Adhesives from Polymeric Methylene Diphenyl Diisocyanate Resin and Recycled Polyols for Plywood

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Abstract

In this study, polyols recycled from decomposed polyurethane (PU) foam wastes were used in preparing adhesives for plywood manufacturing. A polyol was made from chemically decomposed flexible PU foam wastes separated from automobile shredder residue. The recycled polyol was mixed with a commercial polyol at weight ratios of 100/0, 25/75, 50/50, 25/75, and 0/100, respectively. These polyol mixtures were mixed, respectively, with polymeric methylene diphenyl diisocyanate at isocyanate group–to–hydroxyl group (NCO/OH) molar ratios of 1.0, 1.25, and 1.5 to prepare adhesives. The recycled polyol and adhesives were characterized by Fourier transform infrared spectroscopy. Plywood specimens bonded by the adhesives were fabricated and tested. The effects of NCO/OH molar ratio and recycled polyol–to–commercial polyol weight ratio on adhesive gel time and bonding strength before and after water treatments were evaluated. The adhesives prepared from recycled polyol presented shorter gel time and greater dry bonding strength than those prepared from commercial polyol. The adhesives prepared from the recycled polyol–commercial polyol weight ratio of 50/50 and NCO/OH molar ratio of 1.25 showed the best bonding performance after cyclic boiling water treatment. Multilinear regressions showed that NCO/OH molar ratio was the main factor in developing plywood shear strength.

About 5 million tons of automobile shredder residue (ASR) are generated each year in the United States, and most of this material is disposed as waste in landfills, creating a negative environmental impact. Polyurethane (PU) foam materials represent 16 percent of ASR (Hook 2008). Various efforts have been made to reuse PU foam wastes. Angus and Sims (1994) used a moisture-curing isocyanate-terminated prepolymer to bind granulated foam scrap to fabricate foams for carpet underlayment, cushioning materials, and other energy-absorbing products. Reaction injection-moulded PU wastes were ground to fine powders and used as fillers for polyester and polypropylene in new compression moulding compounds (Hulme and Goodhead 2003). Flexible PU foam powders were added to urea-formaldehyde (UF) and phenol-formaldehyde (PF) resins to make plywood and particleboard (Mansouri and Pizzi 2007). PU powders can serve as active fillers or extenders to improve the dry bonding strength of UF resin joints. The water resistance of UF and PF resins is also improved. Mao et al. (2014) mixed polymeric methylene diphenyl diisocyanate (pMDI) with recycled PU foam powders at different ratios for particleboard fabrication. The internal bond strength of particleboard was improved when replacing 5 to 15 percent of pMDI with recycled PU foam powders.

Various chemical procedures to decompose PU foams have been reported (White and Durocher 1997, Behrendt and Naber 2009). These procedures are usually conducted with solvents (water, alcohols, inorganic or organic acids, amines, alkalines, etc.) and a catalyst at high temperatures.

In the decomposing reaction, the solvents break down urethane linkages, resulting in short-chain hydroxyl functional urethane oligomers, and the raw polyols used in the reaction of the original PU foams are thus released (Behrendt and Naber 2009). Recycled polyols have been reused in PU foam manufacturing, with limited success. The manufacturing of PU foams requires precise control of the materials' purity, weight ratios, forming time, setting time, and other conditions. Polyols as the main hydroxyl group-providing component greatly affect the structures and properties of PU foams. Some side reactions that occurred along with the main PU decomposing reaction might produce some amine compounds in the recycled polyols. These amine compounds could catalyze PU foaming reactions and make the process out of control. Currently, recycled polyols can only partially replace commercial polyols in PU foam-forming reactions.

The objective of this study was to investigate the feasibility of using recycled polyols as part of the binder system for plywood. Polyol mixtures were made by mixing a recycled polyol with a commercial polyol at various weight ratios. A series of adhesives was prepared by mixing isocyanate (NCO) and polyol mixtures at different NCO/OH molar ratios. The effects of NCO/OH molar ratio and recycled polyol–commercial polyol weight ratio on adhesive gel time and bonding performance were studied. The results of this study could provide valuable information on alternative ways of utilizing PU foam wastes as well as developing new adhesive systems for plywood manufacturing.

