

Preparation and Adhesive Characteristics of the Acrylic Pressure-Sensitive Adhesives(I)

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(Received February 24, 1983; Accepted May 19, 1983)

Abstract: To prepare acrylic type pressure-sensitive adhesive, terpolymers were synthesized from butyl acrylate(BA), vinyl acetate(VA) and maleic anhydride(MA). These terpolymers were partially crosslinked by a hexamethylol melamine type agent(CL-K). The crosslinking was identified by IR and GPC. Molecular weight was measured by a vapor pressure osmometer. To carry out terpolymerization, the amounts of MA and initiator were held constant, while the amounts of BA and VA were varied over 0.5—1.0 mole and 0.4—1.5 mole, respectively. At BA/VA mole ratio of 1 : 0.5(in case of BVM-3), polymerization for 8 hrs at 75°C with AIBN as a catalyst gave the best results. Adhesive characteristics of the crosslinked BVM-3 (BVMC-2) were 900g/inch in peel strength, more than 24 hours of holding power, 14/32 for tackiness and 85°C for heat resistance. BVMC-2 showed good balanced properties as a permanent pressure-sensitive adhesive. Although the crosslinked polymer exhibited good adhesive characteristics, the uncrosslinked one was not suitable for the pressure-sensitive adhesive.

1. INTRODUCTION

Numerous studies on pressure sensitive adhesives have been reported since Day applied pressure sensitive adhesives to plaster in 1845. Later on, Drew prepared a pressure-sensitive adhesives for masking by adding zinc flowers and coumarone indene to a rubber. Since then, a tape of pressure-sensitive adhesives of plastic film instead of paper and fabric as a base has been prepared and developed rapidly as applying to label, seal, name plate, road sign, album and

wall papers.

In general, the pressure-sensitive adhesive gives lower cohesive strength but higher tackiness than the other general purpose adhesive^{1,2}.

The pressure-sensitive adhesive requires the balanced properties of strength, cohesive strength and keying strength. Dow³ described that an ideal property of the pressure-sensitive adhesive should have keying strength > cohesive strength > adhesive strength > tackiness. The other desired properties are heat-resistance,

cold-resistance, oil-repellency, water-resistance and easy removal.

The pressure-sensitive adhesive can be classified in many different ways. For instance, it can be emulsion type or solvent type in terms of physical state, and permanent type or removable type in final applied form.

The compositional classification of the pressure-sensitive adhesive is given below with some characteristics.

1) Rubber type⁴

The rubber type pressure-sensitive adhesive has most commonly been used for long times. There are two types, natural vs. synthetic. The natural type exhibits good properties of tackiness and adhesive strength, but poor softening property which may be due to degradation of the unreacted functional groups by heat or ultraviolet light.

2) Vinyl type⁵

Copolymer of vinyl chloride with either vinyl acetate or polyvinyl acetates containing plasticizer are available, but acrylic-based polymers with good weather-resistant, oil-repellent and heat resistant properties have recently been introduced.

3) Silicone type^{6,7,8}

A silicone-based pressure-sensitive adhesive consists of rubber type and resin type siloxane. The former imparts film-forming property and cohesive strength, while the latter gives tackiness and adhesive strength.

The silicone type has a wide range of application temperature, weather resistance, water-resistance and good electrical properties. However the cost is relatively high and the curing is required for good tackiness. In general, the silicone type needs heating for curing. i.e. 170°C for 10 min.

4) Acrylic type⁹

The major component is alkyl acrylates.

Notable features of the acrylic type are good weather resistance and oil resistance. Especially, polar functional group can be introduced into the polymer to improve tackiness¹⁰. With further crosslinking one can manipulate adhesive strength and cohesive strength of the adhesive.

The above brief comparisons give the acrylic type an edge over other types in terms of properties and compositional versatility. Thus, a copolymer of acrylic monomer with vinyl functional group appears to be very promising.

However, there is little information available on the acrylic type pressure-sensitive adhesives in the literature. This led us to study crosslinked acrylic pressure-sensitive adhesives. polymers were terpolymers of butyl acrylate (low Tg), vinyl acetate (high Tg) and maleic anhydride with various proportions and then crosslinked by methylol melamine. Conversion, molecular weight distribution and extent of crosslinking were investigated. Furthermore, the three most important characteristics of the pressure-sensitive adhesive¹¹, i.e. peel strength, holding power and tackiness, were studied to examine the performance of the polymers as pressure-sensitive adhesive.

