J. of Korean Oil Chemists' Soc.,
Vol. 32, No. 4. December, 2015. 607~615
ISSN 1225-9098 (Print)
ISSN 2288-1069 (Online)
http://dx.doi.org/10.12925/jkocs.2015.32.4.607

Preparation of Wood Adhesives from the Rice Powder and pMDIs; Characterizations of Their Properties

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(Received September 1, 2015; Revised December 15, 2015; Accepted December 19, 2015)

Abstract : To investigate the adhesion effect of various kinds and contents of polymeric methylene diphenyl diisocyanates (pMDIs) on adhesion performance, wood adhesives (A-1~5) were synthesized and characterized. As results, when the amount of pMDI increased in adhesives, the dry tensile strength was found to be proportionally increased sustaining at around 16.0~21.6 kgf/cm^2. The polyurethane (PU) resin, which used M11S as a source of pMDI showed the best wet tensile strength at 11.9 kgf/cm^2 and cyclic boil tensile strength at 8.1 kgf/cm^2, which satisfied the requirement of over 7 kgf/cm^2. Thermal properties of the rice powder (RP) based polyurethane resins were characterized by differential scanning calorimetry (DSC) and Thermal gravimetric analysis (TGA). Thermal stability of polyurethane resins increased to 250℃ with adding pMDIs. The more pMDI (M5S) was added to adhesive, the higher thermal stability of the resin was observed by TGA.

Keywords : wood adhesive, pMDIs, formaldehyde-free adhesives, biopolymer.

1. Introduction

Most wood adhesives in furniture industry are synthesized from petroleum based sources due to many advantages such as reasonable water resistance, good adhesion and low cost. However the use of formaldehyde based adhesives such as urea-formaldehyde(UF) and phenol-formaldehyde(PF) have recently drown the attention of the public due to environmental issue[1-2]. Formaldehyde can be produced by decompositions and will gradually release to the surrounding environment. On the other hands, natural adhesives derived from the bio-materials such as proteins and carbohydrates are safe and renewable materials with low price. Especially, natural material-based polyurethane(PU) adhesives have been extensively studied due to their unique characteristics, such as amenable curing speeds, formaldehyde emission-free, good weather resistance and excellent adhesion[3-11]. For an example, PU adhesives for bonding wood veneers made from potato starch/natural oil-based polyol and TDI are reported by Desai et al[12-16]. However their synthetic methods require complicated, costly and/or

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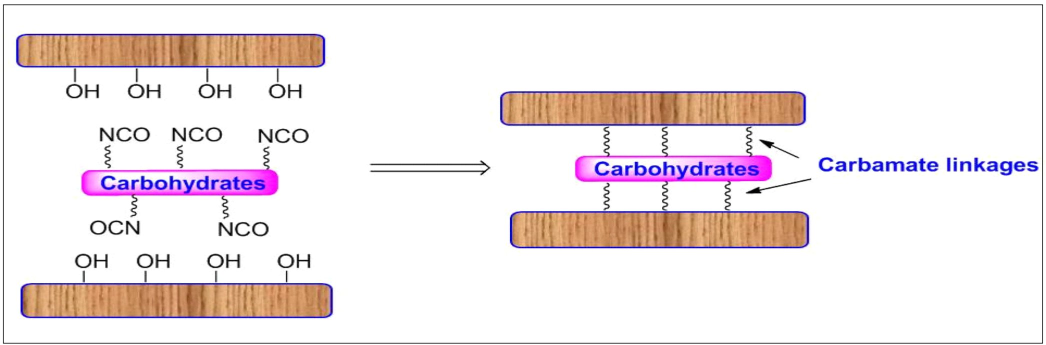

Fig. 1. Illustration of the chemical bonds formation among carbohydrates, pMDI and wood structure.

multi-step processes such as chemical reactions at high temperature and vacuum distillation process, they might not be amenable to the practical applications in furniture industry in terms of cost. Possible reaction mechanisms of isocyanates with carbohydrate in aqueous solutions are shown in Fig. 1.

In this study, rice powder(RP) as a carbohydrate source has been chosen because it is inexpensive and has hydroxyl functional groups that can easily provide chemical cross-linking reactions with isocyanates of pMDI.

