoods produced in Taiwan. Two-pack PU resins were prepared by combining short castor oil-modified alkyd resin serving as a polyol with polymeric 4,4'-diphenylmethane diisocyanate (PMDI) serving as a hardener, by the molar ratio of NCO/OH+COOH of 1.2. Four types of short oil-modified alkyd resins with different polyhydric alcohols (glycerin and pentaerythritol) and polybasic acids (phthalic anhydride and isophthalic acid) were synthesized. Three kinds of medium- and small-diameter softwoods, including China fir, Taiwanina, and Japanese fir with a diameter of 10–15 cm were obtained from Hui-Sun Forest Station, Taiwan. The wood coating of nitrocellulose (NC) lacquer including sanding sealer and top

clear was used. Results show that the surface hardness, homogeneity, moisture excluding efficiency, and antiswelling efficiency of woods were enhanced by PU resin treatments. Among all the PU resins, the isophthalic acid and pentaerythritol-containing PU resin (IPA-P-MDI) achieved the best improved efficiency on dimensional stability of woods. Results of two types of finishing procedure, i.e. NC lacquer sanding sealer plus top clear and top clear only, applied onto the PU-treated woods revealed that the hardness, adhesion, and durability of NC lacquer films on the PU-treated wood were superior to those of untreated one, especially for top clear finishing alone. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2029–2036, 2008

Key words: coatings; dimensional stability; medium- and small-diameter softwood; polyurethanes; resins

INTRODUCTION

Timber is an excellent and environment-friendly building material that lives up to the demands of people in the modern world. For making high-class furniture, timber is the first-rate material that can hardly be replaced by other materials. The demand for timber and its significance to human beings remain great. Additionally, global timber consumption is forecasted to grow at an annual rate of 1.5%.¹ Therefore, the timber demand is full of bright prospects. Correspondingly, the control on timber export has become more rigid in most timber exporters of the world. The domestic timber yield in Taiwan merely accounts for 0.6–0.7% of its timber consumption; hence, most of the timber raw materials required is imported. In view of this, relevant policies shall be formulated to raise the self-sufficiency of domestic timber, such as enlarging the planting area and increasing the utilization of medium- and small-diameter woods, which is a essential

for the sustainable development of forestry industry in Taiwan.

Medium- and small-diameter woods refer to trees which are small in diameter and the age of forest is not old enough to reach maturity. They are usually of low mechanical strength and the annual ring is comparatively wide but not obvious. They are small in specific gravity and light in weight. They tend to warp after being dried. Owing to the low material quality and the high proportion of juvenile wood, they are more heterogeneous than the mature materials in terms of quality. Thus, they tend to swell or shrink as a result of absorption or desorption of moisture. In addition, they easily become discolored and deteriorate.^{2–4} Since its low lumbering rate reduces the possibility of being made into useful large board, the application of medium- and small-diameter woods is quite restricted. On most occasions, they are only used for making boxes or serve as the brackets or pit prop in the building or industrial raw materials. Generally speaking, it is of low use value. Therefore, it is necessary to expand the application and increase the economic value of the heterogeneous medium- and small-diameter woods by pretreatment to improve their dimensional stability and turn them into homogeneous industrial materials for furniture making.

Correspondence to: K.-T. Lu (lukt@nchu.edu.tw).

Contract grant sponsor: National Science Council; contract grant number: NSC 93-2313-B-005.

In view of the rapid growth of softwood, a great deal of forestation performed and enjoyed considerably abundant amount of growing stock in softwoods such as *Cunninghamia lanceolata* (China fir), *Taiwania cryptomerioides* (Taiwania), and *Cryptomeria japonica* (Japanese cedar) in Taiwan. However, they have not been properly utilized. Studies have been conducted on the treatment of softwoods with emphasis on chemical modification utilizing chemical agents to react with hydroxyl group of wood for improving their dimensional stability. For instance, Liu et al.⁵ used acrylonitrile, *n*-butyl chloride, and propylene oxide to etherify Taiwania, and Chang et al.^{6,7} used anhydrides to esterify and acylate China fir. Their results demonstrated that the etherified, esterified, and acylated woods all possessed enhanced dimensional stability. In addition, Chang et al.⁸ used hot ironing treatment to densify the China fir surface. Rowell and Ellis^{9,10} also impregnated Southern pine with methyl isocyanate to improve its dimensional stability. Although these chemical modifications of wood could obtain special performances, the treatment procedure is complicated and it runs the risk of damaging wood texture. In this study, we attempt to synthesize high-performance polyurethane (PU) resins and apply them onto the surfaces of medium- and small-diameter softwoods at room temperature and pressure. It is hoped that through the simple treatment, the PU resins on wood surface can be hardened into a film so as to enhance both the surface homogeneity and dimensional stability of medium- and small-diameter woods.