2. EXPERIMENTAL

2-1. Synthesis of the terpolymer of butyl acrylate, vinyl acetate and maleic anhydride

2-1-1. Raw Materials

vinyl acetate : Analytical grade from Tokyo Kasei Co. was treated first with 10% NaCOO-CH₃ aqueous solution to eliminate the inhibitor, then distilled. Only 72-73°C cut from atmospheric pressure distillation was used for the synthesis.

butyl acrylate : Reagent grade n-butyl acrylate (Kanto Chemical Co.) was distilled twice under

vacuum (9mmHg) and 8mmHg to remove the inhibitor (15 ± 2 ppm p methoxy phenol). The 35°C cut was taken for the experiment.

maleic anhydride : Analytical grade (Kanto Chemical Co.) was used as received.

2,2'-azo-bis-isobutyronitrile (AIBN): Reagent grade AIBN (Merck Co.) was saturated first in chloroform at 40–50°C, then excess ether was added to this solution. AIBN was then recrystallized¹² with slow cooling of the solution.

benzoyl peroxide : Reagent grade (Kanto Chemical Co.) was used as received.

ethylacetate : Reagent grade (Tokyo Kasei Co.) was distilled under atmospheric pressure. The (77–78°C) fraction was used.

toluene : Reagent grade (Katayama Chemical Co.) was distilled under atmospheric pressure. The (110–112°C) fraction was used.

2-1-2. Synthesis of Terpolymer

The typical synthetic method is as follows. (ref. Table 1). 128g (1.0 mole) of butyl acrylate (BA), 43g (0.5 mole) of vinyl acetate (VA) and 4.9g (0.05 mole) of maleic anhydride (MA) were all mixed in a 500 ml 4-neck flask equipped with a stirrer, dropping funnel and a thermometer. 60ml of ethyl acetate and 40ml of toluene as solvent were gradually added to the flask with the stirrer on. Then the initiator AIBN was added and its concentration was adjusted to 1.5×10^{-2} mole/l.

The polymerization reaction was initiated at 60°C under N₂ blanket. The temperature was maintained constant with automatically controlled heating and cooling device. Polymerization was carried out at 60°C for first 1 hr and at 70–80°C for 8 more hrs. The final product (BVM) was colorless, viscous liquid.

2-2. Crosslinking of BVM

The typical method employed for crosslinking of BVM was as follows. (ref. Table 2) : BVM 100g was placed in a 200ml 3-neck flask equi-

pped with a stirrer, a reflux condenser and a thermometer. Colorless liquid crosslinking agent K(CL-K, methylol melamine group) 1.5g was added to BVM to initiate the crosslinking reaction. The reaction was carried out at 100°C for 2hrs. to obtain the partially crosslinked BVM (BVMC).

2-3. Analysis

2-3-1. IR Spectrophotometry

A film used for Diffraction Grating Infrared Spectrophotometer (DS-701 G, JASCO Co.) was prepared by coating 12% polymer solution,

2-3-2. Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography was measured by Shimatzu Liquid Chromatograph 830. The columns used were HSG-30. THF was the solvent with a flow rate of 1.0 ml/min.. Samples were injected at a concentration of 0.25 weight volume percent. Refractive Index detector was also used.

2-3-3. Molecular Weight Determination

Molecular weight of polymers was measured by a Vapor Pressure Osmometer (302 B model, Hewlett Packard Co.) at 45°C with 2 minute intervals. Calibration standard was tetrabromobisphenol A (M.W.=544) dissolved in toluene.

2-4. Property Tests of Pressure-Sensitive Adhesives

2-4-1. Coating of Adhesives

BVMC was coated on polyester film (Toyo Rayon Ruminer #25) by a Doctor Blade Method to give a uniform 25 μ thickness, then dried for 3 minutes at 100°C. This coated film was used as test specimens after storing 24 hrs at room temperature. The thickness was checked by a Peacock Upright Dial Gauge.