Experimental Procedure

Materials

Flexible PU foams were obtained from Metal Management Inc. (Greenville, Mississippi). They were handpicked from ASR. The color of the foams was dark brown. Some rubber, wood, fibers, paper, glass, and other objects in the foams were removed, and the foams were washed with water and acetone. The foams were then air-dried under a hood and ground into powders of a maximum of 1 mm with a laboratory mill (Model 4; Arthur H. Thomas Company, Swedesboro, New Jersey) using a 1-mm screen. The PU foam powders were then dried in an oven at 100°C until all water was removed.

Diethylene glycol (DEG) and sodium hydroxide used as the decomposing solvent and catalyst, respectively, were obtained from Thermo Fisher Scientific (Waltham, Massachusetts). DEG is a low-viscosity transparent liquid with a water content of up to 0.5 percent and a hydroxyl number of about 1,057 mg of KOH/g. The pMDI (Lupranate M20FB) with the NCO content of 31.5 percent was obtained from BASF Chemical Company (Wyandotte, Michigan). It was a dark yellow liquid with a viscosity of 226 mPa·s at 25°C. A commercial polyether polyol (BASF Pluracol GP730, Florham Park, New Jersey) was used together with recycled polyol for adhesive preparation. Yellow poplar (*Liriodendron tulipifera* L.) wood veneers with a moisture content of 8 percent and a thickness of 3.6 mm were used for making plywood.

Decomposition of PU foams and obtaining recycled polyols

The PU foam decomposition reaction was carried out under atmospheric pressure in a three-neck round-bottom jacketed flask equipped with a stirrer and a refluxing condenser (Table 1). A two-blade stainless steel stirrer was used to stir the reaction mixture in the flask. The DEG was placed in the flask and heated by a heating mantle to 210°C. Then the catalyst and PU foam powders were charged in the flask. After the charging was completed, the reaction mixture was maintained at 210°C for 3 hours. The obtained reaction mixture was split into two phases after cooling to room temperature. The upper phase was separated using a separating funnel and restored as the recycled polyol.

Hydroxyl number

The hydroxyl number was measured in accordance with the AOCS Cd 13-60 (American Oil Chemists Society 1993) standard. Pyridine, acetic anhydride, pyridine–acetic anhydride, normal butyl alcohol, ethanolic potassium hydroxide, and the phenolphthalein indicator solution were obtained from Thermo Fisher Scientific. Three replicates were used and averaged for each measurement. The hydroxyl number was calculated as follows:

$$\text{Hydroxyl number} = ([B + \{W \times A/C\} - S] \times N \times 56.1)/W \quad (1)$$

where A is the KOH solution required for the acidity titration (mL), B is the KOH solution required for the reagent blank (mL), C is the weight of sample used for the acidity titration (g), S is the KOH solution required for titration of the acetylated sample (mL), W is the weight of sample used for acetylation (g), and N is the normality of the KOH solution (N).

Viscosity

The viscosity was measured in accordance with ASTM 445 (ASTM International 2009) with a rotational Brookfield viscometer (Brookfield Engineering Laboratories, Inc., Middleboro, Massachusetts). The measurements were performed at 25°C.

Amine number

The amine number was measured in accordance with the procedures described in ASTM D2073 (ASTM 1998a). Acetic acid, acetic anhydride, chloroform, hydrochloric acid, isopropanol, perchloric acid, and salicyl aldehyde were obtained from Fisher Scientific Co. (Waltham, Massachusetts). Three replicates were used and averaged for each measurement. The total amine number was calculated as follows:

$$\text{Total amine number} = (V \times N \times 56.1)/S \quad (2)$$

Table 1.—*Reaction parameters for the decomposition of polyurethane (PU) foams.*

Diethylene glycol–PU wt ratio	4:1
Reaction temperature (°C)	210
Reaction time (h)	3
Catalyst concentration (based on the wt of PU foam powders) (%)	1
Stirring speed (rpm)	800
Charging rate (g/min)	30
System pressure (atm)	1
PU foam powder size (mm in diameter)	1
PU foam powder moisture content (%)	0

where V is the amount of hydrochloric acid required for titration of the sample (mL), N is the normality of the hydrochloric acid solution (N), and S is the sample weight used (g).

pH value

pH value was determined with an Accumet Basic AB15 pH meter (Thermo Fisher Scientific) at 25°C.

FT-IR spectroscopy

Fourier transform infrared (FT-IR) analysis was conducted using a Thermo Fisher Nicolet 6700 spectrophotometer. The liquid samples (polyols) were dropped onto the stage of the spectrophotometer. The cured adhesives were ground to powder and dried in a vacuum oven at 60°C. The solid samples (PU foam powders and adhesive powders) were placed on the stage of the spectrophotometer. A total of 64 scans for each sample from 4,000 to 600 cm^{-1} were recorded.