PU resin designates a polymer wherein the repeating unit is a urethane linkage ($-\text{NHCOO}-$). The synthesis of such polymers is performed by reacting with di and polyfunctional hydroxyl compounds (polyols) with di or polyisocyanates through addition polymerization. PU resins have found extensive applications in many industries mainly because they possess excellent adhesion, abrasion resistance, chemical resistance, a wide range of mechanical strength, and very low-temperature cure.^{11,12} Two-pack PU resin combines one package of an isocyanate-terminated adduct or polymer with another package of hydroxyl-containing polyols at a certain NCO/OH molar ratio, in accordance with specially designed properties. The polyols consist of low to medium molecular weight prepolymers containing an alkyd, polyester, epoxy, or castor oil backbone.

In a number of resins serving as polyols of PU, oil-modified alkyd resins which comprise basic ingredients of polyhydric alcohols, polybasic acids, and oils are quite economical and show excellent performance. Additionally, they are to a greater extent biologically degradable polymers because of the oil and glycerin constituents.¹³ The modification

to the proportion between vegetable oil, polyhydric alcohol, and polybasic acid can increase the content of hydroxyl in oil-modified alkyd resins. It can therefore be used as a polyol of two-pack PU resins. Additionally, the precise combination of the ingredients used, together with the careful control of the reaction, influences the final properties of the alkyd produced.

In our previous reports,^{14–16} blown castor oil, phthalic anhydride, and glycerin were used for synthesizing polyols including short, medium, and long castor oil-modified alkyd resins. These resins and four kinds of polyisocyanates including polymeric toluene diisocyanate (PTDI), polymeric 4,4'-diphenylmethane diisocyanate (PMDI), polymeric isophorone diisocyanate (PIPDI), and polymeric hexamethylene diisocyanate (PHDI) were employed to formulate two-pack PU resins, respectively, by the molar ratio of $\text{NCO}/(\text{OH}+\text{COOH}) = 1.2$. The prepared PU resins were applied to the surfaces of medium- and small-diameter softwoods such as China fir, Taiwania, and Japanese cedar to analyze the influence of PU resin treatment on the surface homogeneity and dimensional stability of these woods. The results revealed that PU resins could readily be cured into a film, thus enhancing the hardness and homogeneity of the wood surfaces, as well as improving the moisture excluding efficiency (MEE) and antismelling efficiency (ASE) of wood. Among all PU resins, the one made by combining short oil-modified alkyd resin and PMDI showed the optimal performances. The present study further explored the synthesis of oil-modified alkyd resins made by combining different polyhydric alcohols and polybasic acids, as well as the physical and chemical properties of the PU resins prepared from each oil-modified alkyd resin and PMDI. This study also analyzed the improved homogeneity, dimensional stability, and finishing performances of medium- and small-diameter softwoods achieved by these PU resin treatments.

EXPERIMENTAL

Materials

Polyhydric alcohols such as glycerin (G) and pentaerythritol (P); polybasic acids including phthalic anhydride (PA) and isophthalic acid (IPA); and solvents such as ethyl acetate, toluene, butyl acetate, xylene, and methyl ethyl ketone were supplied by Shimakyu Pure Chemicals, Japan. Blown castor oil and dibutyl tin dilaurate (DBTDL) were purchased from Deuchen, Taiwan. Polymeric 4,4'-diphenylmethane diisocyanate (PMDI) was supplied by Ann Feng Company, Taiwan. Litharge was supplied by Kanto Company, Japan. All the chemicals used were

of laboratory grade reagent and were used directly from the supplier without further purification. Three kinds of thinning wood of medium- and small-diameter softwoods, with a diameter of 10–15 cm and moisture content of 14.6% including China fir (*Cunninghamia lanceolata*, specific gravity of 0.39), Taiwania (*Taiwania cryptomerioides*, specific gravity of 0.47), and Japanese cedar (*Cryptomeria japonica*, specific gravity of 0.59) were obtained from Hui-Sun Forest Station of Experimental Forest of National Chung Hsing University in Nan-Tou County. Nitrocellulose lacquers (NC lacquer) including sanding sealer and top clear were purchased from Kuo-Roung Paint Manufacture, Taiwan.

Synthesis and characterization of short oil-modified alkyd resins

By the molar ratio of polyhydric alcohol to polybasic acid = 1.3 : 1, four kinds of short oil-modified alkyd resins with the oil content of 40% were synthesized using transesterification¹² according to the recipe shown in Table I. The reaction was carried out in a 1000-mL four-necked round-bottom flask mounted with a motorized stirrer. The experimental setup also includes a nitrogen gas inlet tube, a thermometer, and a separatory trap carrying a water-cooled condenser. In each preparation, the glyceride was first prepared by heating the blown castor oil to 200–210°C within 1 h. Then, litharge was added, followed by the slow addition of 1/2 calculated polyhydric alcohol. The mixture solution was reacted at the temperature of 200–210°C until one volume of reactant could be dissolved into three volumes of methanol. Then, 1/2 calculated polybasic acid and xylene were added when the mixture solution temperature was cooled down to 180°C; and the solution continued to be heated to 200–210°C within 30 min. The time when the polybasic acid was added was taken as the beginning of the reaction.

