

Properties of Reactive Hot Melt Polyurethane Adhesives with Acrylic Polymer or Macromonomer Modifications

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ABSTRACT: The properties of reactive hot melt polyurethane adhesives (RHAs) modified by dihydroxyl-terminated reactive acrylic macromonomers were examined and compared with those of RHAs modified with a nonreactive commercial acrylic copolymer. The melt viscosity and initial bond strength was increased when a portion of the polyols and tackifier was replaced by macromonomers or acrylic copolymers, which have higher glass transition temperatures. When RHA was modified by macromono-

mer, the storage modulus at low shear rate was reduced and set time was increased, which suggests that the chain entanglement was diminished by short-chain branches created by the macromonomers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1757–1763, 2008

Key words: adhesives; macromonomers; viscoelastic properties; polyurethanes; acrylic polymers

INTRODUCTION

Reactive hot melt adhesives (RHAs) are applied in a molten form, solidified by cooling, and are subsequently cured by means of a chemical crosslinking reaction. The first solidification by cooling provides a quick initial bond that is required for the immediate fabrication of a stable bonded assembly. The subsequent crosslinking reaction enhances the bond strength and endows the adhesive with superior mechanical properties and high thermal and solvent resistance, compared with conventional noncuring hot melt adhesives.^{1–3}

The majority of RHAs are moisture-curing polyurethane adhesives whose main components are isocyanate-terminated polyurethane prepolymers; these cure after application by reaction with ambient moisture.^{4–11} Because the polyurethane prepolymers are designed to have a low melt viscosity for facile handling and application, they generally have a molecular weight of only a few thousand daltons, and exhibit poor initial bond strength immediately after cooling compared with conventional nonreactive hot

melt adhesives. To overcome this drawback, polymers with a high glass transition temperature, or with high crystallinity, either of which can accelerate solidification after application upon cooling, are generally incorporated in moisture-cure reactive hot melt polyurethane adhesives (RHAs).^{2,4,10,12} In many patents, it is reported that acrylic copolymers substantially improve the initial bond strength as well as the final bond strength after curing, because they are compatible with and cooperate with polyurethane prepolymers and other components of RHA.^{13,14} Additionally, these improvements are amplified when the acrylic copolymers have hydroxyl groups available to react with isocyanate groups.² Because a reactive acrylic polymer that has more than two hydroxyl groups per molecule can undergo crosslinking via reaction with isocyanate during the preparation of RHA, the hydroxyl functionality of these reactive acrylic polymers should be controlled strictly. However, when the reactive acrylic copolymer is prepared by the radical copolymerization of acrylic monomer containing hydroxyl group, such as hydroxyl-substituted butylacrylate, it is not easy to control the functionality exactly.¹⁵

When an acrylic polymer has two hydroxyl groups that can react with isocyanate group, it will not cause crosslinking and it can be dispersed homogeneously in RHA matrix for the effective enhancement of initial bond strength by accelerated solidification. In addition, the viscosity increase by the added acrylic polymer can be minimized when a

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TABLE I
Characteristics of Macromonomer

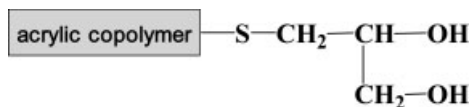
Sample	Composition ^a (wt %)		Molecular weight by			T_g^c (°C)
	MMA	BMA	Titration ^b	GPC		
					\bar{M}_n	\bar{M}_w
MM-1000	53	47	1385	2310	4750	29
MM-3000	48	52	2606	3780	8850	47
MM-5000	49	51	4754	5540	16,040	57

^a Determined by ¹H NMR.

^b Determined by hydroxyl group titration.