Preparation of adhesives and gel time measurement

The adhesives were prepared under laboratory conditions using pMDI and various polyol compositions (Table 2). The NCO/OH molar ratios were 1.0, 1.25, and 1.5, respectively. The recycled polyol and GP730 were respectively mixed at different weight ratios of 0/100, 25/75, 50/50, 75/25, and 100/0. To prepare adhesives, the polyols were first placed in a 250-mL beaker, and the pMDI was added. The mixture was stirred thoroughly with a glass rod for about 1 minute and then applied to the veneer surfaces. The gel times of the adhesives were measured at 25°C and calculated from when the isocyanate was added until the wire drawing phenomenon occurred and the adhesive mixtures could not flow.

Preparation of plywood specimens

Three-layer plywood with dimensions of 38.1 by 38.1 cm (15 by 15 in.) was manufactured using a laboratory hot press (Hydraulic Press Co., Clifton, New Jersey). The adhesive application ratio for double glue line was about 344 g/m^2 (32 g/ft^2). The adhesives were applied uniformly on both sides of the veneer glue line with a brush. The hot press time, temperature, and pressure were 60 minutes, 60°C, and 200 psi, respectively. After pressing, the plywood panels were conditioned at 20°C and 60 percent relative humidity for 1 week.

Measurement of the bonding strength

The bonding strengths were measured by tension test in accordance with ASTM D906 (ASTM 1998b). The plywood was cut into samples with dimensions of 8.89 by 2.54 cm (3.5 by 1 in.). The shear bonding area of the testing samples was 2.54 by 2.54 cm (1 by 1 in.). Both the dry and wet bonding strengths were measured. For the wet bonding strength, samples were immersed in water under two different conditions before testing: (1) water soak at 60°C for 3 hours; and (2) immersion in boiling water for 4 hours, drying in an oven at 63°C for 20 hours, and then immersing in the boiling water again for 4 hours. After the water-immersion treatment, the samples were cooled in water at 20°C and tested by tension to fail in an Instron universal testing machine (Norwood, Massachusetts). The test results were averaged (eight samples for each formulation). The

Table 2.—Composition of the adhesives.

Isocyanate	Recycled polyol–GP730 wt ratio	NCO/OH molar ratio
pMDI[a]	0/100, 25/75, 50/50, 75/25, 100/0	1.0, 1.25, 1.5

[a] pMDI = polymeric methylene diphenyl diisocyanate.

failure mode was identified as cohesive, adhesive, and substrate failures. Cohesive failure was recognized when the failure happened between the wood substrate and the adhesive. Adhesive failure was recognized when the failure happened at the adhesive side. Substrate or wood failure was recognized when the failure happened at the wood substrate side.

Statistical analysis

Means and standard deviations of the data obtained were calculated. Duncan's multiple range tests and multilinear regression tests with SAS 9.4 software (Cary, North Carolina) were used to determine the differences among different treatments.

Results and Discussion

Characterization of PU foam, recycled polyol, and cured adhesives

The decomposition of the PU foams involved intermolecular transesterification of the urethane bonds by a reaction of hydroxyl end groups with glycols (Ulrich et al. 1978). As the reaction progressed, the polyurethane bonds were gradually broken with the DEG and converted into the urethane oligomers (smaller fragments). The general properties of the recycled polyol compared with the commercial polyol (GP730) are shown in Table 3. The recycled polyol had a slightly higher hydroxyl number, viscosity, and pH value than GP730. Some additives (such as cross-linkers, chain extenders, and other polyols in minor amounts) included in the PU foam formulation might affect the hydroxyl number of the recycled polyol. Recycled polyol contained a certain amount of amine compounds, with an amine number of 3.23.

The chemical composition of the ground PU foam powders was characterized by FT-IR (Fig. 1). The absorption bands at 1,720 and 1,537 cm^{-1} correspond to the urethane carbonyl group (C=O in -NH-CO-O-) stretching and N-H bending vibration, respectively. The absorption bands at 1,662 and 3,310 cm^{-1} correspond to the urea carbonyl group (C=O in -NH-CO-NH-) and the stretching vibration of N-H groups, respectively. These groups are the products from the reaction between isocyanate and water (Wu et al. 2003, Wang and Chen 2006, Kwon et al. 2007, Bene et al. 2012). The absorption band at 1,450 cm^{-1}, corresponding to the aromatic ring, indicated the possible aromatic source of the isocyanate as one of the raw materials in the preparation of PU foams (Lee et al. 2005).