The above-mentioned procedures were repeated and the remaining 1/2 calculated polyhydric alcohol was added within 30 min, followed by addition of the remaining 1/2 calculated polybasic acid and xylene within 30 min. The reaction temperature was kept at 200–210°C; the water was then distilled and acid value was measured at an interval of 30 min. When the acid value was lower than 20, another 100 g of xylene was added. When the acid value was dropped to 15, the temperature was cooled down to 140°C and kept for 30 min, and the mixture was then cooled down to room temperature. The speed of the stirrer was kept at 400 rpm throughout the reaction. The resultants of four kinds of short oil-modified alkyd resins according to their ingredients were designated as PA-G, PA-P, IPA-G, and IPA-P as shown in Table I.

TABLE I
Formulation of Short Oil-Modified Alkyd Resins with Different Raw Materials

Raw material	Alkyd resin			
	PA-G	PA-P	IPA-G	IPA-P
Blown castor oil (g)	140.0	156.0	152.0	156.0
Phthalic anhydride (g)	148.0	148.0	–	–
Isophthalic acid (g)	–	–	166.0	166.0
Glycerin (g)	79.8	–	79.8	–
Pentaerythritol (g)	–	88.4	–	88.4
Xylene ^a (g)	37.0	39.2	39.7	41.0
Litharge ^b (g)	0.042	0.047	0.045	0.047

^a Xylene was employed as the azeotropic solvent and 10% (by wt.) of the total amount of ingredients was added.

^b Litharge was employed as the catalyst and 0.03% (by wt.) of blown castor oil was added.

The extent of reaction (P) and average degree of polymerization (DP) with respect to acid value were calculated using the following equation^{17,18}: $P = (Co - Ct)/Co$; $DP = (1 - P)^{-1}$ where Co is the initial acid value of the reactant, and Ct is the acid value after time, t reaction. Molecular weight was measured by means of gel permeation chromatography (GPC; Hitachi, D-2520) and number average molecular weight (M_n) and molecular weight polydispersity (Q) could also be calculated. Viscosity was measured by a Brookfield-LVF meter at 27°C. The hydroxyl number was determined using the acetic anhydride/pyridine method.

Preparation and characterization of PU resins

Four kinds of short oil-modified alkyd resins were blended with polyisocyanate (PMDI) by the molar ratio of $NCO/(OH+COOH) = 1.2$, respectively. The 0.1% PU catalyst of DBTDL (by the weight of the mixed resins) was added and the mixture was stirred evenly. Then, an appropriate amount of PU thinner (ethyl acetate:toluene:butyl acetate:xylene:methyl ethyl ketone = 10:35:25:20:10, v/v) was added to the mixture to adjust the viscosity to 12 s using a No. 4 Ford cup at room temperature and four kinds of PU resins were obtained.

The tensile strength and elongation at break of free PU films were carried out on an EZ Tester (Shimadzu Co.) with a crosshead speed of 5 mm/min. All specimens were of a specified shape and size in accordance with ASTM D638, and five samples were tested for each PU resin and the values were averaged. Gel content was measured by putting each weighted PU film into 100 mL of solvent (ethyl acetate:acetone = 1 : 1, v/v) for 48 h. To remove the remaining solvent, the soaked film was further dried in an 80°C oven for 24 h and the weight retention was calculated. Thermal stability was carried out on a thermogravimetric analysis (TGA) instrument

(Perkin-Elmer Pyris 1) in a nitrogen atmosphere from 50 to 700°C at a heating rate of 20°C/min.

PU resin treatment and characterization of PU-treated wood

All kinds of PU resins with the viscosity well adjusted were applied to the wood surfaces using an air-spray gun with the ratio of compressed air and fluid resin adjusted to obtain a smooth spray flow and films of even thickness. The sample was sprayed twice from top to bottom and from left to right. The amount of resin sprayed averaged 50–60 g m⁻². For moisture absorption and water-soaked tests, the wood was dipped into PU resin for 10 s and then drawn out for weight measurement. The amount of resin adsorbed averaged 200–220 g m⁻². After the treatment, all specimens were conditioned at room temperature for 1 week before testing.

The hardness of the PU-treated wood surfaces was investigated using a König hardness tester (Braive Co.) according to DIN 53157. Ten points were tested with the values averaged for each specimen and a coefficient of variation was also calculated. In moisture absorption tests, the specimens with the dimension of 3.0 cm (*R*) × 3.0 cm (*L*) × 1.0 cm (*T*) were first placed into the oven at the temperature of 103°C ± 2°C. After being oven dried, the specimens were moved into a chamber of constant temperature and humidity chamber for 72 h at 40°C for relative humidity of 65% RH and 95% RH, respectively. The equilibrium moisture content (EMC) and MEE were calculated as follows: EMC (%) = $(W_E - W_o) \times 100 / W_o$, where W_E is the weight of the specimen at a certain relative humidity, and W_o is the oven-dried weight of the specimen. MEE (%) = $(E_c - E_t) \times 100 / E_c$, where E_c is the EMC of untreated specimen, and E_t is the EMC of PU-treated specimen. The measurements were made in triplicate with the values averaged.