2-4-2. Peel Strength

A test specimen (25 μ) was first applied on SUS #27 stainless steel plate (JIS C4305). Adhesion was secured by rolling a 2kg rubber

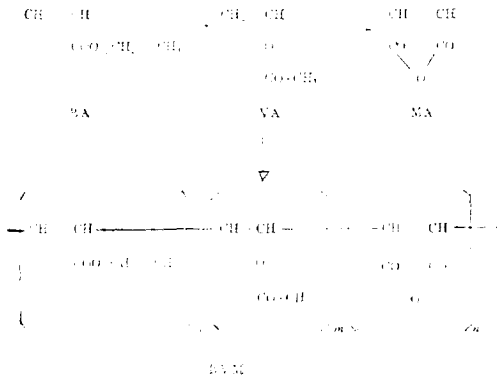


Fig. 1. Synthetic Scheme of BVM.

roller over the sample 8 full times with a Tape Adhesion Roll. Then Auto Graph(P-100 model) was run at 25°C in 180 degree direction at a speed of 300 mm/min. to measure the removable intensity.

2-4-3. Holding Power

A test specimen was applied on SUS #27 stainless steel plate. The adhesion area was 25 × 25mm². The 2kg rubber roller was rolled over the adhesive film 8 full times, then kept in 20°C thermostat for 1 hr. The specimen was held at 0 degree with a weight of 1 kg atta-

ched to the lower end of the test sample. The time for spontaneous fall was measured at 70°C. YSS No. 145-LCT (Yasuda Seiki Co.) was used for the test.

2-4-4. Tackiness

Tackiness was determined at 20°C and 30 degree angle according to the Dow Method³.

2-4-5. Heat Resistance

Heat resistance test was carried out in a similar manner with the holding power test. The specimen was first kept at 20°C for 45 min., then at 40°C for 15min. Temperature was raised from 40°C to 100°C at a rate of 2°C/5min. The temperature of spontaneous fall was measured.

3. RESULTS and DISCUSSION

3-1. Synthesis of BVM

It is generally known that the major composition of acrylic type pressure-sensitive adhesives is alkyl acrylate whose T_g is relatively low. To balance tackiness and cohesive strength, however, they normally are copolymerized. Therefore, BA(T_g: -57°C) and VA(T_g: 20°C)

Table 1. Polymerization Condition and Physical Property of BVM.

Products	Materials				Reactions		Conversion (%)	Viscosity* (cps)	Mol. wt (Mn)	Solvent**
	BA g(mole)	VA g(mole)	MA g(mole)	Initiator	Temp. (°C)	Time (hrs)				
BVM-1	192(1.5)	26(0.3)	4.9(0.05)	AIBN	80	8	87	17000	18000	Tl, Xe, Mx, At
BVM-2	154(1.2)	34(0.4)	4.9(0.05)	"	75	8	92	15000	16300	"
BVM-3	128(1.0)	43(0.5)	4.9(0.05)	"	75	8	91	15000	15400	"
BVM-4	64(0.5)	129(1.5)	4.9(0.05)	"	75	7	86	16600	13000	"
BVM-5	128(1.0)	43(0.5)	4.9(0.05)	"	70	8	86	12000	10000	"
BVM-6	128(1.0)	43(0.5)	4.9(0.05)	"	80	8	93	15000	15500	"
BVM-7	128(1.0)	43(0.5)	4.9(0.05)	"	75	7	85	13000	11000	"
BVM-8	128(1.0)	43(0.5)	4.9(0.05)	"	75	9	88	15000	15700	"
BVM-9	154(1.2)	34(0.4)	4.9(0.05)	BPO	80	8	83	13000	11000	"
BVM-10	128(1.0)	43(0.5)	4.9(0.05)	"	80	8	90	14000	15000	"
BVM-11	128(1.0)	43(0.5)	4.9(0.05)	"	75	8	85	12000	11500	"
BVM-12	128(1.0)	43(0.5)	4.9(0.05)	"	75	7	85	10000	9800	"

* Measured by BH Viscometer at 30°C

** Tl: Toluene, Xe: Xylene, Mx: Methyl ethyl ketone, At: Aceton

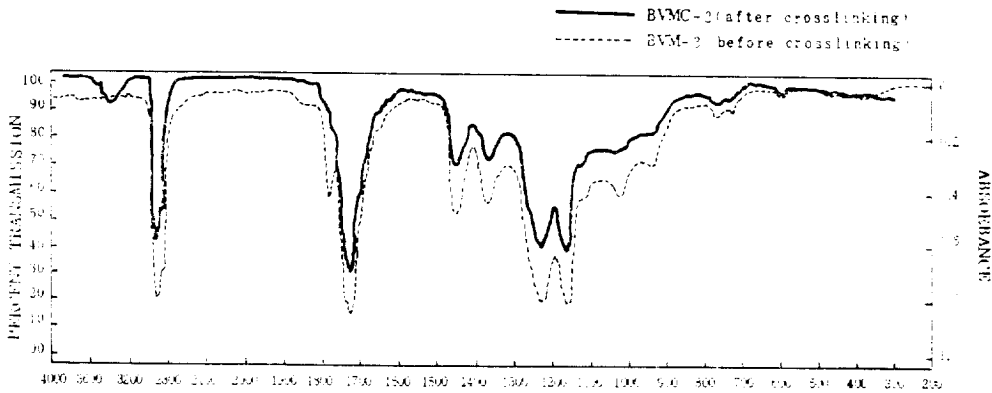


Fig. 2. IR Spectra of BVM-3 and BVMC-2.