^c Determined by DSC.

low-molecular-weight reactive acrylic polymer was used instead of a high-molecular-weight nonreactive acrylic polymer. So, in this study, we prepared reactive acrylic copolymers which do not cause crosslinking. That is, the dihydroxy-terminated acrylic macromonomers of the following chemical structure (chemical structure 1) was prepared by the radical polymerization of acrylic monomers in the presence of a chain transfer agent, 3-mercapto-1,2-propanediol.^{16,17} The effects of this macromonomer on the rheological and physical properties of RHA were examined and compared with those of RHAs modified by a commercial nonreactive acrylic copolymer.



Chemical structure 1

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, Aldrich), *n*-butyl methacrylate (BMA, Aldrich), 2,2'-azobisisobutyronitrile (AIBN, Junsei Chemicals, Tokyo, Japan), 3-mercapto-1,2-propanediol (MPD, Aldrich), and tetrahydrofuran (THF, Aldrich) were used as received. Poly(propylene glycol) (PPG) of two kinds, PPG-3000 (molecular weight: 3000) and PPG-1000 (molecular weight: 1000), were obtained from BASF Korea and Korea Polyol, respectively. A crystalline polyester polyol, Dynacoll-7360 (molecular weight: 3500; melting temperature: 55°C), was obtained from Degussa. Liquid methylene diphenyl diisocyanate (MDI) containing 50% *para*, *para*'-MDI and 50% *ortho*, *para*'-MDI was obtained from BASF Korea. The catalyst 2,2'-dimorpholinoethyl ether (DMEE, Huntsman, USA), tackifier terpene-phenolic resin (Tamanol 803, Arakawa Chemical, Osaka, Japan), and degassing agent Modaflo 2100 (Solutia, USA) were used as received. The

acrylic copolymer Elvacite-2013, a copolymer of 64% BMA and 36% MMA, whose glass transition temperature (T_g) is 76°C and molecular weight is 34,000, was obtained from Ineos Acrylics.^{13,15}

Preparation and characterization of macromonomers

Macromonomers with dihydroxyl terminal groups were prepared by the radical copolymerization of MMA and BMA with AIBN in the presence of the chain transfer agent MPD, which controls the molecular weight of the macromonomer and provides the dihydroxyl terminal group. Briefly, 56 g of MMA, 44 g of BMA, and 0.2 g of AIBN were dissolved in 150 mL of THF, and polymerized under N₂ atmosphere at 70°C in a glass reactor agitated with a magnetic bar. After 4 h, THF and residual monomers were evaporated at 90°C in a vacuum drying oven to obtain the macromonomer. The amounts of MPD mixed with monomers for the synthesis of MM-1000, MM-3000, and MM-5000 (Table I) were 4.8, 2.4, and 1.2 g, respectively.

The properties of the macromonomers shown in Table I were determined as follows. ¹H NMR spectra were recorded on a 500 MHz NMR spectrometer (Varian, Unity Inova 500) using acetone-*d*₆ as a solvent. The areas of the peaks at 3.6 ppm (3H, OCH₃ in MMA) and at 4.0 ppm (2H, OCH₂ in BMA) were utilized to calculate the compositions of MMA and BMA in the macromonomers. To measure the hydroxyl number, the macromonomer was reacted with an excess amount of acetic anhydride in pyridine at 98°C for 1 h, and the residual acetic anhydride was titrated with 1M KOH solution. The molecular weight of the macromonomer was calculated by eq. (1). The number average molecular weight (\bar{M}_n) and weight average molecular weight (\bar{M}_w) were measured at 43°C with gel permeation chromatography (GPC, Waters M510) using THF as an eluent. Differential scanning calorimetry (DSC) was performed with a TA Instrument DSC Q10 under N₂ atmosphere at a heating rate of 10°C/min. T_g was

