Effect of isocyanate index on shear strength plywood properties using *Acacia mangium* polyurethane-based adhesive

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Abstract. Polyurethane adhesive for wood bonding were prepared from the mixture of *Acacia mangium* (AM) polyol and 4,4'-methylene diphenyl diisocynate (pMDI). In this study, *Acacia mangium* polyurethane (AMPU) adhesives were prepared by polymerization between pMDI and AM polyol. Various NCO/OH ratios of AMPU adhesives were used to fabricate 3-ply plywood from *Eucalyptus wyrai* veneers. The effect of different NCO/OH ratios: 1:4, 1:6, 1:8, 2:0, 2:2, 2:4 and 2:6 on lap shear strength and chemical resistance in cold water, hot water, sulfuric acid solution (pH2) and sodium hydroxide solution (pH12) were studied. The commercial PU adhesives were used for comparison purposes. The results show that PU adhesives prepared from pMDI with AM polyol with NCO/OH ratio at 2.4 have higher lap shear strength and chemical resistance by only showing slight degradation (2-8%) compared to commercial PU wood bonding adhesive.

1 Introduction

Polyurethane (PU) is a flexible polymers, widely utilised in a variety of industries, including wear, construction, automobile, and aerospace. The polyols, which are mostly made from non-renewable fossil raw materials, are the essential raw materials for the industrial manufacturing of polyurethanes. Concern of negative effects on the environment and its depletion, were driving forces behind the search for alternative sources for polyol production including agricultural wastes [1], cellulosic waste [2], vegetable oils [3, 4], sawdust [5, 6, 7] and palm oil [8]. Vale *et al.* [9] successfully obtained bio-polyol from cork dust whilst Ye *et al.* [10] lucratively converted 99% of bamboo shoot into polyol.

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PU adhesives are prepared by reacting a low molecular weight of polyol with isocyanate in thepresence of additives such as, curing agent and catalyst. The polymer and isocyanate are combined in two-components PU adhesive before being applied to the adherends. According to Sahoo *et al.*, [3], when producing PU adhesive, the ratio between isocyanate to polyol is vital [3] and the ratio of the actual amount of isocyanate utilised to the theoretical equivalent amount multiplied by 100 is known as the "isocyanate index,". One equivalent isocyanate is equal to one comparable OH group in a theoretical equivalent amount and it significantly affects the mechanical and structural properties of PU. The stiffness and crosslinking density of materials typically improved by high NCO/OH ratio [1, 11].

In this study, *Acacia mangium* polyurethane-based adhesive were prepared by varying the ratio between *A.mangium* polyol and pMDI (NCO/OH 1.4 - 2.6). The adhesive produced were applied onto *Eucalyptus wyrai* veneers surfaces and converted into 3-ply plywood. The effect of *A.mangium* PU-based adhesive at different isocyanate index on lap shear strength and chemical resistance of plywood were evaluated in addition to optimal NCO/OH ratio was determined.

2 Material and methods

2.1 Materials

AM polyol was obtained through a liquefaction process following Palle *et al.* [12] method. 4,4’-methylene diphenyl diisocyanate (pMDI), sulfuric acid, sodium hydroxide and commercial PU adhesive were purchased from an authorized seller and were used as received.

2.2 Preparation of AMPU adhesives

This method was followed Ang *et al.* [8] with some modifications. At room temperature, the AM polyol and pMDI were mixed at different NCO/OH ratio (1:4 to 2:6) and vigorously stirred for 2 min at 200 rpm using a mechanical stirrer before applied onto veneer.

2.3 Fabrication of Plywood

Three-ply plywood was fabricated using *Eucalyptus wyrai* veneers (310 mm x 310 mm x 1.5 mm) bonded with AMPU adhesive at different NCO/OH ratios by using single glue line method, AMPU adhesive was applied onto veneer surface with glue spread of 180 g/m^2. Plywood was pressed for 24 h at room temperature with a specific pressure of 10 kg. Plywood was then cut into sizes for testing after conditioned at room temperature for a week. Plywood bonded with commercial PU adhesives was also prepared at glue spread rate of 180 g/m^2 and used as control.

2.4 Lap shear strength properties

Lap shear strength test were measured following JAS 233:2003 with size of 80 mm x 25 mm in length and width (Figure 1). The lap shear strength was determined by Gotech Universal Testing Machine and the pull rate of 1 mm/min. A total of 60 samples were used for each parameter.

