J. of Korean Oil Chemists' Soc.,
Vol. 30, No. 3. September, 2013. 551~559
ISSN 1225-9098 (Print)
ISSN 2288-1069 (Online)
http://dx.doi.org/10.12925/jkocs.2013.30.3.551

Synthesis of Wood Adhesive Derived from the Milk Protein and the Blocked Isocyanate

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(Received May 21, 2013 ; Revised July 5, 2013 ; Accepted July 6, 2013)

Abstract : To investigate the adhesion effect of sodium bisulfite content in making blocked isocyanate, wood adhesive PB-1, PB-2, PB-3 and PB-4 containing sodium bisulfite content of 15%, 22.5%, 30% and 37.5% were synthesized respectively. As a result, when the amount of sodium bisulfite increased in adhesives, the tensile strength was found to be proportionally increased. The final adhesive mixtures were manufactured using a two-components system which are prepared by mixing two separate protein and BI solutions due to the precipitate in the adhesives. As PVA was added to adhesives to increase tenacity, the plywood dehiscence phenomenon after cold pressing process was declined. By addition of PVA, the tensile strength was improved up to 6.5~7kgf/cm^2 with BI/protein ratio from 1:6 up to 1:8. Phase separation between milk fat and aqueous layer was disappeared after addition of emulsifier, Tween 20. Additon of Tween 20 showed tensile strength up to 5 ~ 6.5 kgf/cm^2 at NCO/protein ratio of 1:12 ~ 1:14 without phase separation.

Keywords : Wood Adhesive, Bisulfite Blocked Isocyanate, Formaldehyde-free Adhesives, Biopolymer.

1. Introduction

These days, most adhesives in furniture industry are synthesized from petroleum based sources. The synthetic adhesives have many advantages such as reasonable water resistance, good adhesion and low cost. However it arises significant environmental problems associated with the use of formaldehyde based adhesives such as urea-formaldehyde(UF) and phenol-formaldehyde(PF)[1-2]. In other hands, natural glues derived from protein and carbohydrates are environmentally-friendly and renewable materials at reasonable costs to compete with synthetic adhesives and meet stringent performance requirements[3-8]. Their utilization is currently limited because of low durability and especially low water resistance. To overcome such problems, research on natural material-based adhesives has been directed toward developing new hybrid polymeric adhesives adding dialdehyde, epichlorohydrine (ECH)5, UF or PF etc for chemical cross-linking[9-11]. Polyurethane adhesives for bonding wood made from potato starch/natural oil-based polyol and TDI are

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also reported by Desai et al[12]. Diisocyantes used for polyurethane adhesives specifically attract our interest because of unique characteristics, such as amenable curing speeds, formaldehyde emission-free, good weather resistance and excellent adhesion[13]. Despite such excellent properties of isocyanates as curing agents, they have a huge disadvantage to use with natural bio-materials together. For example, proteins and carbohydrate are soluble in water whereas Isocyanates are very sensitive to moisture so that they form polyurea and biuret-type structures which compete strongly with the urethane formation.

In this study, milk protein as major bio-materials has been chosen because it is very cheap and can be more suitable raw materials than carbohydrates since proteins have various functional groups that may provide more cross-linking reactions with curing reagents. As cross-linking agents, water-soluble blocked isocyanates (BI) were synthesized. Water-soluble blocked isocyanates (BI) were prepared from pMDI and sodium bisulfite (NaHSO3) aqueous solution[14]. Upon heating BI, it undergoes elimination of sulfite ions to retain free isocyanate functional groups for chemical cross-linking between proteins and wood panels.

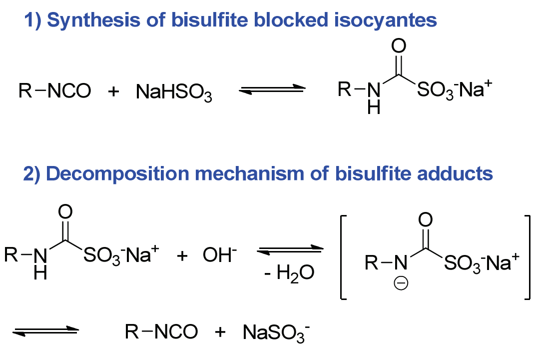

Fig. 1. Possible reaction mechanism of formation of bisulfite blocked isocyante and decomposition of bisulfite adducts.