TABLE II
Formulas for the Preparation of RHAs

Sample	Feed (by weight)										
	PPG-1000	PPG-3000	Dynacoll-7360	Terpene-phenolic resin	Elvacite-2013	Macromonomer			MDI	DMEE	Modaflow
						MM-1000	MM-3000	MM-5000			
RHA-0	20.48	20.48	20.48	20.48	–	–	–	–	17.16	0.125	0.80
RHA-E-5	19.25	19.25	19.25	19.25	5.51	–	–	–	16.66	0.125	0.80
RHA-E-14	17.15	17.15	17.15	17.15	14.73	–	–	–	15.85	0.125	0.80
RHA-E-22	15.47	15.47	15.47	15.47	22.11	–	–	–	15.18	0.125	0.80
RHA-M1-5	19.02	19.02	19.02	19.02	–	5.44	–	–	17.56	0.125	0.80
RHA-M1-14	16.65	16.65	16.65	16.65	–	14.28	–	–	18.22	0.125	0.80
RHA-M1-22	14.80	14.80	14.80	14.80	–	21.16	–	–	18.73	0.125	0.80
RHA-M3-14	16.87	16.87	16.87	16.87	–	–	14.48	–	17.12	0.125	0.80
RHA-M5-14	16.99	16.99	16.99	16.99	–	–	–	14.58	16.55	0.125	0.80

measured in the second heating scan from 20 to 100°C.

$$\text{Molecular weight} = \frac{56,100 \times 2}{\text{Hydroxyl number}} \quad (1)$$

Preparation of reactive hot melt adhesive

A 1-L, round-bottomed, four-necked flask equipped with a mechanical stirrer, a thermometer, a nitrogen gas inlet, and a condenser with a drying tube was used as the reaction vessel; the reaction temperature was controlled with an oil bath. Formulas for the preparation of RHAs are shown in Table II. The reference sample (RHA-0) was prepared as follows: PPG-3000, PPG-1000, Dynacoll 7360, terpene-phenolic resin, and Modaflow 2100 were added to the reactor and agitated for drying under vacuum for 2 h after heating to 100–110°C. After drying, DMEE and liquid MDI were added sequentially into the reactor, and the reaction between the hydroxyl group of the polyol and the isocyanate group of the liquid MDI was carried out for about 1 h at 110°C under a nitrogen atmosphere to obtain the RHA containing the polyurethane prepolymer with terminal isocyanate groups. The isocyanate group content in RHA was controlled by feed recipe to be 3.0% by weight. After the reaction was completed, the RHA was further degassed in the reactor for 1 h at 100–110°C.

Samples containing Elvacite-2013 or macromonomers were prepared by a similar method, except that a portion of the PPG-1000, PPG-3000, Dynacoll-7360, terpene-phenolic resin mixture was replaced by Elvacite-2013 or macromonomers. However, the weight ratio of PPG-1000/PPG-3000/Dynacoll-7360/terpene-phenolic resin was kept at 1 : 1 : 1 : 1 as in the preparation of RHA-0, and the isocyanate group content in RHA was kept at 3.0% by weight.

Measurements

Dynamic rheological properties were measured with a cone and plate rheometer (Physica, MCR 301) at 120°C and 15% strain level. The cone angle and the diameter of the plate were 1.0° and 50 mm, respectively.

The melt viscosity of RHAs was measured using a Brookfield viscometer (DV-11 Pro) with a spindle (SC 4-27) rotating at 20 rpm at 100 or 120°C. The growth of melt viscosity after 1 h at 120°C compared with the initial viscosity was used as the metric for viscosity stability.

Tensile tests were performed with a tensile tester (Shimadzu AGS-1000D, Japan) according to the ASTM D 882 standard. The dumbbell-shaped micro-tensile specimen had the following dimensions: 100 mm length, 10 mm width, and 0.2 mm thickness. The specimen was elongated at a rate of 200 mm/min. The film for this test was obtained by curing the RHA at 25°C in a 55% relative humidity environment for 3 days.