In water-soaked tests, the specimens with the dimension of 3.0 cm (*R*) × 3.0 cm (*L*) × 1.0 cm (*T*) were oven dried with the volume and weight measured. The specimens were soaked in distilled water under reduced pressure for 30 min, and then under normal pressure for 1 h, and again under reduced pressure for another 30 min. Following that, the pressure was restored to normal for 1 day and the distilled water was replaced. The above-mentioned procedures were repeated for 7 days after which the volume and weight of specimens after wetted with water were measured. The water absorption percent (WAP), volumetric swelling coefficient (*S*), and ASE were calculated as follows: WAP (%) = $(W_w - W_o) \times 100 / W_o$, where W_w is the weight of specimen after wetted with water, and W_o is the weight of oven-dried specimen before wetting. S (%) = $(V_w - V_o) \times$

$100 / V_o$, where V_w is the wood volume of specimen after wetted with water, and V_o is the wood volume of oven-dried specimen before wetting. ASE (%) = $(S_c - S_t) \times 100 / S_c$, where S_c is the *S* of the untreated specimen, and S_t is the *S* of the PU-treated specimen.

PU-treated wood finishing and characterization of finishing performances

The viscosity of sanding sealer and top clear of NC lacquer was adjusted to 20 s with thinner using a No.4 Ford cup at room temperature. Two kinds of finishing procedure, i.e. coating with sanding sealer and top clear, and coating with top clear alone, were applied to the PU-treated wood surfaces using the air-spray gun with the proper ratio of compressed air and fluid coatings to obtain a smooth spray flow, and films of even thickness. The coated specimens were then reconditioned at 27°C and 65% RH for 1 week before the properties of films were examined.

The hardness of the tested films was investigated using a König hardness tester (Braive) according to DIN 53157. At least five points were tested for each specimen. The adhesion of tested films was determined by the cross-cut method according to CNS K 6800, and the best adhesion is grade 10 followed by grades 8, 6, 4, 2, and 0. The durability of film was evaluated using hot-and-cold cycle tests, in which the specimens were first placed into a -20°C refrigerator for 2 h, and then transferred to a 50°C oven for another 2 h. The number of cycles undergone when the sample films cracked was recorded.

RESULTS AND DISCUSSION

Fundamental properties of short oil-modified alkyd resins

To prevent gelling of the reactants during the manufacturing procedure, polyhydric alcohols and polybasic acids were added in two stages. The acid value of the reaction mixture dropped markedly during the initial stages, followed by a more gradual decrease in the later stages of reaction, which was in agreement with the results obtained in other studies on preparation of alkyds using rubber seed oil¹⁸ or African locustbean seed oil.¹⁹ When the acid value reached 15, the reaction was stopped. The fundamental properties of the short oil-modified alkyd resin comprising different ingredients are shown in Table II. As can be seen, glycerin-based alkyd resins, PA-G and IPA-G, had higher extent of reaction of 84.86% and 82.15%, respectively, than that of pentaerythritol-based IPA-P (80.6%) and PA-P (78.56%).

TABLE II
Fundamental Properties of Different Short Oil-Modified Alkyd Resins

Property	Alkyd resin ^a			
	PA-G	PA-P	IPA-G	IPA-P
Extent of reaction, <i>P</i> (%)	84.86	78.56	82.15	80.60
Average degree of polymerization, DP	6.61	4.66	5.60	5.15
Number average molecular weight, M_n	1560	1702	1499	1615
Molecular weight polydispersity, <i>Q</i>	2.54	2.36	2.01	2.48
Viscosity ^b (<i>P</i>) (27°C)	747.5	793.2	676.3	783.1
Hydroxy number (KOH mg/g)	143	156	205	143

^a PA, phthalic anhydride; IPA, isophthalic acid; G, glycerin; P, pentaerythritol.

^b Solid content of alkyd resin was adjusted to 70% for viscosity test.

Among all the samples, glycerin-based PA-G had the highest DP of 6.61, followed by IPA-G of 5.60 and pentaerythritol-based IPA-P of 5.15, and PA-P of 4.66. It is possibly because pentaerythritol possesses four primary hydroxyl groups and the transesterification reaction with castor oil for generating glycerides is faster than for glycerin which contains two primary and one secondary hydroxyl groups. The generated glycerides contain less primary hydroxyl groups, which accounts for slow reaction with polybasic acid and lower DP.