Similar spectra were obtained from the recycled polyol and GP730 because of the presence of the same characteristic absorption bands (Fig. 1): (1) intense stretching vibrations of the aliphatic ether groups (-C-O-C-) at 1,100 cm^{-1}, and (2) stretching vibrations of the -OH groups at 3,360 to 3,450 cm^{-1}. Other absorption bands were also normal for the polyols: stretching vibration of C-H bonds in aliphatic carbons at 2,870 to 2,971 cm^{-1} and bending vibrations of methylene and methyl groups in the polyol

Table 3.—Properties of recycled polyol and commercial polyol.

Polyol type	Hydroxyl no. (mg of KOH/g)	Viscosity (mPa·s)	Amine no. (mg of KOH/g)	pH value
Recycled polyol	296	303	3.23	7.5–8.0
GP730	225	270	NA[a]	6.6

[a] NA = not applicable.

chain at 1,374 and 1,456 cm^{-1} (Nikje et al. 2007). The absorption band of the urethane carbonyl groups (C=O in -NH-CO-O-) was not observed because of complete degradation during the reaction. Moreover, some solvents dissolve in the upper phase and thus affect the intensity of the band of the -OH groups (Nikje et al. 2007). If this is the case, even trace amounts of DEG contaminant might increase the hydroxyl number of the recycled polyol. However, this effect was not readily observed in the FT-IR spectrum in this study. Other than these typical bands, the spectrum of the recycled polyol did show some slight differences. The presence of the absorption bands at 1,516 and 1,628 cm^{-1} suggested the presence of amine by-products (Molero et al. 2006).

Figure 2 shows the FT-IR spectra of adhesives prepared at recycled polyol–GP730 weight ratio of 50/50 at NCO/OH molar ratios of 1.0, 1.25, and 1.5, respectively. The characteristic carbonyl stretching of urethane linkage was observed at 1,720 cm^{-1}. An absorption band characteristic of the N-H group stretching was observed at 3,310 cm^{-1}. The NCO group absorption band centered at 2,270 cm^{-1} was clearly present in the adhesive with an NCO/OH molar ratio of 1.5, indicating that the adhesive sample contained residual NCO groups (Kong et al. 2011). This absorption band was much weaker in the spectrum of the sample made with an NCO/OH molar ratio of 1.25 and disappeared in the spectrum of the sample made with an NCO/OH molar ratio of 1.0. This observation shows that few NCO groups remained in the cured adhesive sample made with the NCO/OH molar ratio of 1.25; no NCO groups remained in the sample made with the NCO/OH molar ratio of 1.0.

Gel time of adhesives

For the application of an adhesive system, gel time is an important parameter. It is defined as the maximum length of time the system's viscosity remains in an appropriate range to be applied to a substrate (Kong et al. 2011). Gel times of various adhesives are shown in Table 4. As the NCO/OH molar ratio increased, gel times decreased first and then increased slightly. The NCO/OH ratios of 1.25 and 1.5 were higher than stoichiometric for complete urethane bond formation, resulting in a certain amount of NCO groups remaining in the system as indicated by FT-IR results (Fig. 2). The excess pMDI was in liquid form and may have diluted the adhesive system. Although it gradually reacted with moisture in the air and gelled, this process took a longer time than the reaction between pMDI and polyol. Therefore, excess pMDI in the adhesive mixture resulted in a longer gel time. Moreover, as the weight ratio of recycled polyol–GP730 increased, the gel time decreased. The recycled polyol had a higher hydroxyl number than GP730; a polyol with a higher hydroxyl number yields a more densely cross-linked PU structure (Desai et al. 2003). The formation of more cross-links during the curing process could shorten the gel time (Desai et al. 2003). In addition, because the recycled polyol contained a small amount of amine compounds, as the weight ratio of recycled polyol–GP730 increased, more amine compounds were brought into the reaction system. The catalyzing effect of the amine compounds on the PU reactions might accelerate the reaction and shorten the gel time (Kong et al. 2011, Patel et al. 2009). In this study, all gel times of the adhesives were suitable for adhesive application in plywood manufacturing.
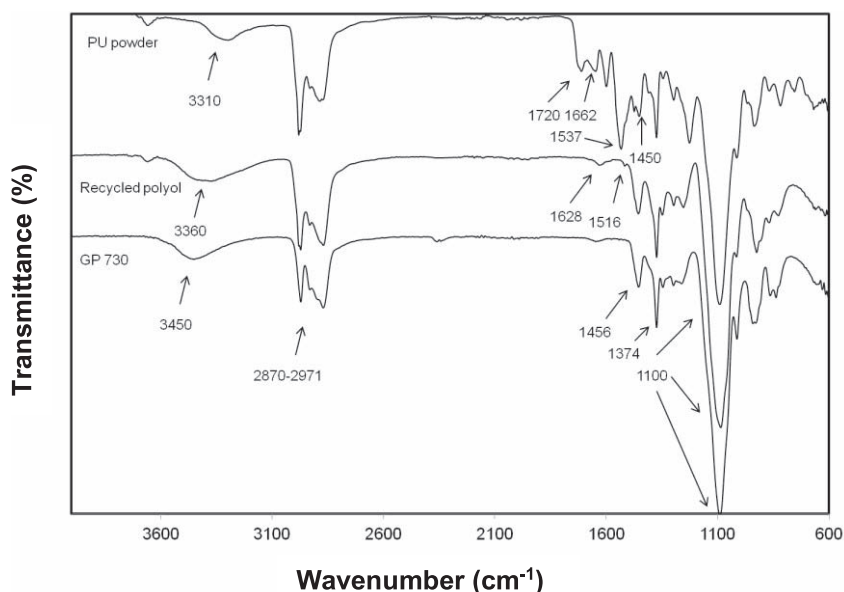