An acrylonitrile-butadiene-styrene copolymer sheet was coated with RHA melted at 150°C to a thickness of 0.2 mm, and poly(ethylene terephthalate) fabric (thickness: 2 mm; width: 10 mm; length: 80 mm) was brought in contact, pressed with a 5-kg roller, and allowed to stand at 25°C in a 55% relative humidity environment. The bond strengths after 2, 5, 10, 15, 30 min, and 3 days were measured by an 180° peel test with a push-pull gauge (Imada, DPS-50, Japan) at a peel rate of about 20 mm/min.

The set time was measured according to the method suggested by Degussa. Briefly, ~ 0.58 mg/mm² of RHA at 100°C was applied to the wide side of a wooden block with the following dimensions: 113 mm width, 22 mm length, and 6 mm height. A second block was attached to the first one and carefully twisted. The set time was defined as the time when the cubes could no longer be twisted.

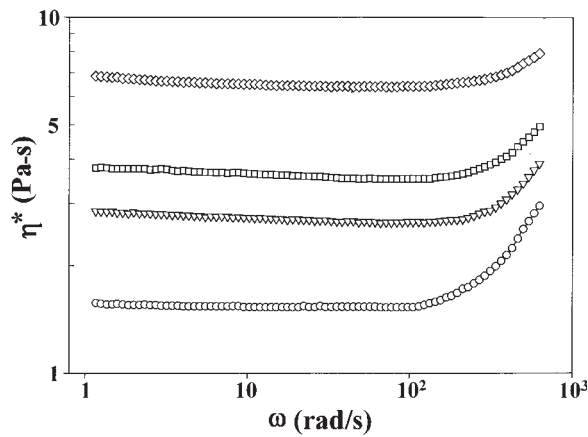


Figure 1 Complex viscosity versus frequency of (○) RHA-0, (▽) RHA-E-5, (□) RHA-E-14, and (◇) RHA-E-22, measured at 120°C.

RESULTS AND DISCUSSION

Rheological properties

The RHA-0 exhibits Newtonian fluid behavior, with a plateau of almost constant complex viscosity (η^*), independent of oscillation frequency ω , persisting up to $\omega = 100$ rad/s (Fig. 1). This behavior shows that the molecular weights of the RHA constituents are not high enough to induce the shear thinning behavior observed in polymers which have a polydispersity of molecular weights. It can be seen (Fig. 1) that η^* increases as the amounts of Elvacite-2013, which substitutes for a portion of the polyols and tackifier, is increased. This shows that Elvacite-2013, whose molecular weight and T_g are higher than other polyols, increases the viscosity of RHA.

The storage shear modulus (G') is also increased as the amount of Elvacite-2013 is increased (Fig. 2). The short-term response at a high shear rate depends on local chain motion; however, the long-term response at a low shear rate is primarily gov-

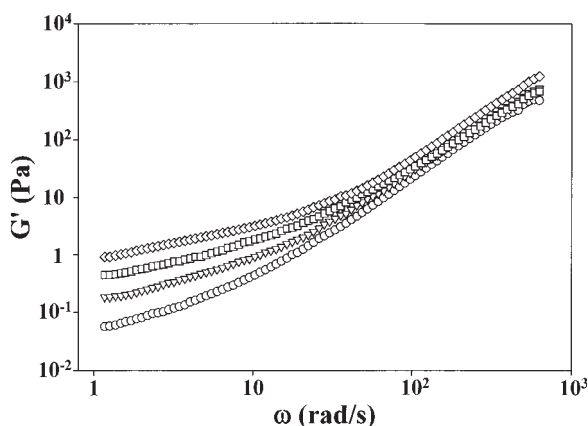


Figure 2 Storage shear modulus versus frequency of (○) RHA-0, (▽) RHA-E-5, (□) RHA-E-14, and (◇) RHA-E-22, measured at 120°C.