The practical synthetic method we developed for PU adhesives is two-component solution process. First of all, pMDIs were rapidly mixed with aqueous RP solutions right before applying to plywood veneers. Upon heating and pressing the plywoods, water in the PU adhesives may undergo rapidly vaporizing and absorbing through wood structure so that NCO functional groups of pMDIs react much more with OH groups of rice powder (RP) and cellulosic part of plywoods than water, forming chemical cross-linkages. Otherwise, isocyanates are reactive to moisture so that they form by-products such as polyurea and biuret-type structures.

Our goal of this study is to develop a practical synthetic method for formaldehyde-free wood adhesives based on the renewable source (RP) and pMDIs as a crosslinker. Furthermore, these adhesives must satisfy the requirement of over 7 kgf/cm^2 of tensile strength for plywood adhesives in both dry and wet tensile strength tests according to the Korean industrial standard KS F 3101. Bonding effects of pMDI content on the wood adhesives were evaluated in terms of tensile property change in dry, wet and cyclic boiled tensile strength tests. In view of these properties we synthesized polyurethane (PU) adhesives from three different pMDIs and rice powder(RP) as a natural polyol. The RP based PU adhesives were characterized by DSC and TGA.

2. Materials and Method

2.1. Materials

Rice powder was purchased from Ant Industry co. and polymeric methylene diphenyl-diisocyanates(pMDI: M5S, M11S and M20S) were gifts from BASF co. and Poly Vinyl Alcohol 500 was purchased from OCI co.

The properties of the pMDI (Lupranate M5S, M11S and M20S) such as NCO content, viscosity and density, are presented in Table 1.

Table 1. Physicochemical properties of pMDIs, M5S, M11S and M20S

Item	Unit	M5S	M11S	M20S
Appearance	-	Brown liquid	Brown liquid	Brown liquid
NCO content	wt%	31.4~32.6	30 ~ 32	30 ~ 32
Viscosity	cps	35 ~ 60	80 ~ 140	170 ~ 250
Density	g/㎤	1.23	1.23	1.23
Acidity as HCl	wt%	〈0.06	〈0.06	Less than 0.06
Total chlorine	wt%	〈0.5	〈0.5	〈0.5
Vapor pressure at 25℃	mbar	〈10^{-4}	〈10^{-4}	Less than 10^{-4}
Flash point	℃	〉200	〉200	〉200

2.2. Preparation of aqueous rice powder (RP) solutions

30 g of PVA 500 was added to 850 g of water and stirred at about 60℃. While heating, 150 g (15wt%) of RP was added lowly to the hot PVA aqueous solutions and agitated. The mixture was stirred for about one hour until RP was almost completely dissolved and then the RP solution was allowed to cool to room temperature.

2.3. Preparation of RP and pMDIs mixed wood adhesives.

Preparation of the final wood adhesives were carried out by mixing the two component solutions, the RP solutions and pMDIs, for about 30 seconds. That is because pMDIs are sensitive to water making by-products when PU adhesives are prepared by one-component system. The pH of the adhesive solutions were maintained neutral.

2.4. Application and strength tests

2.4.1. Dry tensile strength test

The test material we used was lauan rotary veneer, which has thickness of 1.0 mm, the range of 8~10% moisture contents and bulk density of 0.45 g/cm^2 or more. The previously prepared aqueous RP solution and pMDIs were rapidly mixed for about 30 seconds and applied onto the surface of three pieces of the veneers(300mm×300mm×2.7mm) to be glued to the amount of 150 g/m^2. Then the plywood was inserted in a hot press and cured at 130±2℃ under 10 kgf/cm^2 pressure for 3 minutes. The plywood was cut into the samples(80mm×25mm) according to the KS F 3101 as shown in Fig. 2.

2.4.2. Wet tensile strength test

Water resistance of plywood samples was determined with wet tensile strength test. Ten specimens cut from each plywood panel were soaked in water at 60℃ for 3 hours, and then soaked in water at room temperature. Then they were tested for wet tensile strength.

2.4.3. Cyclic boiled tensile strength test.

Water resistance of plywood samples was also determined with cyclic boil tensile strength test. Ten specimens cut from each plywood panel were boiled in hot water at for 4 hours, and then dried at 60℃ for 20 hours. Then they were boiled again in hot water at for 4 hours and immersed in water at room temperature to cool down. The wet specimens then tested for cyclic boil tensile strength test.