Alkyd resins are synthetic polymers and their molecular structure is dependent on the proportion of reactants, speed of agitation of the reaction mixture, changes in temperature, and removal of water during esterification. Owing to these parameters in preparation of alkyd resins, occurrence of intramolecular condensation, cyclization, or branching reaction cause alkyd resins to be heterogeneous and comprise fractions of varying molecular weights.^{18,20} These results were confirmed by GPC analysis and the number average molecular weight (M_n) and polydispersity (*Q*) were calculated as shown in Table II. The M_n ranged between 1499 and 1702 and varied in order of PA-P > IPA-P > PA-G > IPA-G. The phthalic anhydride and pentaerythritol-based alkyd resin had higher M_n than that of the isophthalic acid and glycerin-based one. In addition, the *Q* indices were 2.54, 2.36, 2.01, and 2.48 for PA-G, PA-P, IPA-G, and IPA-P, respectively.

The pentaerythritol-containing alkyd resins tend to have higher viscosities in agreement with higher molecular weights. PA-P had the highest viscosity of 793.2 P and IPA-G had the lowest viscosity of 676.3 P. On the other hand, IPA-G had the highest hydroxyl number of 205 while that of PA-G, PA-P, and IPA-P were 143, 156, and 143, respectively.

Properties of PU resins

The PU resins prepared from different short oil-modified alkyds and polyisocyanate PMDI were designated as PA-G-MDI, PA-P-MDI, IPA-G-MDI, and IPA-P-MDI, respectively, and their properties are listed in Table III. The results indicated that PU resins containing pentaerythritol-based alkyd resins had higher tensile strength than that of glycerin-based ones, such as PA-P-MDI of 54.7 MPa was higher than PA-G-MDI of 53.3 MPa. On the other hand, PU resins with the same polyhydric alcohol and different polybasic acids showed no difference in tensile strength, such as PA-P-MDI of 54.7 MPa was almost equal to IPA-P-MDI of 54.6 MPa. In addition, the PU resin, IPA-G-MDI, containing isophthalic acid and glycerin had the highest elongation at break of 16.13%, which may be due to the IPA-G alkyd resin had the lowest molecular weight and polydispersity (see Table II). PA-P-MDI had the highest gel content of 90.8%, followed by IPA-P-MDI of 89.9%, showing that the PU resins containing pentaerythritol-based alkyd resins had a better crosslinking between the —OH group of alkyd resin and —NCO group of PMDI.

The weight loss percentages for PU resins with different alkyd resins were evaluated by TGA, as summarized in Table IV, and the DTG curves for all kinds of PU resins are shown in Figure 1. As seen in the DTG curves, there are three obvious degradation peaks in PA-G-MDI, while there are only two peaks in the other PU resins. The first degradation peak of all PU resins appeared at 300–350°C and the temperature was the lowest at the first peak of PA-G-MDI, followed by the order of IPA-G-MDI, PA-P-MDI, and IPA-P-MDI. The PU resin containing isophthalic acid and pentaerythritol had the highest temperature of the first peak, which may be attributed to the greater number of hydrogen bonds in the urethane linkage. The second degradation peak of PA-G-MDI appeared at 370–380°C, while the third peak occurred at 400–450°C. However, the temperature of second peaks for IPA-G-MDI and PA-P-MDI was 400–450°C and at 600°C, respectively for IPA-P-MDI.

TABLE III
Tensile Strength, Elongation at Break, and Gel Content of Various PU Resin Films

PU resin ^a	Tensile strength (Mpa)	Elongation at break (%)	Gel content (%)
PA-G-MDI	53.3	10.32	89.4
PA-P-MDI	54.7	9.01	90.8
IPA-G-MDI	52.9	16.13	87.0
IPA-P-MDI	54.6	10.35	89.9

^a PA, phthalic anhydride; IPA, isophthalic acid; G, glycerin; P, pentaerythritol; MDI, polymeric 4,4'-diphenylmethane diisocyanate.

TABLE IV
Weight Loss Percentage of PU Resins at Different Temperatures

PU resin ^a	Temperature (°C)									
	250	300	350	400	450	500	550	600	650	700
PA-G-MDI	8	26	38	57	76	83	85	86	87	88
PA-P-MDI	8	15	42	61	83	97	94	95	95	96
IPA-G-MDI	9	15	36	54	68	81	85	86	87	87
IPA-P-MDI	10	14	33	61	65	70	80	82	92	98

^a PA, phthalic anhydride; IPA, isophthalic acid; G, glycerin; P, pentaerythritol; MDI, polymeric 4,4'-diphenylmethane diisocyanate.

Comparing the weight loss at 450°C of each PU moiety of the compound being decomposed²¹ shows that the lowest value was observed at 65% from IPA-P-MDI (see Table IV). From the results mentioned earlier, it could be concluded that the isophthalic acid and pentaerythritol-containing PU resin had the best thermal stability.

