Bonding Performance of Natural Rubber-Based Aqueous Polymer Isocyanate as Plywood Adhesive

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Abstract. Natural rubber has long been known as biopolymer that can be used as an adhesive. The material is abundantly available in Indonesia. Aqueous Polymer Isocyantae (API) adhesive mainly consists of water soluble polymer and emulsion, which are polyvinyl alcohol (PVA) and polystryrene-co-butadiene rubber (SBR) latex, etc., with isocyanate compounds (pMDI and dibutyl-phtalate 30%) as a crosslinking agent. The aim of this research was to study the bonding performance of Aqueous Polymer Isocayanate (API) adhesive that was prepared from natural rubber latex (NRL) and PVA as base polymers and diisocyanate as crosslinking agent. Adhesive formulas with different ratios and total solid (TS) contents of base polymers (NRL/PVA 0.5-10.7; TS 27.5-40.0%) were prepared. The isocyanate crosslinker was added at the level of 15 wt% of the base polymers. The adhesives were applied on the surface of red meranti (*Shorea* sp.) veneers (250 x120 x1.5 cm face and back; 250 x120 x 2.1 cm core) at a glue spread rate of 300 g/m^2 (double glue line). The veneers were pressed at 14 MPa, room temperature for 24 hours, and plywood samples were conditioned for a week and then they were tested for their bonding performance using cyclic boiling test. The effects of the amount of crosslinking agent and glue spread rate on bonding performance were also studied. Results of this study showed that the ratio of base polymer components (NRL/PVA) affected the bonding performance of the adhesive. Higher bond strengths were observed at ratios of NRL/PVA <4 and >10 and at total solid content between 38 and 43%. Bond strengths are increased due to increase of corsslinker amount. Glue spread rate also influenced bonding strength, and the highest bonding strength was observed at glue spread rate between 250 and 350 g/m^2.

Keywords: Isocyanate crosslinker; natural rubber latex; plywood adhesive; polyvinyl alcohol; shear strength

Introduction

Wood adhesive is one of important parts in wood panels or wood composites industries. It has a great contribution to the price of wood panels, because it can reach as much as 80% of the total production cost of the panels. The most widely used wood adhesive recently are formaldehyde bearing adhesives, such as urea formaldehyde (UF), phenol formladehyde (PF), and melamine formaldehyde (MF), due to their low cost. Nowadays global market of wood panels is very concern with environmental issues, such as formaldehyde emission; thus, the market demands the products that have very low or no formaldehyde emission. Some developed countries, such as Japan and the United States have already produced non formaldehyde wood adhesives, for example the polymeric methylene diphenyl diisocyanate (pMDI) and aqueous polymer isocyanatae (API) adhesives. API adhesive mainly consists of water soluble polymer and emulsion, which are polyvinyl alcohol (PVA) and polystryrene-co-butadiene rubber (SBR) latex, etc., with isocyanate compounds (pMDI and dibutyl-phtalate 30%) as a crosslinking agent [8]. By changing base polymers or amount of crosslinking agents, a wide range of API adhesives can be formulated with various physical properties [9]. API adhesives have good adhesive properties at ambient temperature and excellent resistance to warm/boiling water, is friendly to the environment, and is widely used in the timber-processing industry [10]. According to Taki *et al*. (1994) [8], tensile strength of Birch wood bonded with API adhesive and tested at different temperatures (-100 to 200^{o}C) ranged from 3 to 15 MPa. Hongjiu *et al*. (2006) [10] reported that Rosewood specimens glued by API adhesive and tested at room temperature had compression shear strength ranged from 9 to 15 MPa, while those tested at warm and boiling water ranged from 6 to 9 MPa and from 4 to 5.8 MPa, respectively.

The above commercial wood adhesives are usually made of petroleum based materials, which are non renewable resources. In this study natural rubber, which is a renewable resource, was used as a backbone polymer in the preparation of API adhesive.

Natural rubber is characteristically low in adhesion and cohesion, has poor resistance to stress and heat and fair resistance to moisture, but it has an excellent resistance to organisms and it can make instant bond with a relatively low pressure [1]. Our previous studies show that natural rubber-based adhesive can be mixed well with isocyanate based adhesive and used for gluing some wood panles, such as exterior grade plywood and structural laminated wood [5-7] and could serve as one of base polymers in preparing API adhesives. The use of this adhesive could produce plywood of exterior grade quality.