Possible synthetic reaction mechanisms of bisulfite blocked isocyanate when aqueous solutions of sodium bisulfite ($NaHSO_3$) and isocyante reacts are shown in Fig. 1. The sodium bisulfite adducts is known to decompose forming free isocyanates at high pH or upon heating during curing process. Then the regenerated isocyanates may cross-link between functional groups of proteins and wood structure.

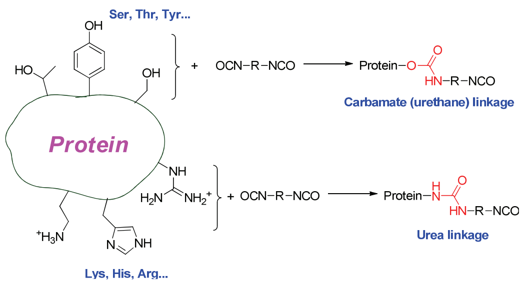

Fig. 2. Illustration of chemical reactions between proteins and isocyanates.

Most proteins consist of linear polymers built from series of up to 20 different amino acids which possess variable side chains with functional groups such as hydroxyl groups, amine groups and thiol groups etc. When hydroxyl groups from amino acids such as serine, threonine and tyrosine react with isocyanates, carbamate groups (so called urethane bonds) are formed, whereas urea linkages are produced when amine groups of lysine, histidine and arginine react with isocyanates. Milk proteins are renewable and low cost bio-materials so that they can be a good source of natural adhesives for wood by combination of water-soluble blocked isocyanates. However, there has been no researches about wood adhesives made of milk proteins and sodium bisulfite blocked isocyanate until now. The present study focused on the synthesis of bisulfite blocked isocyanates and investigation of adhesion effect from diverse ratio of BI and milk proteins mixture using universal test machine to see if the bio-material such as milk protein is suitable renewable source for wood adhesives.

2. Materials and Method

2.1 Materials

Milk protein was a gift from Samick-Milk-Processing co. and polymeric methylene diphenyl-diisocyanate(pMDI, M5S) was a gift from BASF co.. Sodium bisulfite and Poly Vinyl Alcohol 500 were purchased from OCI co.. Tween 20 was purchase from Bio Basic co. and used without further purification.

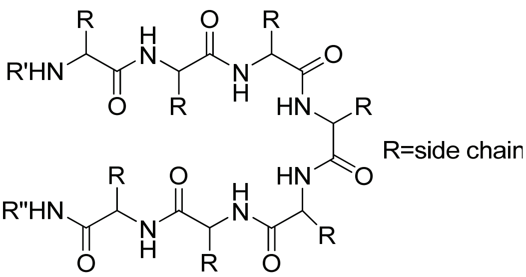

Fig. 3. Peptide bonds of milk proteins.

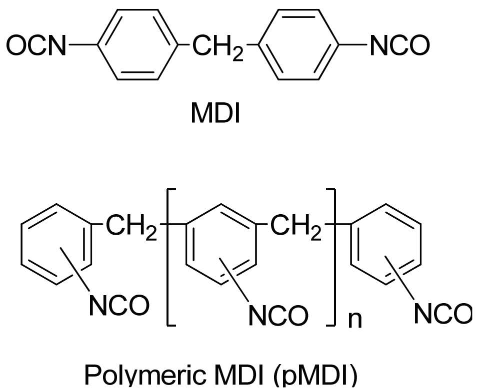

Fig. 4. Chemical structure of MDI and pMDI as a cross-linking agent

Milk protein can be purchased from Samick-Milk-Processing co. with the retail price of less than 30,000 won per 25kg package. General chemical structure of the milk proteins or peptides has shown in Fig. 3. Peptide bonds are covalent bonds formed between amino acids. Each amino acids has side chain that can be reactive toward a variety of isocyanates to form chemical bonds.