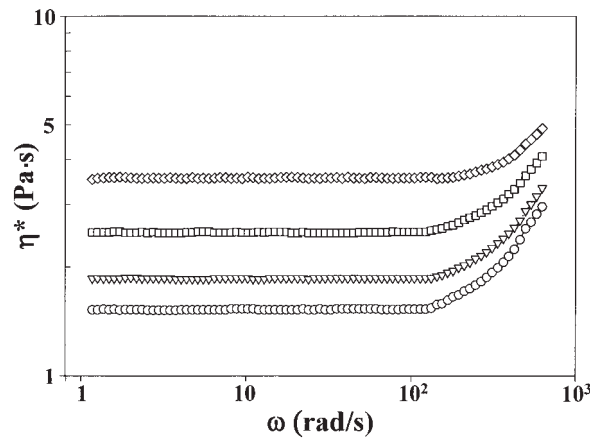


Figure 3 Complex viscosity versus frequency of (○) RHA-0, (▽) RHA-M1-5, (□) RHA-M1-14, and (◇) RHA-M1-22, measured at 120°C.

erned by the behaviors with long relaxation time. So, chain entanglement or crosslinking are important factors which affect the G' at a low shear rate.^{18–20} The observed variation in G' suggests that the increase of G' at high shear rates is mainly due to the more rigid character of Elvacite-2013 chain; however, the increase of G' at a low shear rate is mainly caused by the enhanced chain entanglement because of the higher molecular weight of Elvacite-2013 compared with those of the polyols and tackifier it replaced. The result that the increase of G' at a lower shear rate is more evident than the increase at a higher shear rate shows that Elvacite-2013 can effectively enhance the chain entanglement.

It can also be seen that the macromonomer MM-1000 also increases the viscosity of RHA (Fig. 3), though the degree of increase is smaller than that by Elvacite-2013 (Fig. 1). And, when RHA is modified with MM-1000, G' values are increased at higher shear rates but decreased at lower shear rates (Fig. 4). We can anticipate that MM-1000, whose

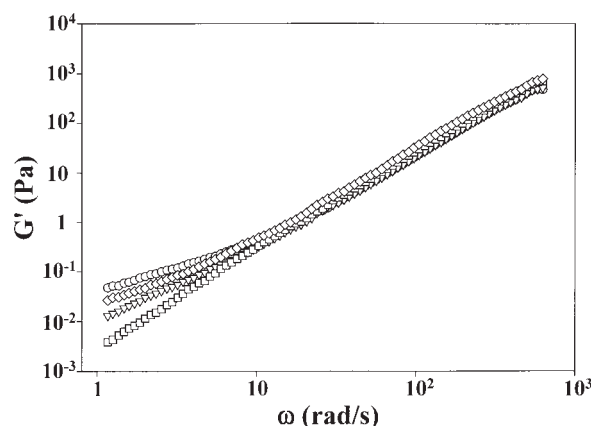


Figure 4 Storage shear modulus versus frequency of (○) RHA-0, (▽) RHA-M1-5, (□) RHA-M1-14, and (◇) RHA-M1-22, measured at 120°C.

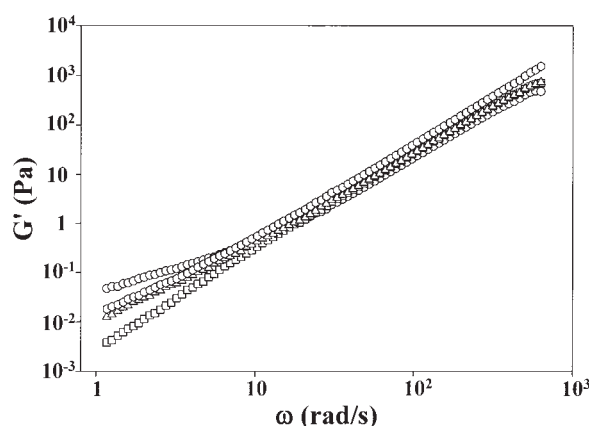


Figure 5 Storage shear modulus versus frequency of (○) RHA-0, (□) RHA-M1-14, (△) RHA-M3-14, and (◇) RHA-M5-14, measured at 120°C.