Unfortunately, these studies only used one NRL/PVA ratio and has not yet come up with the best ratio between rubber as backbone polymer and PVA as hydroxyl or alcohol bearing compound. In fact, this might be very important in producing a good bond strength, since the isocyanate crosslinker is an electrophile which is very reactive toward a variety of nucleophile, such as alcohols, amines, and even water. Besides that, the application of our synthesized API adhesives has not been tried for production of wood panels that should be cured at room temperature. In fact, there is increasing demand of wood adhesive that can be cured at room temperature, since it consumes less energy in wood panel production and can be used by small scale wood panel or furniture industry. The result of this research hopefully will give significant contribution to the development of wood panel industry, especially small scale wood panel industry in Indonesia and regional Asia by providing technology of production of non formaldehyde wood adhesive that can be cured at room temperature of tropical climate with good bonding strength.

Experimental

Materials

Natural rubber latex was purchased from Balai Penelitian Perkebunan Sembawa, South Sumatera. The concentrated latex (61-62% total solid content) was diluted with water to approximately 40, 45, 50, 55 and 60% total solid content. Table 1 shows how much concentrated NRL and how much water should be added to make 1000 mL diluted NRL of certain total solid content. For example, in order to get 1000 mL diluted NRL with total solid content of 40%, as much as 650.41 mL of concentrated NRL was added with 349.59 mL of water. The PVA, purchased from local market in Bogor, was dissolved in warm water to get 15, 20 and 25% total solid content. As much as 150, 200 and 250 g of PVA were dissolved in about 800 mL warm water in three 1000 mL beaker glasses. After the polymer was dissolved completely, each polymer solution was transferred into a 1000 mL volumetric flask, and some more warm water was added until the volume reached 1000 mL. The isocyanate crosslinking agent was a commercial isocyanate crosslinker for API adhesive produced by Koyo bond, Bogor, Indonesia, while the other chemicals were purchased from domestic chemical suppliers in Bogor and Jakarta. Veneers of meranti and albizzia used for the preparation of plywood were obtained from East Kalimantan and West Java, respectively.

Table 1 Preparation of diluted NRL from concentrated NRL.

Expected TS of diluted NRL (%)	TS of concentrated NRL (%)	Vol. of diluted NRL (mL)	Vol. of concentrated NRL (mL)	Added water (mL)
40	61.5	1000	650.41	349.59
45	61.5	1000	731.71	268.29
50	61.5	1000	813.01	186.99
55	61.5	1000	894.31	105.69

60	61.5	1000	975.61	24.39

Methods

Preparation and analysis of adhesives

In order to study the effects of ratios of NRL/PVA, the base polymers of API adhesive were prepared from the above NRL and PVA of different total solid contents to obtained ratios of NRL/PVA ranging from 0.5 to 10.7 with total solid content of base polymers 30, 35 and 40%. The detail of adhesive formulas is presented in Table 2 (without grey highlight). The isocyanate crosslinking agent was added at the level of 15% of the weight of base polymers. To investigate the effect of solid content on adhesive bond strength experiment was conducted at base polymer solid content between 27.5 and 37.5 with narrow range of NRL/PVA ratio to minimize the influence of NRL/PVA ratio on the result of the experiment (Table 2 with grey highlight). Further experiment was conducted to study the effect of crosslinking agent level on bond strength of plywood. Thus, the crosslinking agent was added at the level of 7.5, 10, 15, 17.5 and 20% of base polymer at NRL/PVA ratio of 3.3 with total solid content of base polymer 32.5%. Each adhesive was measured for its total solid content using gravimetric method. Thermal analysis using Differential Scanning Calorimetry (DSC) was also conducted for some adhesives to see the effects of NRL/PVOH ratio and crosslinking agent level on the adhesives. As much as 3 mg of sample was placed into an aluminum crucible and heated from -100°C up to 200°C with heating rate of 10°C/min. Nitrogen was used as purge gas at 20 mL/min.