The properties of The pMDI (Lupranate M5S) such as NCO content, viscosity and density, are presented in Table 1.

Table 1. Physicochemical properties of pMDI, Lupranate M5S

Item	Unit	Content
Appearance	-	Brown liquid
NCO content	wt.%	31.4~32.6
Viscosity	cps	35 ~ 60
Density	g/㎤	1.23
Acidity as HCl	wt.%	<0.06
Total chlorine	wt.%	<0.5
Vapor pressure at 25℃	mbar	$<10^{-4}$
Flash point	℃	>200

2.2. Application and testing

The test material we used was lauan rotary veneer, which has thickness of 1.0 ~ 1.5 mm, the range of 8-10% moisture and bulk density of 0.45g/cm^2 or more. The previously prepared adhesive mixture was applied onto the surface of three pieces of the plywood (300mm x 300mm x 2.7mm) to be glued to the amount of 120g ~ 170g/m^2. Before inserting the pieces of plywood in a hot press, it was pressed at a pressure of 490 to 981kPa for 2 hours at room temperature. Then the plywood was inserted in a hot press and cured at 130 ± 2℃ under 490 ~ 981kPa (5 ~ 10kgf/cm^2) pressure for about 3 minutes. The plywood was cut into the samples (80mm x 25mm) according to the KS M 3701 as shown in Fig. 6.

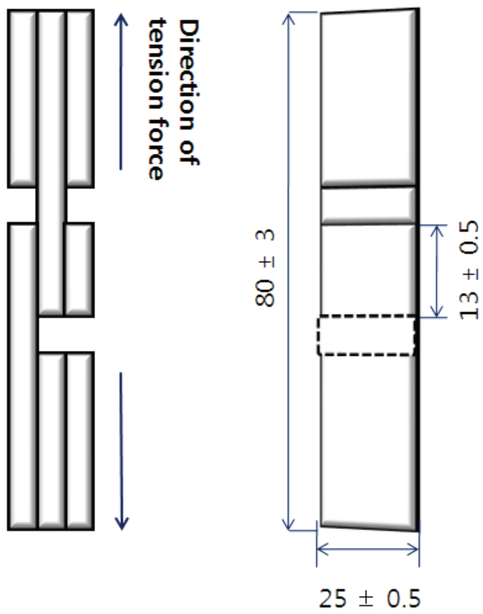

Fig. 5. Preparation of test samples according to the Korean Industrial Standard KS M 3701.

2.3. General method for preparation of bisulfite blocked isocyanate solutions

Bisulfite blocked isocyanate solutions are prepared by reacting aqueous solutions of sodium bisulfite ($NaHSO_3$) with isocyanate. 15g, 22.5g, 30g and 37.5g of $NaHSO_3$ were added to the water 85g, 77.5g, 70g and 62.5g respectively and mixed at room temperature. Water-dispersed bisulfite blocked isocyanate solution was prepared by adding equivalent amount of pMDI 20g, 30g, 40g and 50g to 15%, 22.5%, 30% and 37.5% of $NaHSO_3$ aqueous solutions respectively. pMDI was added dropwise for 30minutes and mixed for another 4~12hours at room temperature.

2.4. General method for preparation of Protein solutions

35g of PVA 500 was added to 965mL of water and stirred at about 60℃. While heating, Emulsifier (Tween 20) 1 ~ 2g (0.1% ~ 0.2%) was added to the PVA aqueous solution. 67g ~ 122g (40 ~ 55 wt%) of milk protein powder was added lowly to 100 mL of the hot PVA aqueous solutions and agitated. The mixture was stirred for about one hour until protein powder was almost completely dissolved and then the protein solution was allowed to cool to room temperature.