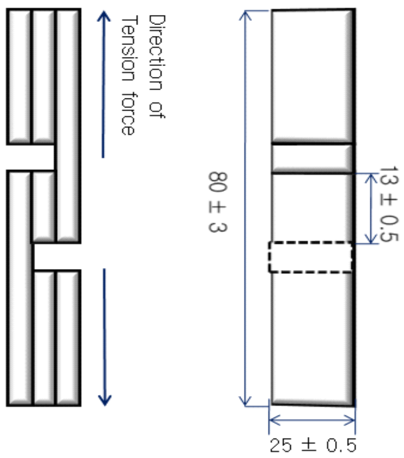

Fig. 2. Preparation of test samples according to the Korean Industrial Standard KS F 3101.

2.5. Differential scanning calorimetry analysis (DSC)

DSC was performed using an Instrument 2910 differential scanning calorimeter (TA instrument, USA). The sample of 5~10 mg in a flow of N_2 (60 mL/min), were heated from 30℃ to 280℃, at 10℃/min.

2.6. Thermogravimetric analysis (TGA)

Measurements of mass loss versus temperature were carried out by using a thermogravimetric analyzer, model 2960 (TA instrument, USA) under N_2 purge. 5~10 mg of samples were placed on a platinum pan and heated from 30℃ to 500℃, at 10℃/min.

3. Results and Discussion

3.1. Preparation of PU adhesives and adhesive performance under the influence of the ratios of pMDI(M5S)/RP in adhesives

Two components RP based PU adhesive solutions were prepared by adding amount of 150 g, 300 g, 450g of pMDI(M5S) to 150 g of aqueous RP solutions respectively. The weight ratios of pMDI/RP in the solution of A-1~3 were 1/1, 2/1 and 3/1 respectively as represented in Table 2. The plywood samples we made were not sticky enough for handling, which require an agglutinant material in the formulation of adhesives. In order to resolve the lack of cohesive problems, water-soluble resin, polyvinyl alchohol(PVA), was added to adhesives. As a result, viscosity and stickiness of PU adhesive solutions was increased as well as adhesion strength (these data were not included). Adhesion performance in dry and wet conditions is important aspects for wood adhesives. For evaluation of adhesion along with various ratios of pMDI/RP, solutions (A-1~3) were prepared and applied onto plywood veneers for hot pressing as mentioned earlier. Hydrophobic pMDI(M5S) is not supposed to be soluble in water; however once pMDI was mixed with a aqueous RP solution,

Table 2. Composition and adhesion properties of PU adhesives with various ratios of M5S/RP

No.	pMDI		RP Sol'n			dry tensile strength (kgf/cm^2)	wet tensile strength (kgf/cm^2)	cyclic boil tensile strength (kgf/cm^2)
	Name	weight (g)	PVA (g)	RP (g)	water (g)			
A-1	M5S	150	30	150	850	16.8±2.5	0	0
A-2	M5S	300	30	150	850	19.2±3.6	4.1±1.9	0.2±0.4
A-3	M5S	450	30	150	850	21.6±2.8	5.7±1.4	5.2±2.4

*RP = rice powder

it became soluble. This phenomenon may attribute to formation of hydrophilic adduct of carbohydrates and pMDI.

Fig. 3 shows the effect of pMDI content on adhesive performance. As pMDI weight ratio over RP increases, adhesive performance in any case of tests improves up to pMDI/RP = 3/1. Dry tensile strength of all test samples (A-1~3) were sustained at around 16.8~21.6 kgf/cm^2. As the ratio of pMDI/RP is increased 100% each time, tensile strength increases 2.4 kgf/cm^2. Moreover, the wet and cyclic boil tensile strength are drastically reduced at low content of pMDI. Therefore, the pMDI/RP content ratio in the adhesive needs to keep up at least 3/1 or higher for the good water resistant property. This result is consistent with what we expected that the higher isocyanate content, the better cross-linking is.

3.2. Adhesive performance under the influence of the pMDIs in adhesives

The adhesion strengths of adhesives with three different pMDIs were determined and the results are shown in Table 3. The adhesives (A-1, A-4 and A-5) used three different pMDIs; M5S, M11S and M20S. Their molecular weights and viscosities increase from M5S to M20S. pMDI/RP ratios were fixed for all three adhesives at 3/1.