Preparation and testing of plywood

The adhesives were spread on the surface of red meranti (*Shorea* sp.) veneers (250 x 120 x 2.1 mm core; 250 x 120 x 1.5 mm face & back) or mixed of red meranti and albizzia (*Paraserianthes falcataria*) veneers of the same sizes for face & back and core, respectively, at the glue spread rate of 300 g/m^2 DGL (double glue line). The veneers with adhesives were cold pressed at 14 MPa for 24 hours. The plywood produced was conditioned at room temperature for about two weeks, then they were measured for their bond strength after cyclic boiling [11] using Shimadzu Universal Testing Machine. Eight test pieces were prepared for each replication of treatment. The test pieces were immersed in boiling water for 4 hours, then they were dried at 60°C for 20 h. Afer that, the test pieces were immersed in boiling water for 4 h, and then immersed in water at room tempereature to cool down. Bond strength measurement was conducted in a wet condition. Shear strength was determined at the maximum load.

To study the effect of glue spread rate on adhesive bond strength, the adhesive was spread at the level of 200, 250, 300, and 350 g/m^2 DGL using the same veneers and other plywood sample preparation and testing procedures as previously explained.

Table 2 Adhesive formulas prepared from NRL and PVA with isocyanate crosslinker.

Ratio	NRL		PVA		Base Polymers		Crosslinker
NRL/PVA*	Weight (g)	TS (%)	Weight (g)	TS (%)	Weight (g)	TS** (%)	(g)
9.0	40.00	45	10.00	20	50	40	7.5
5.4	37.50	45	12.50	25	50	40	7.5
3.0	25.00	60	25.00	20	50	40	7.5
2.2	25.00	55	25.00	25	50	40	7.5
1.8	21.50	60	28.50	25	50	40	7.5
10.7	40.00	40	10.00	15	50	35	7.5
6.0	37.50	40	12.50	20	50	35	7.5
3.7	25.00	55	25.00	15	50	35	7.5
2.5	25.00	50	25.00	20	50	35	7.5
1.3	20.00	50	30.00	25	50	35	7.5
4.0	30.00	40	20.00	15	50	30	7.5
3.0	25.00	45	25.00	15	50	30	7.5
2.0	25.00	40	25.00	20	50	30	7.5
1.0	12.50	60	37.50	20	50	30	7.5
0.5	10.00	50	40.00	25	50	30	7.5
4.0	25.00	60	25.00	15	50	37.50	7.5
3.7	25.00	55	25.00	15	50	35.00	7.5
3.3	25.00	50	25.00	15	50	32.50	7.5
3.0	25.00	45	25.00	15	50	30.00	7.5
2.7	25.00	40	25.00	15	50	27.50	7.5

*(TS of NRL/100 × Weight of NRL)/(TS of PVA/100 × Weight of PVA)
**((TS of NRL/100 × Weight of NRL) + (TS of PVA/100 × Weight of PVA))/Weight of Base Polymer

Results and Discussion

There are some potential reactions can occur during the adhesion with API adhesive, for example the removal of water from the glue line; the formation of a glue film resulted from the coalescence of the emulsion particles of the adhesive; the reactions of NCO group in isocyanate crosslinker with water, with other NCO groups, with hydroxyl groups in PVA or wood cell walls, or with other functional groups in the emulsion polymer [12]. Since isocyanate is very reactive with water, the reaction of water and isocyanate should be considered when bonding wood composite with isocayanate adhesive [13]. In order to obtain a good bond quality, it is important to make a proper mixing of base polymers and proper amount of isocyanate crosslinker.

