

Molecular Parameters and Their Relation to the Adhesive Performance of Emulsion Acrylic Pressure-Sensitive Adhesives. II. Effect of Crosslinking

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ABSTRACT: Acrylic emulsion pressure-sensitive adhesive (PSA) films generally have much lower shear holding power than that of their solvent-borne counterparts for the same peel and tack. This is due to their discrete microgel morphology in the film. In contrast, film cast from solution-polymerized acrylic PSA forms a continuous network as a result of crosslinking acrylic acid and aluminum acetyl acetonate (AAA) in the film following the solvent evaporation. Novel acrylic emulsion PSA was made by copolymerizing ≤ 1 wt % isobutoxy methyl acrylamide (IBMA) in the polymer backbone. The IBMA grafted the linear portion of the acrylic polymer with the microgels upon heating the film, which resulted in a significant increase in the shear holding power. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2558–2564, 2001

Key words: PSAs; acrylic; IBMA; emulsion; network

INTRODUCTION

Over the past 20 years, strict environmental regulations such as the EPA Clean Air Act (Title 5) has made coating solvent-borne acrylic pressure-sensitive adhesives (PSAs) less attractive. The high cost of solvent-borne acrylic PSAs coupled with the slow coating line speed due to limitation of the solvent recovery process bring about the net effect of higher product cost. This economic disadvantage has prompted the replacement of many solvent-borne acrylic PSAs with acrylic emulsion PSAs. Despite the aggressive effort to replace them, there are still high-performance tape and label PSA applications that can only be

met by solvent-borne acrylic PSAs. The majority of these applications require a high shear holding power together with high peel and tack. It is known that solvent-borne acrylic PSA films have a much higher shear-holding power than that of their emulsion counterparts.¹ This is due to their continuous network morphology which is formed by the crosslinking reaction of the acrylic acid and aluminum acetyl acetonate (AAA) in the film once the solvent has evaporated.² In contrast, emulsion polymerization of acrylics such as *n*-butyl acrylate (BA) and 2-ethyl hexyl acrylate (2-EHA) produce microgels which retain their discrete morphology in the film.¹ In styrene-butadiene rubber (SBR) technology, SBR latex made using a thermal initiator contained $\geq 50\%$ microgels. In contrast, gel free emulsion could be made by using a redox-initiated system which was polymerized only to low conversion ($\leq 30\%$). Vulca-

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nized rubber products from thermally initiated SBR latex showed a lower tensile property compared to that made of a redox-initiated system.³

Crosslinking acrylic emulsion PSAs in the film increased their shear holding power at the expense of lower peel and tack.⁴ A well-known method is to postadd aluminum acetate into the acrylic emulsion.⁴ Another known method is to blend the acrylic emulsion with a polyoxazoline emulsion where crosslinking was provided by the reaction between the acrylic acid and oxazoline in the film.⁵ In both prior arts, reduction of peel and tack was expected due to a significant increase in the gel content and crosslink density.

In this research, the shear-holding power of acrylic emulsion PSAs was found to be increased significantly without a significant trade-off in their peel and loop tack if the microgels were interconnected by the linear polymer in the film upon heating. To facilitate these interconnections, a low level of isobutoxy methyl acrylamide (IBMA) was copolymerized in the acrylic backbone at a very low level (≤ 1 wt %). IBMA is capable of a self-condensation reaction as well as reacting with the acrylic acid (AA) in the film upon heating. The successful outcome in establishing these interconnections depends on the interplay among several molecular parameters such as the entanglement molecular weight (M_e), weight-average molecular weight (M_w), molecular weight between crosslinks (M_c), and gel content. As will be shown later, these novel acrylic emulsion PSA films have comparable adhesive performance in terms of peel, tack, and shear-holding power to their solvent-borne acrylic counterparts.

EXPERIMENTAL

The IBMA was a commercial grade available from CYTEC (West Paterson, NJ). A detailed polymerization procedure, characterization methods, and physical testings were described previously.¹ Only emulsion PSAs had the IBMA incorporated into the polymer backbone. The IBMA monomer was added only in the feed delay, not in the initial kettle charge, to ensure its random placement in the polymer backbone.