Figure 1.—Fourier transform infrared spectra of polyurethane powder, recycled polyol, and GP730.
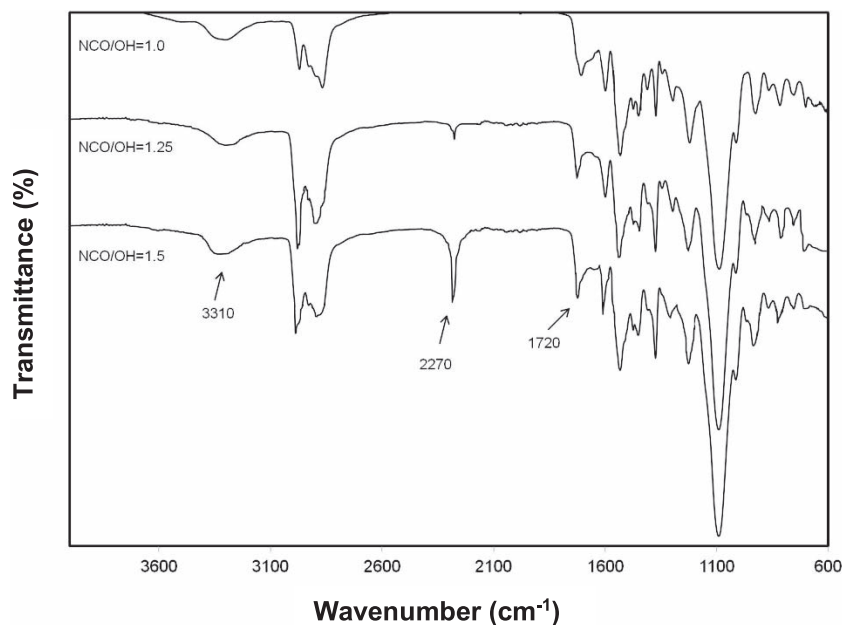
Figure 2.—Fourier transform infrared spectra of adhesives prepared at recycled polyol–GP730 weight ratio of 50/50 at NCO/OH molar ratios of 1.0, 1.25, and 1.5.

Bonding strength of adhesives before water immersion treatment

The average shear strengths of the plywood specimens with various NCO/OH molar ratios and recycled polyol–GP730 weight ratios before water treatment (dry strength) are listed in Table 5. At the same recycled polyol level, generally, the shear strength increased with NCO/OH molar ratio. Statistical analyses showed that as the NCO/OH molar ratio increased from 1.0 to 1.25, the shear strength increase was significant at $\alpha = 0.05$; further increasing the NCO/OH molar ratio from 1.25 to 1.5 did not increase shear strength significantly at $\alpha = 0.05$. This is probably because, at an NCO/OH of 1.0, most isocyanate groups reacted with hydroxyl groups of polyol, forming urethane bonds, leaving not enough free isocyanate groups to react with wood. Chemical functional groups, such as hydroxyl groups, are present on the wood surface (Rowell and Ellis 1981). Isocyanate groups in pMDI resin could react with the hydroxyl groups on wood surfaces and form urethane linkages (Yoshida et al. 1987). Moreover, the resin could cure by reacting with water in wood and the urea linkages formed to create a rigid and polar network. At an NCO/OH molar ratio of 1.0, most wood failure modes were adhesive failure, indicating weak bond strength between wood