Surface hardness and dimensional stability of PU-treated wood

The surface hardness of various PU-treated woods is shown in Table V. The hardness of untreated China fir, Taiwania, and Japanese cedar were 33, 42, and 52 s, respectively, and were remarkably enhanced by PU treatments. Take Japanese cedar for instance, when treated by PA-G-MDI, PA-P-MDI, IPA-G-MDI, and IPA-P-MDI, its surface hardness was increased from 52 s to 129, 133, 103, and 135 s, respectively. Comparing the same polybasic acid-containing PU treatments reveals that the hardness of pentaerythritol-containing PU-treated wood was higher than that of glycerin-containing one. After the same glycerin-containing PU treatments, the hardness of phthalic anhydride-containing PA-G-MDI-treated wood was higher than that of isophthalic acid-containing IPA-G-MDI-treated one. However, with the same pentaerythritol-containing PU treatments, the hardness of isophthalic acid-containing PU was higher than that

of phthalic anhydride-containing PU, which may be attributed to the fact that the application of isophthalic acid alkyd resin with pentaerythritol yielded harder film than that applied with orthophthalic anhydride alkyd resin.

The surface hardness of PU-treated wood increased with increasing specific gravity of wood; for example, the hardness of PA-P-MDI-treated China fir, Taiwania, and Japanese cedar were 95, 102, and 133 s, respectively. In addition, the IPA-P-MDI-treated wood had the highest percent of increase in hardness, and the value reached 203, 181, and 160% for China fir, Taiwania, and Japanese cedar, respectively. Moreover, the coefficients of variation in surface hardness of PU treated woods were lowered. To be more specific, the coefficient of variation for China fir decreased from 22.40% to 10.67–14.22%; from 17.78% to 12.12–16.77% for Taiwania; and from 25.12% to 18.79–20.48% for Japanese cedar. These results revealed that more homogeneous wood surfaces would be obtained by PU treatments. Moreover, the lower the specific gravity of wood, the smaller the coefficient of variation is obtained for the IPA-G-MDI- and IPA-P-MDI-treated wood, meaning that woods with low specific gravity had the best improved efficiency on the homogeneity of medium- and small-diameter softwood surfaces.

The EMC and MEE of PU-treated woods at 65% RH and 95% RH tests are displayed in Table VI. The EMCs of untreated woods were higher than those of the PU-treated woods at 65% RH. For instance, the EMC of the untreated Taiwania was 8.11%; after PU treatments, the EMCs of the treated wood were reduced to 7.83% (PA-G-MDI), 7.72% (PA-P-MDI), 7.96% (IPA-G-MDI), and 8.01% (IPA-P-MDI). The results indicated that PU resin could be hardened into a film on the surface and void of the wood, thus delaying and reducing moisture absorption. The EMCs of the PU-treated wood in the high-humidity environment of 95% RH showed the same trend as those in the environment of 65% RH, but it had higher EMC values. Either in the environment of 65% RH or 95% RH and after the same phthalic anhydride-containing PU treatments, the MEEs of pentaerythritol-containing PU-treated woods were

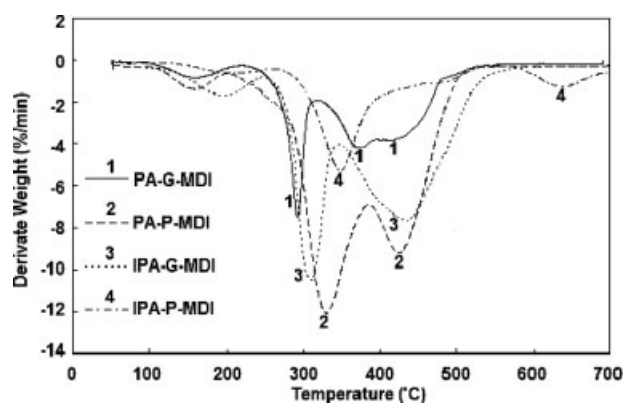


Figure 1 DTG curves of various PU resins.

TABLE V
Surface Hardness and Percentage of Increase in Hardness of PU-Treated Woods

PU resin ^a	China fir		Taiwania		Japanese cedar	
	Hardness (s)	Increase in hardness (%) ^b	Hardness (s)	Increase in hardness (%)	Hardness (s)	Increase in hardness (%)
Control	33 (22.40) ^c	–	42 (17.78)	–	52 (25.12)	–
PA-G-MDI	92 (14.22)	178	107 (13.56)	155	129 (20.48)	148
PA-P-MDI	95 (12.62)	188	102 (12.12)	143	133 (19.63)	156
IPA-G-MDI	90 (12.00)	173	92 (16.77)	119	103 (20.14)	117
IPA-P-MDI	100 (10.67)	203	118 (13.59)	181	135 (18.79)	160

^a PA, phthalic anhydride; IPA, isophthalic acid; G, glycerin; P, pentaerythritol; MDI, polymeric 4,4'-diphenylmethane diisocyanate.

^b Increase in hardness (%) = (Surface hardness of wood after PU treatments – Surface hardness of wood before PU treatments) × 100 / Surface hardness of wood before PU treatments.