As results, the best test sample for dry tensile strength was A-1 at 21.6 kgf/cm^2 along with good adhesion of other two adhesives, A-4 and A-5. Wet tensile strength

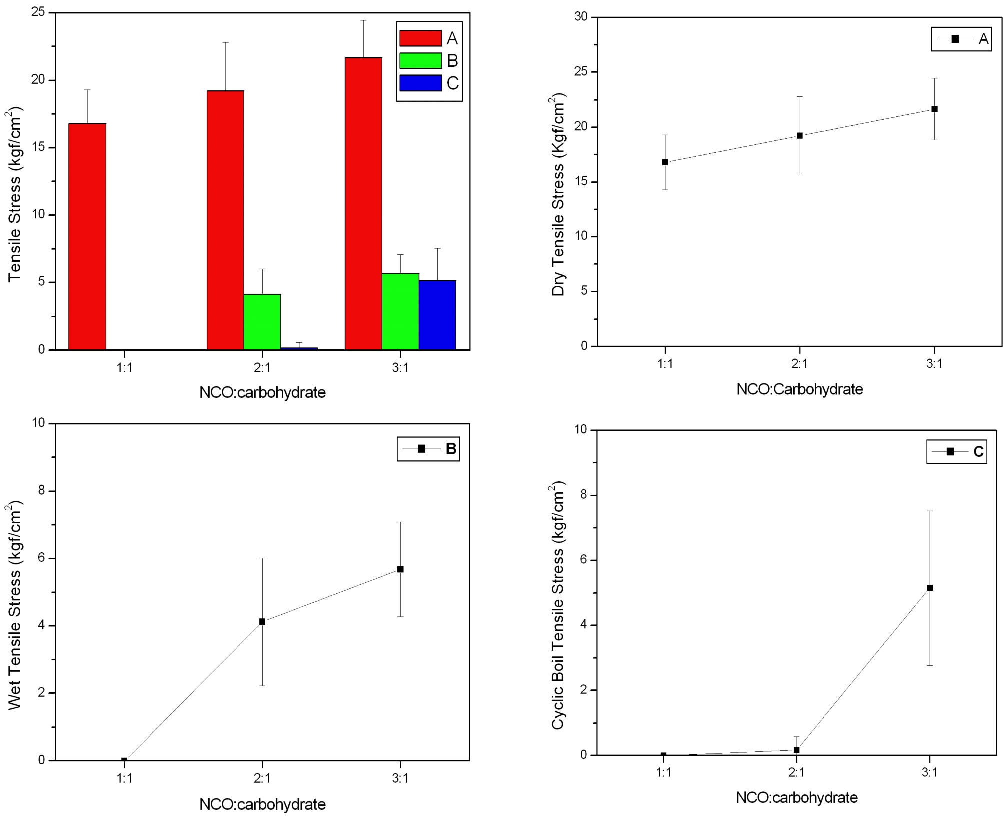

Fig. 3. Effects of pMDI/RP ratio on adhesion. pMDI is M5S. A; Dry tensile strength of PU adhesives. B; Wet tensile strength of PU adhesives. C; Cyclic boil tensile strength of PU adhesives.

Table 3. Composition and adhesion properties of PU adhesives with various pMDIs

No.	pMDI		RP Sol'n			dry tensile strength (kgf/cm^2)	wet tensile strength (kgf/cm^2)	cyclic boil tensile strength (kgf/cm^2)
	Name	weight (g)	PVA (g)	RP (g)	water (g)			
A-1	M5S	450	30	150	850	21.6±2.8	5.7±1.4	5.2±2.4
A-4	M11S	450	30	150	850	16.0±1.9	11.9±1.4	8.1±1.6
A-5	M20S	450	30	150	850	17.0±2.1	8.6±0.8	3.8±2.6

*RP = rice powder

and cyclic boil tensile strength are the most important properties for wood adhesives. The adhesive A-4, which used M11S as a source of pMDI showed the best wet tensile strength at 11.9 kgf/cm^2 and cyclic boil tensile strength at 8.1 kgf/cm^2. Both results well satisfied the requirement of over 7 kgf/cm^2 of tensile strength for plywood adhesives in both wet tensile strength and cyclic boil tensile strength tests according to the Korean industrial