substrates and adhesives, and some cohesive failures were observed. This was probably because the less cross-linked structure of adhesive with lower NCO content tended to fail within the adhesive material itself. At the NCO/OH molar ratio of 1.25, shear strengths were about 20 percent higher than those obtained at 1.0. The wood failure mode became adhesive failure mixed with some substrate failure, probably because at an NCO/OH molar ratio of 1.25, the cross-linked density of cured adhesives increased, and some excessive NCO groups reacted with hydroxyl groups or water in wood, forming strong urethane or urea bonds. The adhesive system at an NCO/OH molar ratio of 1.5 presented similar strength values and wood failure mode as those obtained at an NCO/OH molar ratio of 1.25. The extra excessive NCO groups at the NCO/OH molar ratio of 1.5 did not contribute further to the dry bonding strength of plywood.

At the same NCO/OH molar ratio, as the weight ratio of recycled polyol–GP730 increased from 0 to 100 percent, the bond strength increased (Table 5). Statistical analyses showed that as the weight ratio of recycled polyol increased from 0 to 100 percent, at most NCO/OH molar ratios, the shear strength increase was significant at $\alpha = 0.05$. This is probably because of the formation of a more cross-linked structure at a higher hydroxyl number of polyols resulting from a higher recycled polyol–GP730 weight ratio (Desai et al. 2003). Recycled polyol had a hydroxyl number of about 296 mg of KOH/g, which was higher than that of GP730 (225 mg of KOH/g). As the weight percentage of recycled polyol in polyol mixtures increased, the hydroxyl number of the polyol mixtures increased. Another reason may be that the recycled polyol contained a small amount of amine compounds, which might serve as reaction catalyst, so that a more fully cured adhesive structure was obtained. For the dry bonding strength, adhesives made with recycled polyol had higher strength than those made by GP730. This indicates that using recycled polyol in adhesive development had advantages over using virgin polyol in terms of shear strength.

Table 4.—Gel time of adhesives.

Recycled polyol–GP730 wt ratio	Gel time (min) at an NCO/OH molar ratio of[a]:		
	1.0	1.25	1.5
0/100	45	43	52
25/75	37	34	42
50/50	30	30	32
75/25	23	20	24
100/0	9	7	10

[a] Each gel time is the average of three replicates.

Table 5.—Bonding strength before water immersion treatment.

| Recycled polyol–GP730 wt ratio | NCO/OH molar ratio[a]: | | | | | | | | |
| | 1.0 | | | 1.25 | | | 1.5 | | |
	Strength (psi)	Failure mode	Duncan's test	Strength (psi)	Failure mode	Duncan's test	Strength (psi)	Failure mode	Duncan's test
0/100	454 (15)	A+C	D d	575 (17)	A+S	E d	587 (19)	A+C+S	E d
25/75	531 (16)	A+C	D e	623 (24)	A+S	E e	631 (20)	S	E e
50/50	571 (22)	A+C	D f	679 (17)	S	E f	670 (24)	S	E f
75/25	591 (24)	A	D f	707 (19)	S	E g	708 (25)	S	E g
100/0	634 (21)	A+S	D g	741 (27)	A+S	E h	754 (21)	A+S	E h

[a] $n = 8$. Numbers in parentheses are standard deviations. A = adhesive failure; C = cohesive failure of adhesive; S = substrate failure. Shear strengths in the same row with the same capital letter are not statistically different at $\alpha = 0.05$ based on Duncan's test; shear strengths in the same column with the same lowercase letter are not statistically different at $\alpha = 0.05$ based on Duncan's tests.

On the basis of the shear strength data before water immersion treatment, multilinear regression showed a statistically significant relationship between shear strength and recycled polyol and the NCO/OH molar ratio as follows:

$$\text{Shear strength} = 262.8 + 227.6 \times \text{NCO/OH} + 17 \times \text{recycled polyol}$$
$$(R^2 = 0.841) \qquad (3)$$

Before water immersion, the shear strength increased with the molar ratio of NCO/OH and the recycled polyol ratio. NCO/OH was the main factor to determine shear strength. Changing the molar ratio of NCO/OH had a greater impact than changing the recycled polyol ratio on plywood shear strength.