^c Figure in bracket means coefficient of variation (%) = Standard deviation × 100 / Average.

higher than those of glycerin-containing PU-treated ones. However, the same isophthalic acid-containing PU treatments yielded the reverse results. The trend of the MEEs of phthalic anhydride-containing PU-treated woods being higher than those of isophthalic acid-containing PU-treated woods was also observed. From the results mentioned earlier, it could be concluded that the phthalic anhydride and pentaerythritol-containing PU (PA-P-MDI)-treated medium- and small-diameter softwoods had the highest MEE values at different RH levels.

The dimensional stability of PU-treated wood is also evaluated by the water-soaked tests, and the water absorption percent (WAP), volumetric swelling coefficient (*S*) and ASE are shown in Table VII. As can be seen, the lower the specific gravity of wood, the

higher WAP of untreated wood was obtained, such as the WAP of 185, 182, and 136% for China fir (sp. gr. of 0.39), Taiwania (sp. gr. of 0.47), and Japanese cedar (sp. gr. of 0.59), respectively. After PU resin treatments, the WAPs of all specimens were decreased, which was because the surface and void of wood were filled with PU film. However, the untreated wood with high specific gravity had higher *S* value, and the *S*s of woods after PU treatments were also decreased; for instance, the *S* of Taiwania was reduced from 12.54% to 10.69–11.31%. The results also showed that the wood with high specific gravity had higher ASE value, such as the ASE of PU-treated Japanese cedar was 18.9–21.67%, meaning that it had greater improved efficiency on dimensional stability after PU treatments. Furthermore, after the same polybasic acid-containing PU treatments, the ASEs of pentaerythritol-containing PU-treated woods were higher

TABLE VI
EMC and MEE of PU-Treated Woods

Wood	PU resin ^a	65% RH ^b		95% RH ^b	
		EMC (%)	MEE (%)	EMC (%)	MEE (%)
China fir	Control	7.71	–	16.84	–
	PA-G-MDI	7.30	5.32	15.58	7.48
	PA-P-MDI	7.25	5.97	15.43	8.37
	IPA-G-MDI	7.49	2.85	16.38	2.73
	IPA-P-MDI	7.55	2.08	16.58	1.54
Taiwania	Control	8.11	–	19.68	–
	PA-G-MDI	7.83	3.45	19.40	1.42
	PA-P-MDI	7.72	4.81	19.31	1.88
	IPA-G-MDI	7.96	1.85	19.49	0.97
	IPA-P-MDI	8.01	1.23	19.55	0.66
Japanese cedar	Control	8.05	–	19.48	–
	PA-G-MDI	7.89	1.99	17.56	9.86
	PA-P-MDI	7.66	4.84	17.51	10.11
	IPA-G-MDI	7.73	3.98	18.37	5.70
	IPA-P-MDI	7.92	1.61	18.48	5.13

^a PA, phthalic anhydride; IPA, isophthalic acid; G, glycerin; P, pentaerythritol; MDI, polymeric 4,4'-diphenylmethane diisocyanate.

^b EMC, equilibrium moisture content; MEE, moisture excluding efficiency.

TABLE VII
WAP, *S*, and ASE of PU-Treated Woods

Wood	PU resin ^a	WAP (%) ^b	<i>S</i> (%) ^b	ASE (%) ^b
China fir	Control	185	9.81	–
	PA-G-MDI	145	9.37	4.49
	PA-P-MDI	102	9.29	5.30
	IPA-G-MDI	155	9.40	4.18
	IPA-P-MDI	134	9.22	6.01
Taiwania	Control	182	12.54	–
	PA-G-MDI	152	10.87	13.32
	PA-P-MDI	159	10.85	13.48
	IPA-G-MDI	167	11.31	9.81
	IPA-P-MDI	169	10.69	14.75
Japanese cedar	Control	136	20.21	–
	PA-G-MDI	115	15.91	21.28
	PA-P-MDI	123	16.01	20.78
	IPA-G-MDI	128	16.39	18.90
	IPA-P-MDI	117	15.83	21.67

^a PA, phthalic anhydride; IPA, isophthalic acid; G, glycerin; P, pentaerythritol; MDI, polymeric 4,4'-diphenylmethane diisocyanate.

^b WAP, water absorption percentage; *S*, volumetric swelling coefficient; ASE, antiswelling efficiency.

TABLE VIII
Finishing Performances of PU-Treated Woods

Wood	Hardness (s)			Adhesion (grade)			Hot and cold cycles		
	Sanding sealer + top clear		Top clear	Sanding sealer + Top clear		Top clear	Sanding sealer + Top clear		Top clear
	Control	PU ^a	PU	Control	PU	PU	Control	PU	PU
China fir	53	62	98	4	6	8	3	5	16
Taiwania	60	63	99	6	8	10	3	5	17
Japanese cedar	64	68	103	6	6	8	3	5	17

^a PU means IPA-P-MDI-treated.

than those of glycerin-containing PU-treated ones. It revealed that the PU with high mechanical properties had the best improved efficiency on dimensional stability of wood.

