

# Characteristics of Non-plasticizer PVAc Resin for Wood Products\*<sup>1</sup>

Sumin Kim\*<sup>2</sup>, Hyun-Joong Kim\*<sup>2†</sup>, Youn Mee Choi\*<sup>3</sup>, and Sung-Wook Jang\*<sup>3</sup>

## ABSTRACT

The applicable scope of adhesives in the current society is broad and currently, several types of PVAc resin are sold in the market for adhesives. PVAc resin is primarily used for wood works and paper adhesion. However, the PVAc resin itself has the disadvantages that its viscosity is highly temperature-dependent and the work condition and viscosity get worse at the low temperature in the winter seasons. Although phthalate-based plasticizer is used to complement these disadvantages, adhesion strength and heat-resistance are weakened by adding the phthalate-based plasticizer and in the winter period, the amount of quantity should be increased. Also in a high-density product, it worsens the work condition by causing a rise of viscosity and delays curing and in a low-density product, it worsens the storage stability by causing separate precipitation. In addition to these, the phthalate-based plasticizer as a material of causing environmental hormones is currently restricted in the advanced countries for its amount of use and also in the domestic market, it is necessary to prepare for the situation. This study has not only eliminated the disadvantages of PVAc resin emulsion without adding a phthalate-based plasticizer of causing these problems, but also synthesized the PVAc resin for timber adhesion that is excellent in woodwork, thermal-resistance, water-resistance, storage stability, and adhesion performance. As the result, it has proven an excellent performance in thermal resistance, water resistance, storage stability, and minimum film forming temperature.

*Keywords* : non-plasticizer, PVAc, wood, adhesive

## 1. INTRODUCTION

PVAc resin, as the one manufactured and industrialized first in Germany in 1924, is widely used for adhesives, paints and resins due to its excellent viscosity although it can not be used

as a forming material since its glass transition temperature is about the room temperature [1]. PVAc monomer becomes a colorless transparent resin by polymerization if heated by adding a small quantity of benzoyl peroxide. On the other hand, if it is polymerized under the water,

\*1 Received on November 30, 2006; accepted on January 10, 2007.

\*2 Lab. of Adhesion & Bio-Composites, Program in Environmental Materials Science, Department of Forest Sciences, Seoul National University, Seoul 151-921, South Korea

\*3 R&D Center, OKONG Corp., Incheon 402-023, South Korea

† Corresponding author : Hyun-Joong Kim (hjokim@snu.ac.kr)

Table 1. Advantages and disadvantages of PVAc resin-based emulsion adhesive [9,10]

Advantages	<ol style="list-style-type: none"> <li>(1) The undiluted solution can be directly used while it requires no joining time and does not limit the pot-life.</li> <li>(2) Its use is broad since various materials can be bonded.</li> <li>(3) Since it is water-soluble, it has no toxicity and risk of fire and the mechanism can be cleaned by a brush or water.</li> <li>(4) Since it appears colorless and transparent after drying, no contamination is made on the material such as timber.</li> <li>(5) It can be easily mixed with plasticizer (DBP) and the drying film holds plasticity.</li> </ol>
Disadvantages	<ol style="list-style-type: none"> <li>(1) Since it is thermo-plastic, it loses adhesive strength at a high temperature of 70°C or higher due to its nature of losing heat-resistance.</li> <li>(2) The speed of adhesion is slow on the paper (printing paper) with low absorptive property.</li> <li>(3) It can not be used in a bathroom or outdoor due to its limited water-resisting qualities.</li> <li>(4) Since it can not hold a heavy load for a long period of time, it is not suitable for a structural use.</li> </ol>

the monomer is emulsified from an aid of a surface active agent and polymerized by catalyst and heat. This emulsified and polymerized material appears to be milk white and is generally referred to as emulsion. And if polymerized in acetic ethyl or methanol, it becomes a colorless transparent viscous solution [2,3].