Bonding strength of adhesives after water immersion at 60°C

After the water soaking treatment at 60°C for 3 hours, the bond strength decreased (Table 6). At the same recycled polyol ratio, the bonding strengths of the plywood specimens bonded with the adhesives at an NCO/OH molar ratio of 1.0 were still the lowest among all molar ratios, which was statistically significant at $\alpha = 0.05$. The shear strength of the NCO/OH molar ratio of 1.5 was a slightly lower strength value than that obtained at NCO/OH molar ratio of 1.25; however, it was not statistically significant at $\alpha = 0.05$. This is probably because at the NCO/OH molar ratio of 1.5, the adhesive system had a higher amount of excessive NCO groups than those at the NCO/OH molar ratio of 1.25. The excessive isocyanate could not react with anything (because of a certain amount of available hydroxyl groups in polyol and wood substrate) but moisture in the air, which makes the adhesive material brittle after it hardens. Wood and cured adhesive behave differently when they are subjected to water treatment. Wood may swell when it absorbs water, whereas cured adhesive is more resistant to hygroscopic swelling. The different behaviors of those two materials during water immersion treatment could cause movements at their interface, resulting in a weaker adhesive strength.

At the same NCO/OH molar ratio, as the weight ratio of recycled polyol–GP730 increased, the bond strengths increased, reaching peak values at a recycled polyol–GP730 weight ratio of 75/25, and then decreased, which was statistically significant at $\alpha = 0.05$ in most cases. This result shows that a certain amount of polyol GP730 was helpful in

developing wet shear strength of plywood. As the weight percentage of recycled polyol in polyol mixtures increased, more cross-linked structures were formed via the reaction between isocyanate and polyols. The cured adhesives could have lost some flexibility, making the adhesive failure easier to occur, which needs further research to verify.

On the basis of the shear strength data after water immersion treatment, multilinear regression demonstrated a statistically significant relationship between shear strength and the amount of recycled polyol and NCO/OH molar ratio as follows:

$$\text{Shear strength} = 275.4 + 174.86 \times \text{NCO/OH} \times \text{recycled polyol}$$
$$(R^2 = 0.60) \qquad (4)$$

Thus, after water immersion, the shear strength increased with the molar ratio of NCO/OH and the recycled polyol ratio. NCO/OH was the main factor to change shear strength. Concerning its influence on shear strength after water immersion, the relative impact of NCO/OH, compared with recycled polyol weight ratio, was increased from 133 (227.6/1.7) (Eq. 3) to 224 (174.86/0.78) (Eq. 4) indicating that the molar ratio of NCO/OH was more crucial to plywood wet shear strength.

Bonding strength of adhesives after cyclic boiling water treatment

Table 7 shows the shear strength results after the cyclic boiling water treatment. The strengths of all adhesives significantly decreased after the treatment. The overall trends of the strength values at various NCO/OH molar ratios and recycled polyol–GP730 weight ratios were similar to those after the water immersion treatment at 60°C. However, compared with the 60°C water treatment data in Table 6, the biggest differences in boiling water treatment was that the shear strength was decreased and the shear strength differences at different levels of NCO/OH were significant at $\alpha = 0.05$, indicating that boiling water affected the differences in shear strength at different NCO/OH molar ratios. At an NCO/OH molar ratio of 1.25, the maximum shear strength was obtained. When the NCO/OH molar ratio increased to 1.5, strength decreased, but it was still higher than at the NCO/OH molar ratio of 1.0. The cyclic boiling water treatment was much more severe than the water immersion treatment at 60°C (Table 6). The wood substrate in the plywood test sample was subject to swelling when it was immersed in the water and shrinking when it was oven-

Table 6.—Bonding strength after water immersion treatment at 60°C.

| Recycled polyol–GP730 wt ratio | NCO/OH molar ratio[a]: | | | | | | | | |
| | 1.0 | | | 1.25 | | | 1.5 | | |
	Strength (psi)	Failure mode	Duncan's test[c]	Strength (psi)	Failure mode	Duncan's test	Strength (psi)	Failure mode	Duncan's test
0/100	404 (16)	A+C	D d	515 (19)	A+S	E d	507 (22)	A+C+S	E d
25/75	462 (17)	A+C	D e	553 (19)	A+S	E e	549 (20)	A+S	E e
50/50	481 (19)	A	D f	589 (26)	A+S	E fg	571 (23)	A+S	E f
75/25	511 (19)	A	D g	607 (14)	A+S	E g	598 (16)	A+S	E g
100/0	494 (18)	A	D fg	581 (15)	A+S	E f	564 (20)	A	E e

[a] $n = 8$. Numbers in parentheses are standard deviations. A = adhesive failure; C = cohesive failure of adhesive; S = substrate failure. Shear strengths in the same row with the same capital letter are not statistically different at $\alpha = 0.05$ based on Duncan's test; shear strengths in the same column with the same lowercase letter are not statistically different at $\alpha = 0.05$ based on Duncan's tests.

dried at 60°C. As discussed above, movement might occur between the wood substrate and the adhesive phases, causing an adhesive failure. The bond strength was thus lowered.