Finishing performances of PU-treated wood

From the conclusion of the results mentioned above, all the isophthalic acid and pentaerythritol-containing PU (IPA-P-MDI)-treated woods had the best surface homogeneity and dimensional stability. Therefore, the following analyses on finishing performances of woods were carried out using IPA-P-MDI-treated woods, and the results are listed in Table VIII. The hardness of NC lacquer films on the untreated woods were 53, 60, and 64 s for China fir, Taiwania, and Japanese cedar, respectively. After PU treatment, the hardness increased for all specimens after NC lacquer finishing with either sanding sealer plus top clear or top clear alone applied. Especially, for finishing with top clear alone, the hardness increased obviously, such as from 53 to 98 for China fir, from 60 to 99 for Taiwania, and from 64 to 103 for Japanese cedar. The same tendencies were observed in the adhesion and hot-and-cold cycles tests. The results revealed that the adhesion and durability of NC films on PU-treated woods improved because of better dimensional stability achieved by the treatment. From the viewpoint of practical utilization, the PU resin could be used as wood sealer for furniture or interior decoration finishing, especially, for open porous wood finishing, with only top clear applied to the PU-treated woods. Hence, the finishing processes can be easy and economical with significantly improved finishing performances achieved in medium- and small-diameter softwoods.

CONCLUSIONS

In this study, the synthesis of four types of short oil-modified alkyd resins with different polyhydric alcohols and polybasic acids was examined. The number average molecular weights (M_n) of alkyd resins ranged between 1499 and 1702, average degree of polymerization (DP) from 4.66 to 6.61, and polydis-

persity (Q) from 2.01 to 2.54. The results of the physical properties of PU resins prepared from each alkyd resin with polyisocyanates (PMDI) indicated that the pentaerythritol-containing PU resins, such as PA-P-MDI and IPA-P-MDI, had higher tensile strength, gel content, and thermal stability, but lower elongation at break. According to the moisture absorption and water-soaked tests, the EMC, MEE, and ASE values of medium- and small-diameter softwoods were decreased by PU resin treatments. In particular, the isophthalic acid and pentaerythritol-containing PU resin (IPA-P-MDI) had the best improved efficiency on dimensional stability of woods. In addition, the finishing performances such as hardness, adhesion, and durability of NC lacquer films on the PU-treated woods could be greatly enhanced by finishing with only top clear applied.

References

1. Forestry bureau. Forestry white paper of Taiwan region. 2003, <http://www.forestry.org.tw>.
2. Wang, S. Y. *For Prod Ind* 1982, 1, 69.
3. Comn, D. J.; Haslett, A. N.; Kimberley, M. O.; McConchie, D. L. *Ann Sci For* 1996, 53, 177.
4. Dumail, J. F.; Castéra, P.; Morlier, P. *Ann Sci For* 1998, 55, 911.
5. Liu, C. T.; Lee, W. J.; Lin, F. Y. *For Prod Ind* 1998, 17, 305.
6. Chang, H. T.; Chang, S. T.; Chia, S. J. *Q J Chin For* 2000, 33, 383.
7. Chang, H. T.; Chang, S. T. *Q J Chin For* 2002, 35, 299.
8. Chang, S. T.; Chang, H. T.; Huang, Y. S. *For Prod Ind* 1997, 16, 157.
9. Rowell, R. M.; Ellis, W. D. *Wood Sci* 1979, 12, 52.
10. Rowell, R. M.; Ellis, W. D. *Wood Sci* 1980, 13, 102.
11. Oil and Colour Chemists' Association, Australia. *Surface Coatings, Vol I: Raw Materials and Their Usage*; Chapman and Hall: New York, 1983; Chapter 11.
12. Paul, S. *Surface Coatings, Science and Technology*; Wiley: New York, 1985. Chapters 2.1, 2.6, pp 70, 261.
13. Aydin, S.; Akçay, H.; Özkan, E.; Güner, F. S.; Erciyes, A. T. *Prog Org Coat* 2004, 51, 273.
14. Lu, K. T.; Lin, S. L. *Q J Forest Res* 2006, 28, 63.
15. Lu, K. T.; Lin, S. L. *For Prod Ind* 2006, 25, 29.
16. Lu, K. T.; Lin, S. L. *Q J Chin For* 2006, 39, 233.
17. Bobalek, E. G.; Moore, E. R.; Levy, S. S.; Lee, C. C. *J Appl Polym Sci* 1964, 8, 625.
18. Aigbodion, A. I.; Okieimen, F. E. *Eur Polym J* 1996, 32, 1105.
19. Aigbodion, A. I.; Okieimen, F. E. *Ind Crops Prod* 2001, 13, 29.
20. Okieimen, F. E.; Aigbodion, A. I. *Ind Crops Prod* 1997, 6, 155.
21. Mishra, D. K.; Mishra, B. K.; Lenka, S.; Nayak, P. L. *Polym Eng Sci* 1996, 36, 1047.