Effect of NRL/PVA ratio on adhesive bond strength

Scattered diagram which correlates between ratio of NRL/PVA and shear strength of plywood bonded with the synthesized API adhesive (Figure 1A) shows that the ratio of base polymer components (NRL/PVA) affected bonding performance of the adhesive. Lower ratios of NRL/PVA (<4) tended to produce adhesive of higher bond strength, which could meet JAS requirement (> 0.7 N/mm^2). Bond strength of the adhesives tended to decrease due to increase of NRL/PVA ratio. This might be due to the lower hydroxyl group available, which is important in curing or hardening process of the adhesive. The glass transition temperature (*Tg*) measurements of some samples supported the result of bond strength measurements. The samples having NRL/PVA ratio of 1.3 had much higher *Tg* (60.87^{o}C) than that having NRL/PVA ratio of 3.7 with *Tg* value of 34.35^{o}C. Similar phenomenon was also reported in the gluing of rosewood using API adhesives with different content of PVA in the adhesive mixtures [10], which showed that shear strength and percent of wood failure were increased with increasing amount of PVA up to certain critical value of PVA content, then shear strength and wood failure were decreased when PVA content higher than the critical value. The study suggested that when PVA content was less than the critical value, there was increases of urethane bonds due to increases of hydroxyl groups from PVA. When there was more hydroxyl groups, the isocyanate groups were not enough for reaction with the excess of hydroxyl groups from PVA. However, in our study there was an increase of bond strength when the ratio of NRL/PVA was >10, and the bond strength could meet JAS requirement. The Tg of this sample (39.66^{o}C) was higher than that of NRL/PVA 3.7, but lower than NRL/PVA ratio 1.3. This phenomenon needs further elucidation.

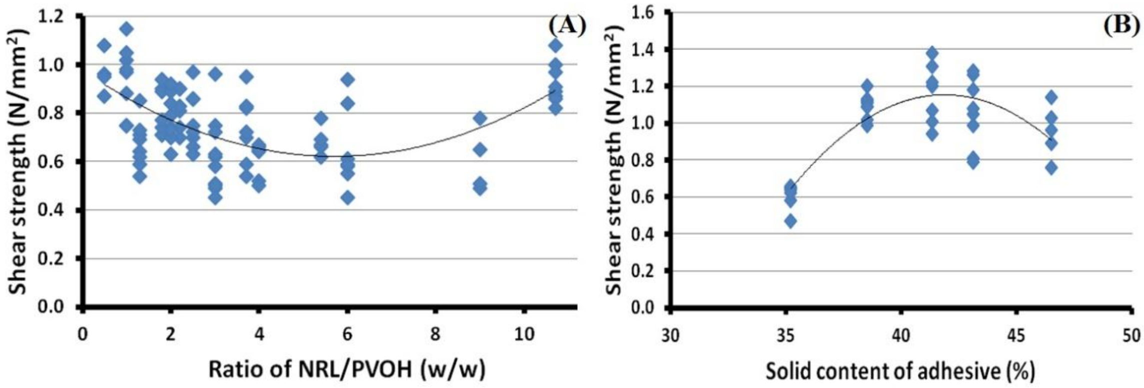

Figure 1. Relationship between shear strength and ratio of NRL/PVA (A) solid content of adhesive (B).

Effect of solid content on adhesive bond strength

Bond strength of adhesive increased due to increase of adhesive total solid (TS) content up TS of about 42%, then decreased at higher TS content (Figure 1B). When adhesive of low TS used, there was less adhesive applied on wood surfaces, caused not enough adhesive on the wood surfaces to make a good adhesion. On the other hand, too high solid content made the adhesive had lower mobility and made the particles harder to penetrate into wood pores, or caused uneven distribution of the adhesive on the wood surfaces, which in turn reduced the bond strength.

Effect of crosslinker amount on adhesive bond strength

The isocyanate crosslinker was usually used at the level of 15% of the weight of base polymers. The increase of the amount of isocyanate crosslinker tended to increase bond strength of API adhesives prepared from NRL and PVA (Figure 2A). This result was not in agreement with studies on API adhesives prepared from polyvinyl acetate (PVAc) latex, which contain certain amount of PVA, where excessive of isocyanate crosslinker could weaken the bonding of the adhesives on wood samples [10]. The study suggested that the increase of isocyanate crosslinker above the critical limit caused the PVAc homopolymer fairly hard, brittle, and less elastics; thus, weaken the bond strength. In our study we used NRL which had a good elastic property, so that it could stand the detrimental effects of excessive isocyanate crosslinker on the glue line. Unfortunately, the DSC thermograms (Figure 3) as well as *Tg* of the adhesive with crosslinking agent of 5, 10 and 15% (38.68; 37.75; 37.38^{o}C) did not give clear contribution for explaining the effects of the amount of crosslinker on bond strength of the adhesives.