By polymerizing PVAc monomer while dispersing it in the water, the milk-white PVAc resin emulsion high in viscosity can be obtained. The PVAc resin-based emulsion adhesive can be either made of PVAc resin or reformed so that it can hold a certain property of performance according to its use. For example, the copolymerized emulsion, which is obtained by the emulsified polymerization of PVAc with other monomers (ether acrylate, mallein ester and fatty acid ester), makes the membrane soft by plasticizing the PVAc resin internally and reduces the film forming temperature. Also, the emulsion of holding cross-linkable property by adopting the activator among the molecules of PVAc resin has been developed and the EVA emulsion obtained by copolymerizing PVAc resin monomer with ethylene has been widely adopted [4-6].

The characteristics of emulsion adhesives are not determined by only the polymerized monomer and they are greatly affected by various additives that are added according to the type, quantity and use of necessary protective colloid, surface active agent, and catalyst. Especially, the type and quantity of plasticizer greatly affects on the viscosity of adhesives. In addition to the adhesive woodworks such as for the assembly, boards of furniture, building material, musical instrument and toy, they are also used for bookbinding and non-woven fabric. Also, those copolymerized with ester acrylate are used for gluing soft vinyl sheet to plywood or paper and for joining vinyl faced papers [7,8]. Table 1 is shown advantages and disadvantages of PVAc resin-based emulsion adhesive.

Although phthalate-based plasticizer is used to complement these disadvantages, adhesion strength and heat-resistance are weakened by adding the phthalate-based plasticizer and in the winter period, the amount of quantity should be increased. The phthalate-based plasticizer as a material of causing environmental hormones is currently restricted in the advanced countries for its amount of use and also in the domestic mar-

ket, it is necessary to prepare for the situation. This study has not only eliminated the disadvantages of PVAc resin emulsion without adding a phthalate-based plasticizer of causing these problems, but also synthesized the PVAc resin for timber adhesion that is excellent in woodwork, thermal-resistance, water-resistance, storage stability, and adhesion performance.

## 2. EXPERIMENTAL

### 2.1. Material

Polyvinyl alcohol (PVA) has used the saponification of 88% (product: P24, P20, P17) with the polymerization of 2400, 2000 and 1700 and the saponification of 98% (product: AH22) with the polymerization of 2200; emulsifier has used the products of polyoxyethylene nonylphenyl ether HBL=17.8 and 12.3. As for the monomer, it has used vinyl acetate monomer and butyl acrylate monomer; for the acrylic acid, has used the products of Junsei Chemical with its purity of 99.5%; and for the vinyl acetate-ethylene emulsion(VAE), has used EP706 ( $T_g$ , 0°C) and AF401 ( $T_g$ , -15°C) among from Air products Co. Ltd. As for the plasticizer, dibutyl phthalate (DBP, Junsei Chemical) is used and ammonium persulfate (APS, 98.0%, Junsei Chemical) is used for the initiator.

### 2.2 Adhesive Synthesis

Sample A (Hereinafter Referred to as 'A')

Put 330 g of water in the reactor installed with a stirrer and then, add 13 g of PVA P17 and 9 g of P24, and 0.7 g of emulsifier (HBL=17.8). While keeping up the stirring speed of 130 rpm, dissolve the contents within the reactor by raising the temperature up to 80°C. After completely dissolving the contents, add APS and check the reaction while dropping 220

g of vinyl acetate monomer for duration of 4 hours. After completely checking the reaction, cool the contents down to the temperature of 50°C or below and then, add 22 g of DBP.

Sample B (Hereinafter Referred to as 'B')

After synthesizing in the same way as 'A' and checking the reaction, cool the contents down to the temperature of 50°C or below and then, add 26 g of DBP.

Sample C (Hereinafter Referred to as 'C')

Put 330 g of water in the reactor installed with a stirrer and then, add 20 g of PVA P24 and 15 g of P20, and 0.9 g of emulsifier (HBL=12.3). While keeping up the stirring speed of 130 rpm, dissolve the contents within the reactor by raising the temperature up to 80°C. After completely dissolving the contents, add APS and check the reaction while dropping 180 g of vinyl acetate monomer, 16 g of butyl acrylate monomer and 5 g of acrylic acid for duration of 4 h. After completely checking the reaction, cool the contents down to the temperature of 50°C or below and then, add 8 g of DBP.