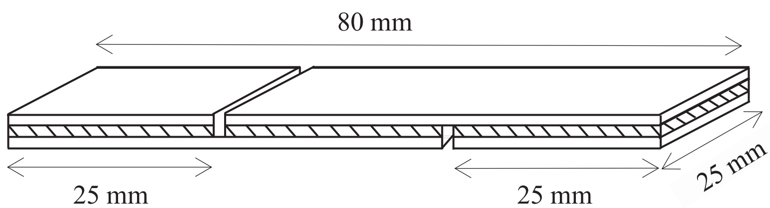

Fig. 1. Sample dimensions for the 3-ply plywood lap shear strength test.

2.5 Chemical resistance

AMPU adhesive prepared at different NCO/OH ratio to study its endurance towards hydrolysis in various circumstances: cold water, boiling water, sulfuric acid (H_2SO_4) solution (pH2) and sodium hydroxide (NaOH) solution (pH12) and conducted following Ang *et al.* [8]. Plywood bonded with AMPU adhesive at different NCO/OH ratio were divided into four groups: (1) *Cold water* – Sample was submerged in distilled water for 24 h. (2) *Boiling water* - Sample was submerged in boiling water for 1 h. (3) *Sulfuric acid solution (pH2)* – Sample was immersed in an acidic solution at 80 º C for 1 h. (4) *Sodium hydroxide (pH12)* - Sample was immersed in an alkaline solution at 80 º C for 1 h. All samples (all conditions) were dry at room temperature for 24 h before the lap joint strength were measured.

2.6 Data analysis

Statistical Analysis Software (SAS) were used to analyse the data. Analysis of variance (ANOVA) with mean separation using least significant difference (LSD) were carried out to evaluate the effect of different NCO/OH ratios on shear strength plywood panel properties.

3 Results and discussion

3.1 Lap shear strength of plywood panel bonded with AMPU adhesive at different NCO/OH ratio

The lap shear strength of plywood bonded with AMPU adhesive depends significantly on the NCO/OH ratio. The lap shear strength of plywood was increased with increasing NCO/OH ratio to a specific ratio (Table 1). Plywood with NCO/OH 1.4 showed the lowest lap shear strength which is 0.37 N/mm^2, whereas the highest was NCO/OH 2.4, 2.28 N/mm^2. The ANOVA results revealed that different NCO/OH ratio of AMPU adhesive did affect the lap shear strength of plywood at $p \leq 0.05$. The increment of microphase separation in the co-polymers might correspond to the high lap shear strength at high isocyanate index. According to Palle *et al.* [11] and Jiang *et al.* [13], the formation of urea increased as the NCO/OH ratio enhanced, leading to a stronger hydrogen-bonded urea and urethane hard segment in the network. The interconnectivity among the hard segments might correspond to the high lap shear strength of plywood at high isocyanate index. Nevertheless, the lap shear strength of plywood had reduced to 1.30 N/mm^2 after rising NCO/OH ratio to 2.6. The free unreacted isocyanate group tends to form more allophanate linkage with the urethane bond at high NCO/OH ratio caused the adhesive layer to be brittle and crack easily when shear strength force is applied [8, 14-15], and these might be the reason for the lessening of lap shear strength of plywood at NCO/OH ratio 2.6. Therefore, the optimum lap shear strength was 2.28 N/mm^2 using AMPU adhesive at NCO/OH 2.4.

The lap shear strength of plywood using AMPU adhesive at NCO/OH 1.4 to 2.0 is 26%

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76% less than PUC adhesive. Low NCO/OH ratio prevented the formation of a strong urethane network due to low NCO groups to interact with the hydroxyl groups of the polyol [5, 8, 13].

Table 1. Lap shear strength of plywood bonded with AMPU adhesive at different NCO/OH ratio.

NCO/OH	Shear strength (N/mm^2)
PUC	$1.67 \pm 0.52^{a*}$
1.4	0.37 ± 0.10^{b}
1.6	0.39 ± 0.12^{b}
1.8	1.13 ± 0.17^{c}
2.0	1.24 ± 0.07^{cd}
2.2	1.60 ± 0.44^{ad}
2.4	2.28 ± 0.55^{e}
2.6	1.30 ± 0.22^{acd}

*Means with the different letters ^{a,b,c,d,e} in the same column were significantly different ($p \leq 0.05$).