2.5. General method for preparation of protein and block isocyanate mixed wood adhesives

Preparation of the final wood adhesives were carried out by mixing the previously made two solutions, milk protein solution (40 ~55 %) and bisulfite blocked isocyanate solution. That is because there are a lump of solids in the final mixture when adhesives were prepared by one-component system. However, when the final adhesive mixture was manufactured using a two-component system, which were prepared and mixed from two separate protein and BI solutions, almost no solids were observed in the final adhesive mixture. The pH of the adhesive solutions was maintained neutral.

3. Results and Discussion

3.1. Synthesis of $NaHSO_3$ blocked isocyanate(BI) aqueous solutions

To compare the adhesion strength under the influence of the concentration of $NaHSO_3$ on the synthesis of water-dispersed isocyanates, bisulfite blocked aqueous isocyanate solution was synthesized in the same condition as in Table 3. This blocked isocyante (BI) will be used adding to protein solutions to investigate the performance of the final adhesives later on. Prior to adding isocyanate to water, 13, 22.5, 30 and 37.5 wt% of $NaHSO_3$ were dissolved in water, which are named as N-1, N-2, N-3 and N-4 solutions respectively. $NaHSO_3$ content of N-1~4 are shown in Table 2.

Table 2. $NaHSO_3$ content in the solution N-1~4

Sol'n No.	$NaHSO_3$ (wt %)	H_2O (wt %)	total weight (g)
N-1	15	85	100
N-2	22.5	77.5	100
N-3	30	70	100
N-4	37.5	62.5	100

Table 3. Composition of water-dispersed $NaHSO_3$ blocked isocyanate solutions

Sol'n No.	$NaHSO_3$ Sol'n		pMDI (g)	Total weight (g)
	$NaHSO_3$ Sol'n No.	$NaHSO_3$ Sol'n (g)		
BI-1	N-1	100	20	120
BI-2	N-2	100	30	130
BI-3	N-3	100	40	140
BI-4	N-4	100	50	150

Table 4. Composition of $NaHSO_3$ blocked isocyanate and protein solution mixed adhesives

Sol'n No.	Blocked Isocyanate (BI)		water (g)	Protein (g)	Total weight (g)
	BI Sol'n No.	BI Sol'n (g)			
PB-1	BI-1	50	80	80	210
PB-2	BI-2	50	120	120	290
PB-3	BI-3	50	160	160	370
PB-4	BI-4	50	200	200	450

*Protein and blocked isocyanate weight ration was maintained at 8:1.

Water-dispersed bisulfite blocked isocyanate solutions were prepared by adding equivalent amount of 20g, 30g, 40g and 50g pMDI to 15%, 22.5%, 30% and 37.5% of $NaHSO_3$ aqueous solutions (100g) respectively. pMDsI were added dropwise for 30minutes and mixed for another 4hours at room temperature to give BI-1~4 solutions as represented in Table 3.

3.2. Adhesive performance under the influence of the concentration of $NaHSO_3$ in adhesives

After taken by 50g of the solutions of BI-1, BI-2, BI-3 and BI-4 each, they were added to water 80g, 120g, 160g and 200g for dilution. Each Milk protein powder, 80g, 120g, 160g and 200g was added to BI solutions BI-1, BI-2, BI-3 and BI-4 respectively to prepare PB-1~4 solutions. Weight ratio between all protein and blocked isocyanate solutions were maintained at 8:1. Table. 4 represents the composition of $NaHSO_3$ blocked-isocyanate/protein solution mixed adhesives.

Each bonded plywood specimen was tested for dry tensile strength using universal test machine according to the Koean industrial standard KS M 3701. This standard requires over 7kgf/cm^2 of tensile strength for plywood adhesives. Our first test results show below 3kgf/cm^2 of tensile strength, moreover the adhesives (PB-1~4) were not sticky enough for hot press processing after cold-pressing. This means to require an agglutinant material in the formulation of adhesives.