Sample D (Hereinafter Referred to as 'D')

Put 330 g of water in the reactor installed with a stirrer and then, add 17 g of PVA P24, 11 g of P17, 9 g of AH22, and 0.5 g of emulsifier (HBL=12.3). While keeping up the stirring speed of 130 rpm, dissolve the contents within the reactor by raising the temperature up to 80°C. After completely dissolving the contents, add 100 g of EP706 and APS and then, check the reaction while dropping 167 g of vinyl acetate monomer and 1 g of acrylic acid for duration of 4 hours.

Table 2. Composition of synthesized adhesives

	Sample A	Sample B	Sample C	Sample D	Sample E
Water (g)	330	330	330	330	330
PVA (poly(vinyl) alcohol)	22	22	35	37	37
VAM (Vinyl acetate monomer)	220	220	180	167	167
Acrylate	-	-	16	-	-
Acrylic acid	-	-	5	1	1
DBP (Dibutyl phthalate)	22	26	8	-	-
VAE (Vinyl acetate-ethylene emulsion)	-	-	-	100 ( $T_g$ , 0°C)	100 ( $T_g$ , -15°C)

Sample E (Hereinafter Referred to as 'E')

Synthesize in the same way as 'D' while using 100 g of AF401 instead of EP706.

Vinyl acetate monomer and PVA are commonly used for the respective sample ingredients and for the case of 'C,' a small amount of high viscosity PVA has been applied additionally. In order to see the physical property change in varying plasticizer and  $T_g$ , the amount of DBP for A and B has been changed by 10% and 12% as compared to that of monomer and for the cases of C, D and E, the amount of plasticizer has been reduced or not added. In the cases of D and E,  $T_g$  has been used with 2 other VAE products. The amounts of respective uses are listed on Table 2.

## 2.3 Characteristic Tests

### 2.3.1. Physical Property Measurement

As for the viscosity test, RION viscotester VT-04 has been used and the measurement temperature has been set to 25°C. As for the solid content (%), it has been dried at the temperature

of 150°C for 30 minutes and the amount has been measured. The glass transition temperature ( $T_g$ ) has been measured by using DSC-2010 (TA Instrument) and its particle size has been measured by using the particle sizer (Shinadzu SALD1100).

### 2.3.2. Test Sample Preparation

As for the test sample material, a timber with the size of 25 mm×30 mm and specific gravity of 0.5 or higher that has been dried up to the moisture percentage of 15% has been used. Affix together by applying about 100 g/m<sup>2</sup> adhesive well-mixed in advance on both sides of adhesion and leave it at the temperature of 20 ± 2°C for 24 hours after compressing it within 10 minutes with a load of 5 ~ 10 kgf/cm<sup>2</sup>. After removing the pressure, it has been left alone for 48 hours and tested for the waterproof adhesion strength.

### 2.3.3. Adhesion Force

#### 2.3.3.1. Adhesion Strength

The compression shear strength has been

Table 3. Properties of synthesized adhesives

	Sample A	Sample B	Sample C	Sample D	Sample E
Viscosity (cp)	25,000	24,000	86,000	28,000	24,000
Solid content (%)	41.2	41.0	42.0	41.7	41.2
Plasticizer <sup>1)</sup>	DBP (10%)	DBP (12%)	DBP (4%)	-	-
Particle size ( $\mu\text{m}$ )	3.12	3.23	3.16	2.58	2.41

<sup>1)</sup> The amount of plasticizer is shown as the ratio of monomer weight.

measured by using a Universal Test Machine (UTM, Shimadzu AG-2000A) while using the test sample prepared.

#### 2.3.3.2 Waterproof Adhesion Strength

After dipping the test sample prepared again in the water with the temperature of  $20 \pm 1^\circ\text{C}$  for 10 minutes after dipping it in the water with the temperature of  $30 \pm 1^\circ\text{C}$  for 3 hours, the compression shear strength has been checked by using the universal test machine (UTM, Shimadzu AG-2000A).

#### 2.3.4. Minimum Film Forming Temperature (MFT)

After applying the sample widely on one side of the sample on a clean slide glass, make a uniform membrane with a thickness of 0.1~0.3 mm by drying it while maintaining at the specific temperature and humidity. Check it visually whether the dried object is a uniform continuous membrane and the membrane is whitened.