chain rigidity and T_g are higher than those of the polyols and tackifier, will increase η^* and G' ; however, G' behavior at low shear rate cannot be explained this way. When short-chain branches, whose molecular weight is smaller than the critical molecular weight for intermolecular chain entanglement, are introduced into a polymer chain, reduction of G' is generally observed at low shear rates because the molecular cross-sectional area is increased and the intermolecular chain entanglement of main chain is restricted by the presence of short-chain branches.^{19–22} So, this reduced intermolecular chain entanglement in the presence of short-chain branches, resulting from modification with MM-1000, seems to be the main cause of G' reduction at low shear rates (Fig. 4) compared with that of RHA-0 (Fig. 2), and relatively small increases of η^* (Fig. 3) compared with those of RHAs modified with Elvacite-2013 (Fig. 1).

It can be seen (Fig. 5) that the decrease of G' compared with that of RHA-0 is reduced and is restricted to a narrower frequency range as the molec-

ular weight of the macromonomer is increased. The increased molecular weight and decreased number of branches relative to the amount of macromonomer present seem to explain these results.

The steady shear viscosity, as measured by a Brookfield viscometer, is shown (Table III). One can see, as with the results for η^* , that RHA viscosity is increased by modification with Elvacite-2013 or macromonomers. And this increase is most evident with Elvacite-2013 and less evident when the molecular weight of the macromonomers is lower.

The temperature dependency of viscosity is a factor that should be considered for the practical utilization of an RHA, because low viscosity at the time of application is a desirable attribute for its ability to be processed, and development of early viscosity during cooling can improve the initial bond strength for fast setting. The activation energy for flow E , calculated by eq. (2), where R is the gas constant, increased when RHA was modified with Elvacite-2013 or macromonomers, and this increase is more evident with Elvacite-2013 compared with macromonomers (Table III).

$$\ln \frac{\eta_{373}}{\eta_{393}} = \frac{E}{R} \left(\frac{1}{373} - \frac{1}{393} \right) \quad (2)$$

The melt viscosity stability at application temperature is a factor that must be evaluated in the practical application of an RHA. The growth of viscosity for 1 h at 120°C under a constant shear rate by a spindle rotating at 20 rpm is shown (Table III); one can see that viscosity growth is generally reduced by modification with Elvacite-2013 or macromonomers. Note that the rise of η^* at high shear rate, probably due to chain extension reaction induced by shear force, is reduced as the content of Elvacite-2013 or MM-1000 is increased (Figs. 1 and 3). This also shows that the melt stability is enhanced by modification with Elvacite-2013 or MM-1000.

TABLE III
Physical Properties of RHAs

Sample	Melt viscosity (Pa s)		E (kJ/mol)	Viscosity growth at 120°C (%)	Tensile properties		
	At 100°C	At 120°C			10% secant modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
RHA-0	2.5	1.1	50.0	9.1	41.2	4.8	499
RHA-E-5	3.5	1.5	51.6	9.1	44.1	5.7	576
RHA-E-14	6.9	2.7	57.2	4.7	65.7	8.0	536
RHA-E-22	16.1	5.2	68.9	4.8	89.2	9.8	500
RHA-M1-5	2.9	1.2	53.8	12.2	36.3	4.3	410
RHA-M1-14	4.2	1.7	55.1	5.1	26.5	4.5	521
RHA-M1-22	7.0	2.6	60.4	4.8	19.6	4.5	548
RHA-M3-14	5.2	2.1	55.3	14.0	26.5	5.0	515
RHA-M5-14	5.2	2.1	55.3	8.9	31.4	5.6	481