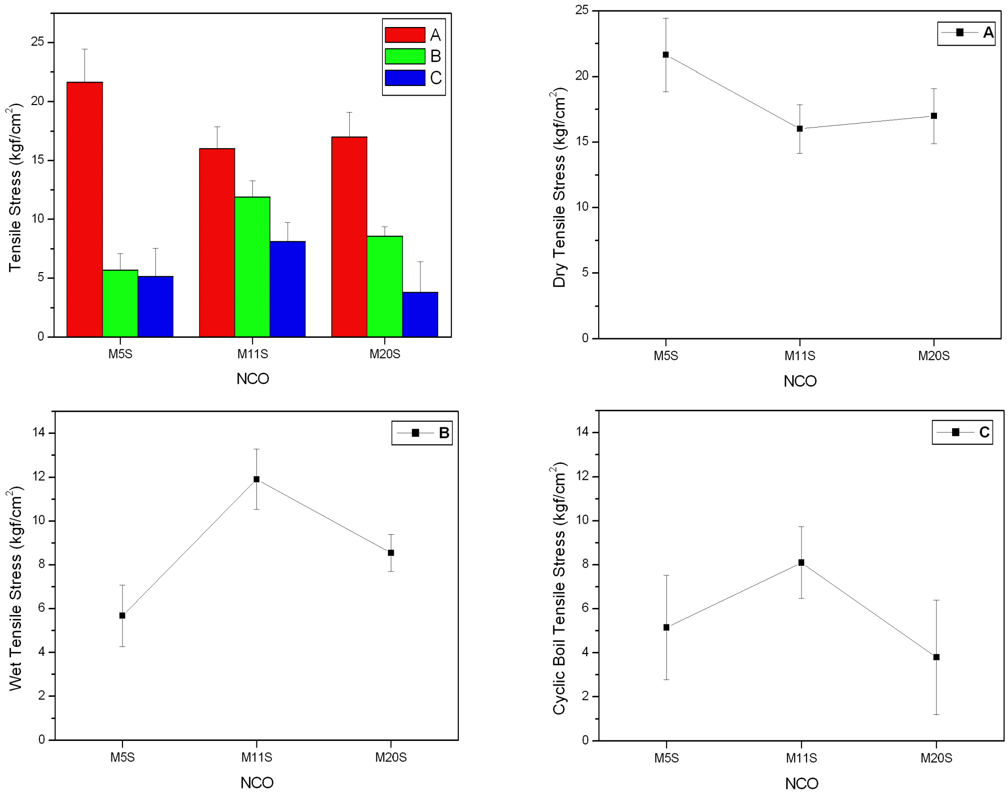

Fig. 4. Effects of various pMDIs on adhesion. pMDIs/RP weight ratio was maintained at 3/1. A; Dry tensile strength of PU adhesives. B; Wet tensile strength of PU adhesives. C; Cyclic boil strength of PU adhesives.

standard KS F 3101 as shown in Fig. 4. We speculate that pMDI(M11S) among others may have optimum molecular weight and viscosity for chemical crosslink reactions between RP and wood components. Generally, isocyanates compete with both the hydroxyl groups and water in adhesives. In our case, hot pressing of the plywoods could easily remove the moisture from the adhesives so that isocyanate may have much more chance to react with the hydroxyl groups than water to give the good water resistant property.

3.3. Physical properties of pMDIs/RP adhesives

The DSC scanning curves for the wood adhesives with different pMDIs are shown in Fig. 5. Tc(crystalline temperature) of rice powder showed at 114.4℃. When M5S was added to adhesive, Tc of the resin (resin B) slightly decreased to 107.3℃. In comparison with the resin B, the resin C that mixed with M20S showed much lower Tc at 99.6℃. Similarly Tm decreased from resin B to resin C. Tm of resin C was 237.3℃, whereas that of resin B was 243.9℃.

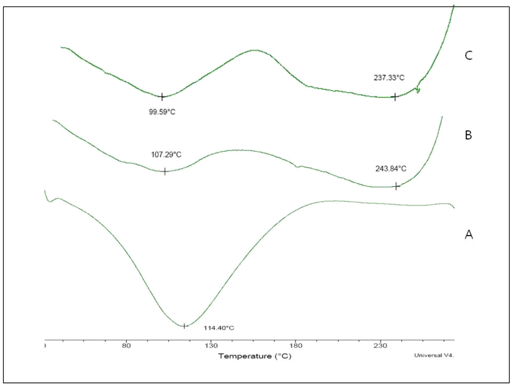

Fig. 5. DSC scanning curves for the RP/pMDIs mixtures. A: Rice Powder (RP), B: RP:M5S=1:3, C: RP/M20S=1:3.