#### 2.3.5. Glass Transition Temperature ( $T_g$ )

$T_g$  of the blends was determined by a DSC with TA Instrument Q-1000, with a scan rate of  $10^\circ\text{C}^{-1}$  over a temperature range of  $-50$  to  $100^\circ\text{C}$ . The  $T_g$  was taken as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated

liquid and glass lines.

#### 2.3.6. Particle Size

The particle size was determined using a laser diffraction particle size analyzer (Shimadzu SALD 1100). The size of the microparticles was determined in paraffin oil (viscosity 5 mPa s) as a non-dissolving dispersion medium. Particles were suspended by sanification and magnetic stirring during the measurement.

## 3. RESULTS and CONSIDERATION

### 3.1. General Properties

The basic properties for the synthetic product are listed in the Table 3. Viscosity may differ in part from the type and use amount of PVA and generally, the final synthesized product comes out to be high in viscosity when a highly viscous PVA or relatively larger amount of PVA is used. In the case of C, it has used more of a highly viscous PVA and acrylic acid so that hydrogen cohesion can be generated more between A and B, leading to high in viscosity. The non-plasticized synthetic resins D and E, although they have used more PVA in comparison to A and B, are synthesized in a similar viscosity within the range of 25,000~30,000 cp due to the influence of VAE emulsion that is low in viscosity. Solid content (%) has been kept within 40~42% to adjust to the test con-

Table 4. Minimum film forming temperatures of synthesized adhesives

	Sample A	Sample B	Sample C	Sample D	Sample E
MFT (°C)	>5	>4	>5	>5	>0

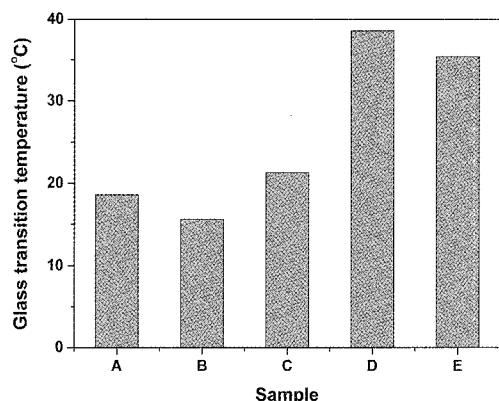


Fig. 1. Glass transition temperature of synthesized adhesives.

ditions of adhesive strength.

The glass transition temperatures ( $T_g$ ) of each synthesis resins are shown in Fig. 1. While the  $T_g$  of polyvinyl acetate that has not added a plasticizer generally appears to be 35~40°C, the cases of A and B makes a low  $T_g$  of 15~20°C that is suitable to use by applying DBP. Although it is known to make the resin with lower  $T_g$  as more DBP is added, it is not possible to make the resin with an unlimited low rate of  $T_g$ . In the case of C, a resin with a relatively low rate of  $T_g$  is synthesized by copolymerizing acrylate although the amount of DBP input is small. On the other hand, D and E have synthesized the resin high in  $T_g$  since no plasticizer were added and the case E that has used the VAE emulsion with a low  $T_g$  appears to be lower in  $T_g$ . The particle sizes for D and E that have copolymerized VAE emulsion appeared to be 0.5  $\mu\text{m}$  smaller than those of A, B, and C and it is judged that the result has come out to be in this way because they have used the VAE emulsion smaller in the particle size.

### 3.2. Minimum Film Forming Temperature (MFT)

In order for the water-based adhesive (emulsion type) to demonstrate its adhesive strength, it has to be bonded to the adherend by forming a film as water gets volatilized; but the whitening observed frequently, when using the adhesive in the winter season, is an example of adhesion defect that occurs when water is not volatilized and caught in the film. Therefore, the adhesive strength of water-based adhesive has a close relationship with the use temperature of adhesives. This whitening condition appears more apparently at the low temperature that water is not easily volatilized and the temperature of 0°C that water starts to freeze is known to be the limit of using water-based adhesives. MFT becomes an important criterion whether water-based adhesive can demonstrate its adhesive strength by forming a film up to a certain degree of low temperature. Previously, it is generally accepted that the lower  $T_g$  of resin emulsion holds the better low-temperature MFT property.