A maximum strength was obtained at a recycled polyol–GP730 weight ratio of 50/50 at three different NCO/OH molar ratios. At recycled polyol–GP730 weight ratios higher than 50/50, strength values decreased significantly because of the higher cross-link density of the cured adhesive structures. After the cyclic boiling water immersion treatment, adhesives made with polyol mixtures with slightly excessive isocyanate had a better bond performance than the other formulations. Excessive isocyanate groups could react with hydroxyl groups and water in wood, forming urethane and urea bonds. The bond strength between the wood and adhesive could be enhanced. However, the cross-link density of cured adhesive could play an important role to the bond strength. Cross-link density in a suitable range could provide enough cohesive strength and, at the same time, minimize stress between wood and adhesive interface. In this study, the cross-link density of the cured adhesives could be adjusted by changing the recycled polyol–GP730 weight ratio.

On the basis of the shear strength data after cyclic boiling water treatment, multilinear regression indicated a statistically significant relationship between shear strength and recycled polyol and NCO/OH molar ratio as follows:

$$\text{Shear strength} = 65.9 + 195.2 \times \text{NCO/OH}$$
$$- 0.56 \times \text{recycled polyol}$$
$$(R^2 = 0.334) \qquad (5)$$

Thus, after boiling water immersion, the shear strength increased with the molar ratio of NCO/OH and decreased with the recycled polyol ratio. The molar ratio of NCO/OH was the only positive factor to change shear strength, indicating that to develop durable adhesives for engineered wood products, the molar ratio of NCO/OH merits further study.

On the basis of the results of this study, PU foam wastes could be decomposed into recycled polyols and formulated into adhesives for bonding plywood with comparable or even improved performances. This could help provide a potential new way of utilizing PU wastes as well as developing new adhesive systems for plywood manufacturing, thus adding more sustainable manufacturing components into plywood manufacturing.

Conclusions

1. Adhesives with slightly excessive isocyanate groups with an NCO/OH molar ratio of 1.25 showed better bonding performance between the wood substrate and adhesive materials.
2. Adhesives prepared from recycled polyol had shorter gel time and greater dry bonding strength than those of adhesives prepared from a commercial polyol.
3. Adhesives prepared from polyol mixtures at a recycled polyol–commercial polyol weight ratio of 50/50 and an NCO/OH molar ratio of 1.25 showed the best bonding performance among all the formulations after cyclic boiling water treatment
4. Multilinear regressions showed that NCO/OH was the main factor in developing plywood shear strength.

Table 7.—Bonding strength after cyclic boiling water treatment.

| Recycled polyol–GP730 wt ratio | NCO/OH molar ratio[a]: | | | | | | | | |
| | 1.0 | | | 1.25 | | | 1.5 | | |
	Strength (psi)	Failure mode	Duncan's test	Strength (psi)	Failure mode	Duncan's test	Strength (psi)	Failure mode	Duncan's test
0/100	51 (14)	A+C	D d	211 (16)	A+S	E d	167 (19)	A+C	F d
25/75	83 (13)	A+C	D e	231 (13)	A+S	E e	201 (23)	A+S	F e
50/50	109 (15)	A+C	D f	274 (23)	A+S	E f	220 (15)	A+S	F f
75/25	66 (14)	A	D g	232 (21)	A+S	E e	158 (21)	A	F d
100/0	23 (10)	A	D h	151 (20)	A	E g	74 (14)	A	F g

[a] $n = 8$. Numbers in parentheses are standard deviations. C = cohesive failure of adhesive; A = adhesive failure; S = substrate failure. Shear strengths in the same row with the same capital letter are not statistically different at $\alpha = 0.05$ based on Duncan's test; shear strengths in the same column with the same lowercase letter are not statistically different at $\alpha = 0.05$ based on Duncan's tests.

Acknowledgments

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