TGA can check the thermal decomposition and thermal stability of adhesives. It was found that RP derived PU adhesives differing only by their RP/pMDI ratios showed almost identical thermal properties. All of the decompositions started at approximately 150℃ and ended with approximately 72~74% of the weight loss at 500℃. The DTG curve shows that there are two obvious mass losses at TGA curves show two main degradation processes as shown in Fig. 6. The first stage of degradation is due to the carbohydrate decomposition starting at 150℃ and reaching at maximum degradation temperature of 230℃. The second stage of degradation starts

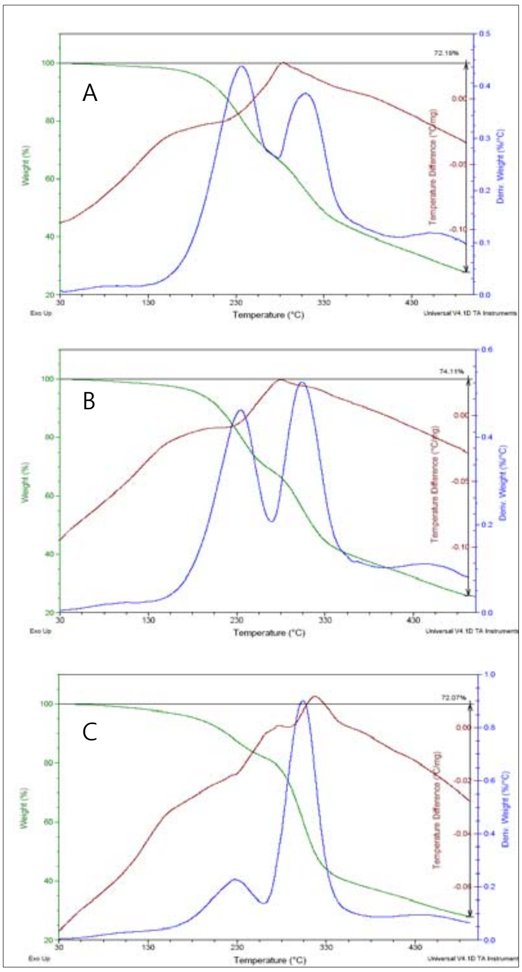

Fig. 6. TGA curves for the RP/pMDIs mixtures. A: RP/M5S=1/1, B: RP/M5S=1/2, C: RP/M5S=1/3.

with breaking of urethane linkages between alcohols and isocyanates, which shows maximum degradation temperature of around 300℃. Differences of weight loss in those three curves indicate the influence of RP/pMDIs ratios, which vary from 1/1~1/3.

In summary, this research carried out to develop the *in situ* synthetic method for pMDI/RP based wood adhesives. To use as a cross-linker between wood structure and rice powder, pMDIs were mixed with aqueous RP solution and applied on to the plywood for hot pressing. The results showed that as the ratio of pMDIs/RP increased to 3/1, the tensile strength in dry, wet and cyclic boil tensile strength was found to be increased as we expected. RP can be a good natural source for formaldehyde-free wood adhesives with excellent water resistant properties especially when it was combined with the pMDI(M11S).

4. Conclusions

1. The adhesion effect of pMDI content on adhesive performance was investigated. When the amount of pMDI increased in adhesives, the dry tensile strengths were found to be proportionally increased sustaining at around 16.0~ 21.6 kgf/cm^2 in any cases. The wet and cyclic boil tensile strength are drastically weak at low content of pMDI(M5S). Therefore, the pMDI/RP content ratio in the adhesive needs to keep up at least 3/1 or higher for the good water resistant property.

2. The adhesion strengths of adhesives with three different pMDIs(M5S, M11S and M20S) were determined. Among them, The PU resin, which used M11S as a source of pMDI showed the best wet tensile strength at 11.9 kgf/cm^2 and cyclic boil tensile strength at 8.1 kgf/cm^2. These results well satisfied the requirement of over 7 kgf/cm^2 for wet tensile strength and cyclic boil tensile strength tests according to KS F 3101.

3. Tc of the resin (RP:M5S=1:3) showed at 107.3℃, whereas the resin (RP/M20S = 1:3) showed much lower Tc at 99.6℃.

4. Thermal stability of PU resins increased to 250℃ with adding pMDIs. The more pMDI(M5S) was added to adhesive, the higher thermal stability of the resin was observed by TGA.

Acknowledgements

This research was supported by a grant from the research programs of Korea Forest Research Institute (201305040001).

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