As shown on the Table 4, the more plasticizer (DBP) is used, the better the lower-temperature MFT property has come out; when using DBP and acrylate, the low temperature MFT property is more influenced by plasticizer than acrylate. It corresponds to the result of showing better lower-temperature MFT property as  $T_g$  gets lower. On the other hand, the cases D and E that have copolymerized VAE emulsion with vinyl acetate monomer have shown quite good low-temperature MFT property despite of a low  $T_g$ . In the case of D, the film has been formed up to the limit 0°C of using wa-

## Characteristics of Non-plasticizer PVAc Resin for Wood Products

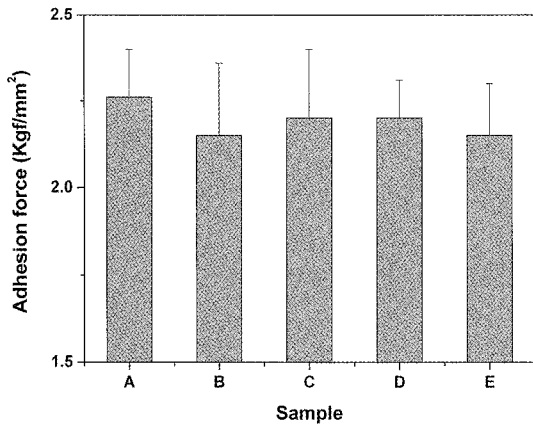


Fig. 2. Adhesion force of synthesized adhesives.

ter-based adhesive.

### 3.3. Adhesion Force

Plasticizer (DBP) is required to improve the physical resin properties as its amount of use increases and this comes out to be a disadvantage in the perspective of adhesive strength. As shown on the Fig. 2, B that uses more plasticizer appears to be lacking in the perspective of adhesive strength in the cases A and B. Also in case of plasticizer, it is known to cause a property change in the adhesive strength and adhesion resin due to the migration occurring in the inner side of wooden part after passing a long period of time upon adhesion and occasionally, this property can be a problem. The reason that the adhesive strength of C is low in spite of its low application of plasticizer is judged that it is the resin copolymerized with acrylate low in the adhesive strength.

The non-plasticized synthetic resins D and E show relatively low adhesive strength in comparison to the synthetic products on the market that have added plasticizer; but, all show the numbers of exceeding the limit that damages adherend. In the cases of D and E, it can be observed that E lower in the amount of Tg is lacking in the perspective of adhesive strength.

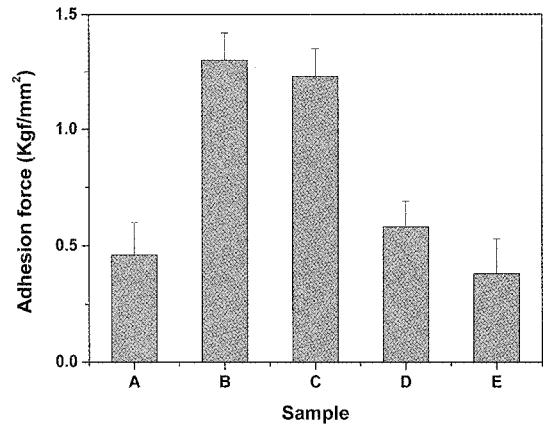


Fig. 3. Waterproof adhesion strength of synthesized adhesives.

Plasticizer (DBP), as its use increases, causes an adverse effect on the waterproof adhesion strength; as shown on the Fig. 3, A as compared to B shows better waterproof adhesion strength. Additionally, C shows better waterproof adhesion strength than B in connection to the reduced use of DBP and polymerization of low-water acrylate. Although the non-plasticized synthetic resins D and E hold relatively lower adhesive strength than the existing products of adding plasticizer (DBP), their waterproof adhesion strength appears to be far greater than others (refer to the Fig. 3). It is judged that waterproofness is greatly enhanced from the influence of VAE ethylene chain that holds low-water.