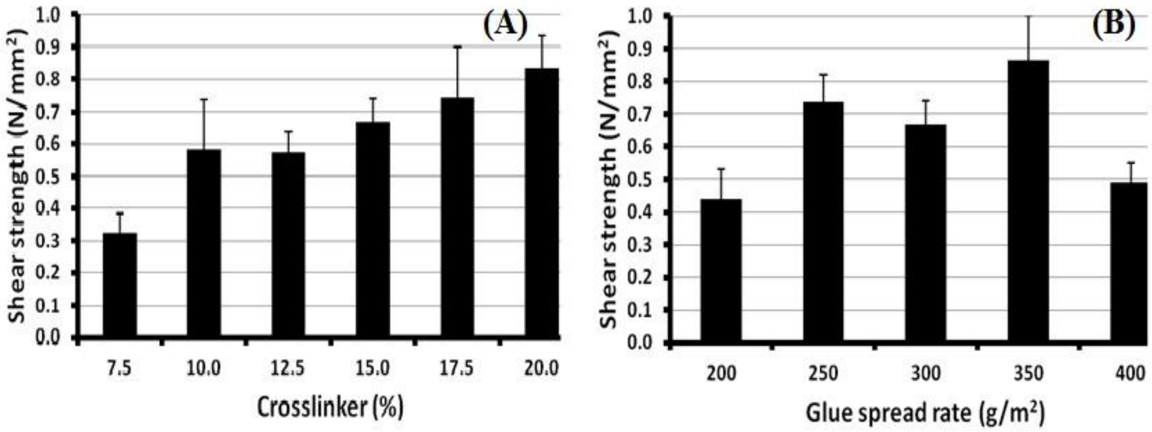

Figure 2. The effect of crosslinker amount (A) and glue spread rate (B) on adhesive bond strength.

Effect of glue spread rate on adhesive bond strength

The effect of glue spread rate on bond strength of adhesive is shown in Figure 2B. The bond strengths of the adhesives were increased with increasing of glue spread rate up to glue spread rate of 350 g/m^2, but then decrease at higher glue spread rate. This might be due to the excessive amount of the adhesive on the glue line, which might influence the solidification of the adhesive in the glue line during the pressing process. As we know, the final step of an adhesion process is solidification of the adhesives in the glue line. In this case since the adhesive is solidify due to combination of chemical reaction and loss of water, too much adhesive in the glue line also means that there was also too much water to be evaporated to cure or harden the adhesive; thus the adhesive was not solidify properly and weaken the bond strength.

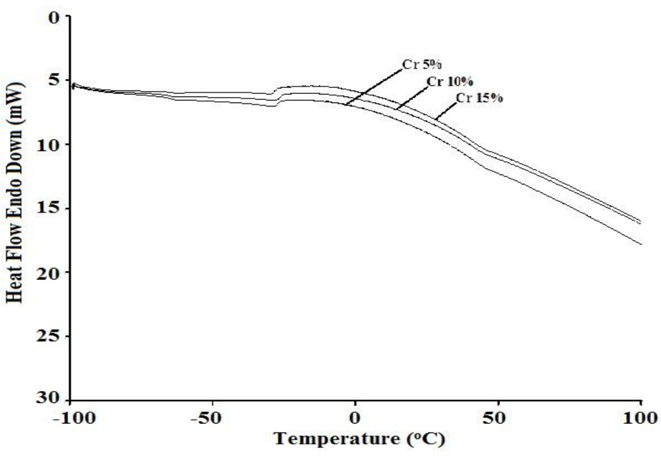

Figure 3. DSC thermogram of API adhesives with different amount of crosslinking agent.

Conclusion

Aqueous Polymer Isocyanate (API) adhesive could be prepared from natural rubber latex and polivinyl alcohol with isocyanate crosslinker and applied as plywood adhesive. The adhesive has good bond strength, which could meet standard for exterior applications. The amount of hydroxyl groups in the base polymers, solid content, the amount of isocyanate crosslinker, and glue spread rate of adhesive in plywood preparation affected bond strength of the adhesive. In order to produce adhesive that could meet the standard for exterior application, it is suggested to use tha ratio of NRL/PVA <4 or >10 as base polymers and 15-17.5% isocyanate crosslinker with adhesive loading between 250 and 350 g/m^2.

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