are chosen for the study. Synthetic scheme of BVM from BA, VA and MA are described in Figure 1.

Table 1 shows reaction conditions, conversion, viscosity and the molecular weight. Use of BPO as initiator instead of AIBN gives little difference except the molecular weight and viscosity whose values are lower with BPO than with AIBN. The primary role of MA in the copolymer is to provide a crosslinking site. The reason for determining reaction time with viscosity is because the viscosity is an important characteristic of the pressure-sensitive adhesive. In this work, the best reaction condition of synthesis of BVM is 8 hrs of reaction time at 75°C. Figure 2 shows IR spectrum of BVM-3.

The presence of $\nu_{C=O}$ band¹³ at $1,780\text{cm}^{-1}$ and ester $\left(\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{C}-\text{O}-\text{C}- \end{array} \right)$ band¹³ at $1,020\text{cm}^{-1}$ indicates the presence of acid anhydride ring. On the other hand the presence of $\nu_{C=C}$ absorption¹⁴ at $1,730\text{cm}^{-1}$ and ν_{C-O} absorption¹⁴ at $1,160\text{cm}^{-1}$ identifies the presence of vinyl ester and acrylate respectively.

3-2. Synthesis of BVMC

The crosslinking reaction of BVM and CL-K is described in Figure 3.

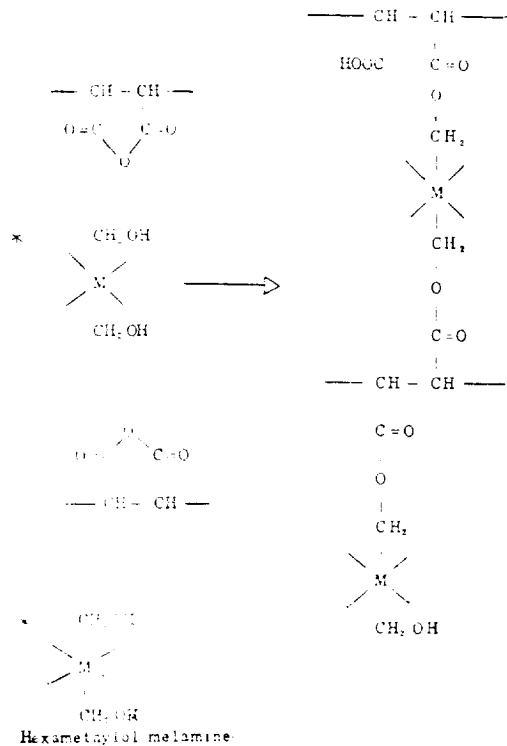


Fig. 3. Synthetic scheme of BVMC.

The crosslinking temperature, time, viscosity and molecular weight are listed in Table 2.

As can be seen in Table 2, the viscosity and molecular weight were increased by the crosslinking. As shown in Figure 3, the me-

Table 2. Crosslinking Conditions and Physical Property of BVMC.

Products	Materials		Reactions		Viscosity* (cps)	Mol. wt. (\bar{M}_n)
	BVM(g)	CL-K(g)	Temp(°C)	Time(hrs)		
BVMC-1	BVM-2(100)	1.5	100	2	22000	28000
BVMC-2	BVM-3(100)	1.5	100	2	20000	27000
BVMC-3	BVM-4(100)	1.5	100	2	19000	22000
BVMC-4	BVM-5(100)	1.5	100	2	15000	19000
BVMC-5	BVM-8(100)	1.5	100	2	22000	28000
BVMC-6	BVM-10(100)	1.5	100	2	20000	26000
BVMC-7	BVM-11(100)	1.5	100	2	14000	17000

* Measured by BH Viscometer at 60°C

thylol group of CL-K reacts with butanedionic anhydride ring in BVM to form carboxylic acid in one part and esteric bond in the other part. This carboxylic acid can react further with the methylol group of CL-K leading to additional crosslinking.