Fig. 4 is the result that the storage stability of non-plasticized synthetic resin has been checked the viscosity change while keeping it at 4°C and 50°C for one month. These two resins, synthetic resins D and E, were shown no significant difference during storage period of one month at 4°C and 50°C. These resins showed good storage stability.

## 4. CONCLUSION

Through this experiment, we can resolve the

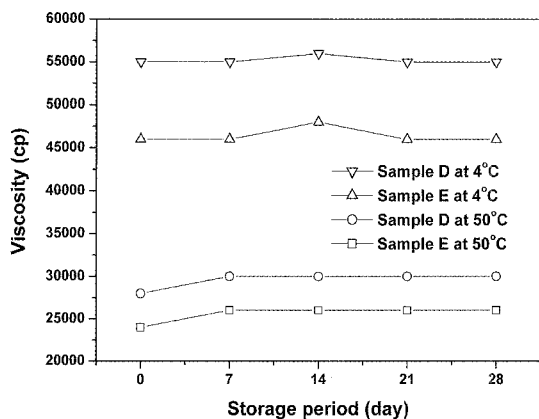


Fig. 4. Storage Stability of synthesized adhesives at 4°C and 50°C.

problem of low adhesive strength caused by adding plasticizer by copolymerizing vinyl acetate monomer and VAE emulsion when using adhesives in the winter season for woodworks and especially, the waterproof adhesion strength can be greatly improved. Furthermore, we can synthesize the PVAc resin adhesive of holding excellent minimum film forming temperature up to 0°C without adding more plasticizer (DBP) for the minimum film formation temperature that has been a big concern in using adhesives in the winter season. It has shown the performance that is not poorer than those of existing products in the perspectives of adhesive strength and storage stability and has allowed preparing for the property change problem of adhesion resin due to the possible plasticizer migration by adding plasticizer. Additionally, its area of application is expected to get larger in the domestic market as an environment-friendly product.

## ACKNOWLEDGMENTS

This work was supported by the research program of Agricultural R&D Promotion Center. Sumin Kim is grateful for the graduate fellow-

ship provided by the Ministry of Education through the Brain Korea 21 project.

## REFERENCES

1. Pizzi, A. 1983. Wood Adhesives - Chemistry and Technology. Marcel Dekker, Inc., New York.
2. Pizzi, A. and K. L. Mittal, 2003. Adhesive Technology and Application. Marcel Dekker, Inc., New York.
3. Blomquist, R. F., A. W. Christiansen, R. H. Gillespie, and G. E. Myers, 1961. Adhesive bonding of wood and other structural materials, EMMSE, The Pennsylvania State University, University Park, PA.
4. Verma, S. K. and S. C. Bisarya, 1986. Improvement in properties of poly(vinyl acetate): Emulsion with dibasic acids. *Journal of Applied Polymer Science* 31(8): 2675 ~ 2684.
5. Tuncer, D. and H. Salim. 2004. Effect of density and some of the production parameters on bending strength of laminated window profiles. *Building and Environment* 39: 1199 ~ 1205.
6. Yalçın, Ö., A. Musa, and Ö. Ayhan, 2000. Bonding strength of poly(vinyl acetate)- based adhesives in some wood materials treated with impregnation. *Journal of Applied Polymer Science* 76(9): 1472 ~ 1479.
7. Skeist, I. 1990. Handbook of Adhesives, Van Nostrand Reinhold, New York.
8. Daniels, W. E. 1983. Poly(Vinyl Acetate) in Kirkothmer Encyclopedia of chemical technology, 3rd Ed., John Wiley and Sons, New York.
9. Kim, S. and H.-J. Kim. 2005. Effect of addition of polyvinyl Acetate to melamine-formaldehyde resin on the adhesion and formaldehyde emission in engineered flooring. *International Journal of Adhesion and Adhesives* 25(5), 456 ~ 461.
10. Kim, S. and H.-J. Kim, 2006. Study of Miscibility of melamine-formaldehyde resin and poly(vinyl acetate) for adhesive in engineered flooring. *Journal of Adhesion Science and Technology* 20(2-3), 209 ~ 219.