TABLE IV
Adhesion Properties of RHAs

Sample	Bond strength (N/m) after						Setting time (min)
	2 min	5 min	10 min	15 min	30 min	3 day	
RHA-0	128	147	324	471	667	fracture	30
RHA-E-5	304	314	530	942	961	fracture	58
RHA-E-14	834	922	1030	1157	1304	fracture	50
RHA-E-22	892	1030	1226	1383	1520	fracture	6
RHA-M1-5	235	286	343	618	892	fracture	longer than 60
RHA-M1-14	392	461	628	853	1216	fracture	longer than 60
RHA-M1-22	991	1098	1267	1393	1785	fracture	longer than 60
RHA-M3-14	569	581	618	716	995	fracture	longer than 60
RHA-M5-14	363	412	611	687	971	fracture	longer than 60

Tensile and adhesion properties

Modulus and tensile strength are increased, and elongation at break is reduced, as the content of Elvacite-2013 in cured RHA is increased (Table III). These results seem to be due to the rigid character of Elvacite-2013, relative to the polyols and tackifier it replaces. Oppositely, as the content of MM-1000 is increased, the modulus is decreased and elongation at break is increased. This seems to be caused by the reduced chain entanglements in the presence of short-chain branches, as observed in the behavior of G' (Fig. 4). Also the modulus is increased and elongation at break is reduced as the molecular weight of macromonomer is increased (Table III). Enhanced chain entanglement due to fewer short-chain branches seems to explain this, because the number of short-chain branches created by the macromonomers will decrease as the molecular weight of the macromonomers is increased with the total macromonomer amount held constant.

The initial bond strength of RHA up to 30 min is generally enhanced by the modification with Elvacite-2013, and this effect is more evident with higher Elvacite-2013 contents (Table IV). Enhanced cohesive strength in the presence of Elvacite-2013, which is rigid and has high T_g relative to the polyols and tackifier it replaces, may be a cause of these improved bond strengths. When MM-1000 is used instead of Elvacite-2013, this initial bond strength increase can be enhanced because the segment of reactive macromonomer can be dispersed more homogeneously in the matrix of RHA and increase the cohesive strength. However, the reduced entanglement caused by the presence of short-chain branches, as discussed before, can diminish the cohesive strength. So, our finding (Table IV) that MM-1000 is more effective for initial bond strength improvement at high content and is less effective at low content, compared with Elvacite-2013, and another finding (Table IV) that the initial bond strength is influenced not systematically by the molecular weight of macro-

monomer, seem to be due to the complicated contributions of the aforementioned factors.

The set time of RHA-E-22 is effectively reduced compared with RHA-0 by the high content of Elvacite-2013 (Table IV), although the content of crystalline polyol, Dynacoll-7360, is reduced. This shows that enhanced chain entanglement and increased cohesive strength by Elvacite-2013, with its high molecular weight and high T_g , can effectively reduce the set time. However, the set time is increased when RHA is modified with macromonomers. Reduced chain entanglement by macromonomer short-chain branches seems to be a main cause of the increase in set time.

CONCLUSIONS

The melt viscosity and initial bond strength of RHA was increased when some amounts of polyols and tackifier were replaced by acrylic copolymers or reactive acrylic macromonomers. These results show that the cohesive force displayed by cooled RHA is increased by modification with acrylic copolymers or macromonomers, because they have more rigid chain structures and consequently higher T_g compared with those of the replaced polyols and tackifier. However, when RHA was modified with macromonomers, the set time became longer and G' at low shear rate was reduced. These results show that chain entanglement is reduced by the short-chain branches the macromonomer creates.

As the molecular weight of macromonomer was increased, the reduction of G' at low shear rate, the reductions of modulus and tensile strength, and the increase of elongation at break by the added macromonomers were diminished, because the number of short-chain branches created by the macromonomers were decreased with the total macromonomer amount held constant. However, the initial bond strength was influenced not systematically by the molecular weight of macromonomer. This seems to

be due to the complicated effects that the dispersion of rigid acrylic polymer is improved, whereas the chain entanglement is reduced as the molecular weight of macromonomer was decreased.

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