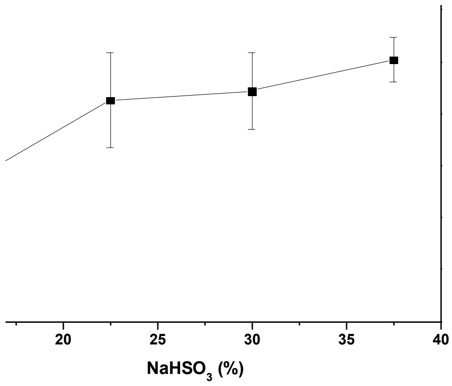

Fig. 6. Dry tensile strength of mixed adhesives. *PB-1, PB-2, PB-3 and PB-4 contain BI-1 (15% of $NaHSO_3$), BI-2 (22.5% of $NaHSO_3$), BI-3 (30% of $NaHSO_3$) and (37.5% of $NaHSO_3$) respectively.

In order to resolve the lack of cohesive problems, water-soluble resin, polyvinyl alchohol (PVA), was added to adhesives. PVA 500 resin has repeating units of [{$CH_2CH(OH)$}n] and dissolves in water increasing viscosity and stickiness. In addition, the number of alcohol groups can react with the isocyanates during hot pressing, which may also help increase tension strength.

As the plywood dehiscence phenomenon after cold pressing process was reduced by the addition of PVA , adhesive solution was prepared by adding PVA 500. 3.5% PVA aqueous solution was prepared by adding PVA 35g to water 1L while heated and agitated at 60℃. And milk protein powder was added to PVA aqueous solutions to make protein solution B as shown in Table 5. Then, by adding BI solution A to protein solution B, mixed final adhesives PB-9~12 were obtained.

Plywood pieces bonded with the Mixed adhesives have BI/protein content ratio varying from 1:6 to 1:12. Dry adhesion strength was determined as mentioned earlier. Adhesives was mixed with BI/protein content ratio varying from 1:6 to 1:12 and tested for tensile strength. As a result, the tensile strength was sustained at 6.5~7kgf/cm^2 with BI/protein ratio from 1:6 up to 1:8, however it was drastically reduced at BI/protein ratio of 1:10 or higher. Therefore, the BI/protein content ratio in the adhesive seems to be appropriate to keep it 1:8 or below. This result is consistent with what we expected that the higher isocyanate content, the better cross-linking is.

However, phase separation phenomenon has occurred after the final adhesive was kept at room temperature for a while. We speculate that as the milk protein powder was added to the salty ($NaHSO_3$) aqueous solution, milk fat was separated from the homogeneous protein

Table 5. Composition of adhesives comprising PVA 500

Sol'n No.	Sol'n A		Sol'n B			BI : Protein (ratio)
	BI-4 sol'n (g)	pMDI content (g)	Protein (g)	water (g)	PVA (g)	
PB-9	50	25	150	150	5.25	1 : 6
PB-10	50	25	200	200	7.00	1 : 8
PB-11	50	25	250	250	8.75	1 : 10
PB-12	50	25	300	300	10.5	1 : 12

solution without mixing in water. Therefore, the addition of the emulsifier was needed to prevent phase separation.

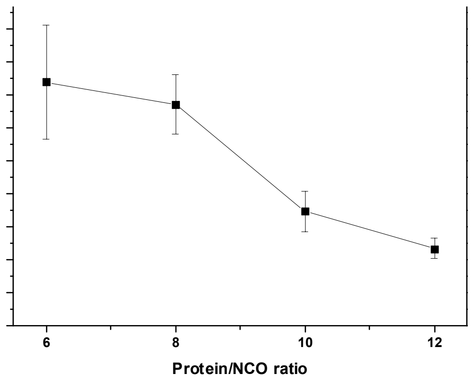

Fig. 7. Adhesion effect according to various BI(or NCO)/protein ratio.
*PB-9, PB-10, PB-11 and PB-12 contain the weight ratio of BI(or NCO) over protein, 6, 8, 10 and 12 respectively.

3.3. The effect of adhesion by the addition of an emulsifier.

Consequently, Tween 20 was added to the protein solution B to solve the phase separation. It is speculated that Tween 20 is strengthened adhesion by cross-linking as well as it emulsifies the milk fat because of it's large number of hydroxyl groups. To investigate the effect of Tween 20 on the adhesive, solutions, PB-13, PB-14, PB-15 and PB-16, were prepared as shown in Table 6.