Figure 2 includes IR spectrum of BVMC-2. IR spectra of BVM and BVMC seem to be almost same because content of MA in two polymers are low and the polar groups of two materials are same. However, the absorption band of acid anhydride ring disappears after crosslinking ($1,780\text{cm}^{-1}$ & $1,020\text{cm}^{-1}$), indicating that the acid anhydride ring reacts with CL-K to give an ester linkage^{15,16}.

On the other hand, the GPC chromatograms of BVM-3 and BVMC-2 were presented in Figure 4.

It is shown that the average molecular weight of crosslinked sample is higher than that of the uncrosslinked (BVM-3). However, no appreciable difference in elution volume is observed between two polymers as shown in Figure 4. This might be due to the fact that the polymers were only partially crosslinked by use of relatively low amount of crosslinking agent to optimize the adhesion characteristics. It may also be deduced from the molecular weight-viscosity relationship presented in Table 1 and 2.

3-3. Properties of Pressure-Sensitive Adhesives

Three important physical properties of pressure-sensitive adhesives based on BVM and BVMC are given in Table 3.

It is well accepted in the pressure-sensitive adhesive market that a pressure-sensitive adhe-

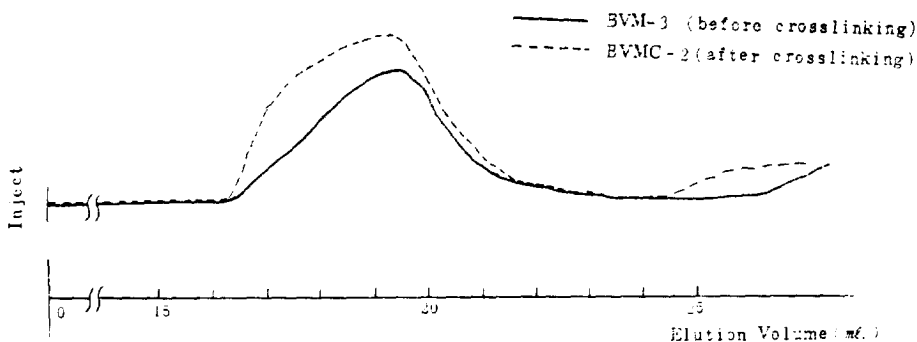


Fig. 4. Gel permeation chromatograms of BVM-3 and BVMC-2.

Table 3. Properties of Pressure-Sensitive Adhesive

Base Polymer	Peel strength (g/inch)	Holding power (hrs)	Tackiness	Heat resistance (°C)
B V M— 2	2100	1.0	16/32	40
B V M— 3	2300	1.0	16/32	45
B V M— 4	1600	0.5	12/32	40
B V M—10	2100	0.8	14/32	35
BVMC— 1	900	24 over	12/32	85
BVMC— 2	900	24 over	14/32	85
BVMC— 3	450	24 over	8/32	75
BVMC— 4	1300	12	14/32	60
BVMC— 5	400	24 over	7/32	85
BVMC— 6	800	24 over	10/32	70
BVMC— 7	1400	12	14/32	50

sive should exhibit the adhesive strength of (\pm) 1000g/inch, holding power of more than 24 hrs and tackiness 14/32-18/32. Therefore from Table 3, overall performance of the adhesives tested which show order of BVMC-2>BVMC-1>BVMC-6>BVMC-3. BVMC-2 and BVMC-1 exhibited a strong potential as a practical pressure-sensitive adhesive with good heat resistant property.

The uncrosslinked BVM showed rather poor performance, especially in holding power and heat resistance. In general, the crosslinking increases holding power but reduces adhesive strength, which explains why BVM has high adhesive strength but low holding power.

4. CONCLUSIONS

A series of pressure-sensitive adhesive has been prepared by terpolymerization of butyl acrylate, vinyl acetate and maleic anhydride, followed by crosslinking with hexamethylol melamine. When the adhesive strength, holding power and tackiness of the compounds were measured and compared, the following results were obtained.

1. The optimal terpolymerization condition of BA,VA and MA was for 8 hrs of reaction time at 75°C with AIBN initiator.

2. The crosslinked polymer showed a good balance of adhesive properties, but the uncross-linked polymer was not suitable for the use as a pressure-sensitive adhesive due to poor holding power and low heat resistance.

3. BVMC-1 and BVMC-2 gave excellent performance suggesting the possibility as a practical pressure-sensitive adhesive.

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