3.2 Chemical resistance of AMPU adhesive at different NCO/OH ratio

Figure 2 shows the effect of chemical hydrolysis on lap shear strength of plywood panel bonded with AMPU adhesive at various NCO/OH. In general, the results shows that plywood bonded with AMPU at various NCO/OH ratios were resistance towards NaOH solution (pH12) and cold water. The lap shear strength enhances until NCO/OH 2.4 before reduce slightly. As can be seen, a minor decrease in lap shear strength in alkali and cold-water solutions compared to acid and boil-water conditions. According to Daneshvar *et al.* [5], the polyester polyols were easily hydrolysed under acidic condition, resulting in a decrease in lap shear strength in the H_2SO_4 solution. In addition, the mechanical strength of the adhesives is weakened by severe hydrolysis such as boiling condition [8, 16] and this scenario might correspond to the decrement in lap shear strength of plywood panel after immersing samples in boiling water for 1 h.

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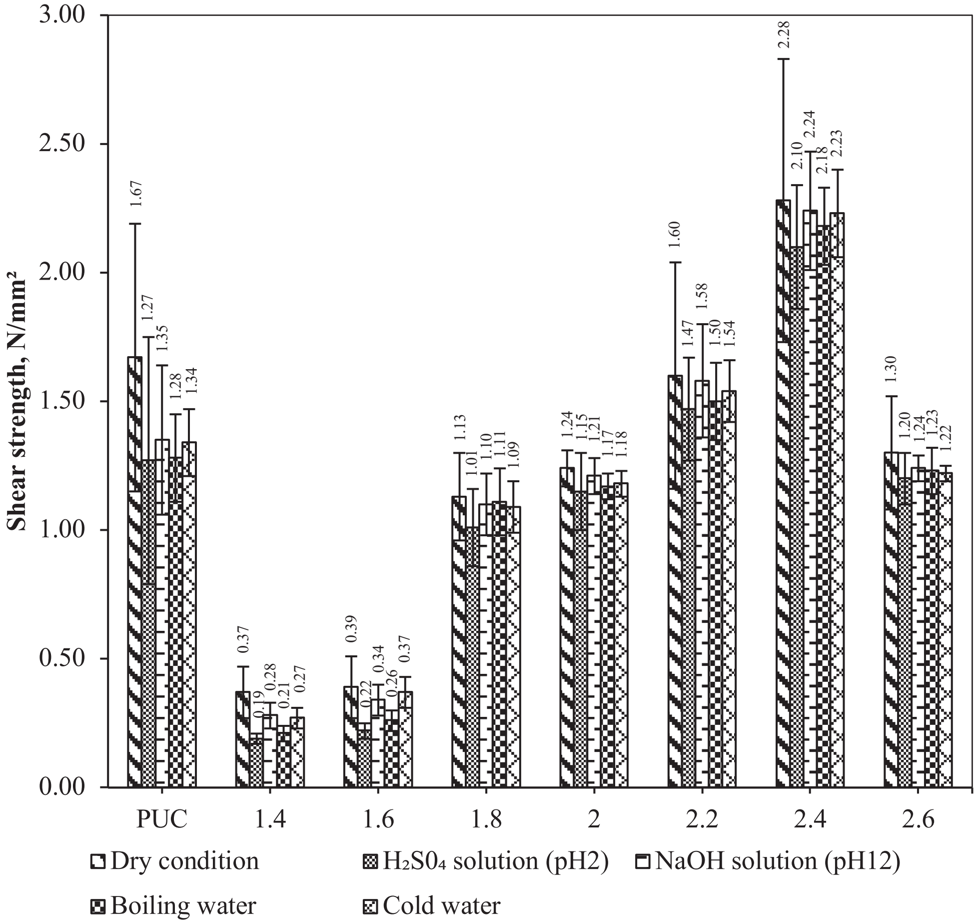

Fig. 2. Effect of chemical hydrolysis on the lap shear strength of plywood bonded with AMPU adhesive at various NCO/OH ratios.

4 Conclusion

Increasing NCO/OH ratio of AMPU adhesive substantially intensified the formation of hard segment. High lap shear strength of plywood panel at high NCO/OH ratio reflecting the improvement of rigidity. The optimal lap shear strength of plywood was 2.28 N/mm^2 which bonded with AMPU adhesive with NCO/OH 2.4. Too much allophanate linkages with urethane at high NCO/OH ratio (>2.4) might be responsible to the decrement of lap shear strength of plywood panel. The findings of this study also indicate that plywood bonded with AMPU adhesive are resistance towards NaOH and cold water compared to boiling water and sulfuric acid.

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