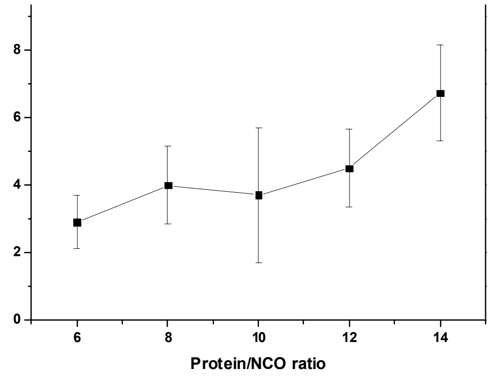

Fig. 10. Adhesion effect of the addition of emulsifier, Tween 20.
*PB-13, PB-14, PB-15 and PB-16 contain the weight ratio of BI(or NCO) over protein, 6, 8, 10, 12 and 14 respectively.

By adding Tween 20, The adhesive solution was well mixed without phase separation. As a result of measuring tensile strength, even isocyanate/protein ratio increased, adhesive strength was maintained or rather increased. Although adhesive strength appeared to be rapidly increasing in the ratio of protein/NCO of 12/1, the proper ratio of isocyanate solution may also be required to use because it may degrade water-resistance, if the amount of the isocyanate is too small. In summary, this research carried out to investigate the possibility that the bio-material such as milk protein is suitable renewable source for wood adhesives. To use as a cross-linker between

Table 6. Composition of adhesives comprising an emulsifier, Tween 20

Sol'n No.	Sol'n A		Sol'n B				BI:Protein (ratio)
	BI-4 sol'n (g)	pMDI content (g)	Protein (g)	water (g)	PVA 500 (g)	T20 (g)	
PB-13	50	25	150	150	5.25	0.3	1:6
PB-14	50	25	200	200	7.00	0.4	1:8
PB-15	50	25	250	250	8.75	0.5	1:10
PB-16	50	25	300	300	10.5	0.6	1:12

*T20 : Tween 20

wood structure and milk proteins, water-dispersed bisulfite blocked isocyanate was synthesized by mixing sodium bisulfite aqueous solutions and pMDI. As the amount of sodium bisulfite increased in making blocked isocyanate aqueous solutions, so the tensile strength was found to be increased as we expected. Added PVA in adhesive solution has proven to be a good additive for increasing adherence between two wood plates before hot pressing. The tensile strength are sustained at 6.5~7kgf/cm^2 with high ratio of blocked isocyanate/protein, which shows high content of isocyanates enhance the tensile strength through more chemical bondings. In conclusion, milk protein can be a good natural source for formaldehyde-free wood adhesives with the help of a couple of additives such as blocked pMDI, PVA and Tween20.

4. Conclusions

1. To investigate the adhesion effect of sodium bisulfite content in making blocked isocyanate, wood adhesive PB-1, PB-2, PB-3 and PB-4 containing sodium bisulfite content of 15%, 22.5%, 30% and 37.5% were synthesized respectively. As a result, when the amount of sodium bisulfite increased in adhesives, the tensile strength was found to be proportionally increased.

2. The final adhesive mixtures were manufactured using a two-component system which are prepared by mixing two separate protein and BI solution due to the precipitate in the adhesives.

3. As PVA was added to adhesives to increase tenacity, the plywood dehiscence phenomenon after cold pressing process was declined. By addition of PVA, the tensile strength was improved up to 6.5~7kgf/cm^2 with BI/protein ratio from 1:6 up to 1:8

4. Phase separation between milk fat and aqueous layer was disappeared by addition of emulsifier, Tween 20. Additon of Tween 20 showed tensile strength up to 5~6.5kgf/cm^2 at isocyanate/protein ratio of 1:12 ~ 1:14 without phase separation.

Acknowledgements

This research was supported by a grant from the research programs of Korea Forest Research Institute (03-2012-0015).

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