RESULTS AND DISCUSSION

Emulsion Polymerization of IBMA Containing Acrylic Lattices

The main advantage for using the V-50[®] initiator was the lower gel content in the polymerization

Table I Effect of Reaction Condition on the Gel Content of Acrylic Lattices Containing a Low Level of the IBMA Copolymer

Polymer Composition ^a	Gel Content (%) ^b
I. KPS at 80°C	
2EHA-AA-IBMA- <i>n</i> DDM (96.8-2.5-0.5-0.2)	30
2EHA-AA-IBMA- <i>n</i> DDM (96.4-2.5-1-0.1)	54
2EHA-AA- <i>n</i> DDM (97.4-2.5-0.1)	31
BA-AA-IBMA- <i>n</i> DDM (96.4-2.5-1-0.1)	45
BA-AA- <i>n</i> DDM (97.4-2.5-0.1)	2
II. V-50 [®] at 60°C	
2EHA-AA-IBMA- <i>n</i> DDM (96.8-2.5-0.5-0.2)	2
2EHA-AA-IBMA (97-2.5-0.5)	67
2EHA-AA (97.5-2.5)	62
BA-AA-IBMA (97-2.5-0.5)	54
BA-AA (97.5-2.5)	42

^a Emulsion polymerized using a semicontinuous process. *n*-DDM is the chain-transfer agent. All compositions are in a weight ratio.

^b Films were cast and dried at room temperature.

of 2EHA-*stat*-IBMA-*stat*-AA and BA-*stat*-IBMA-*stat*-AA using a semicontinuous emulsion process. As shown in Table I, emulsion polymerization of a acrylic-*stat*-IBMA monomer using a KPS initiator at 80°C led to a significantly higher gel content than that of the corresponding composition without IBMA. Comparative examples are shown in the parentheses. On the other hand, the use of V-50[®] had a significantly reduced premature IBMA crosslinking reaction during polymerization as shown in 2EHA-AA-IBMA-*n*-dodecyl mercaptan (*n*-DDM) at 96.8-2.5-0.5-0.2. The purpose of copolymerizing with IBMA is to induce additional crosslinking in the film after drying the emulsion at elevated temperature. Premature crosslinking of the IBMA during polymerization was therefore undesirable. Acrylic-*stat*-IBMA copolymer lattices prepared by using V-50[®] showed smaller differences in the gel content compared to the corresponding acrylic compositions without IBMA as shown in Table I. A lower reaction temperature (60°C) was postulated to be the reason for this behavior. The onset of IBMA crosslinking

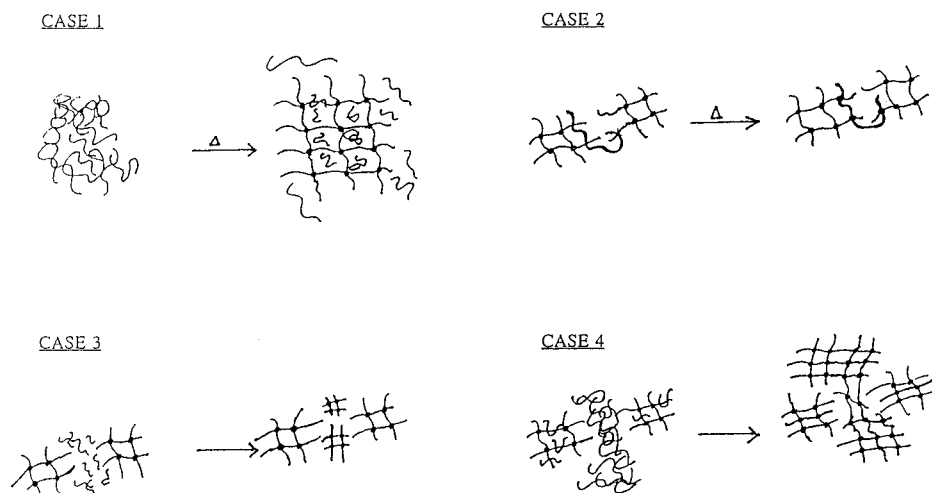


Figure 1 Network formation in the film.

depends on the reaction temperature.⁶ Although IBMA is endcapped and it normally would require 175°C to react, the reaction could be activated at much lower temperature in the presence of an acid such as acrylic acid. Therefore, it is advantageous to polymerize the acrylic-*stat*-IBMA monomer using V-50[®] as the initiator at lower temperature to avoid a premature reaction of the IBMA.

Effect of Network Morphology on Adhesive Performance

Network morphology plays a significant role in influencing the shear-holding power and its balance with peel and loop tack properties in acrylic

PSAs. In this section, the formation of a network in the film as a result of the reactions of IBMA in the film due to heating the film was explored. It is well known that under high temperature (ca. 175°C) IBMA can undergo a self-crosslinking reaction as well as a reaction with carboxylic acid to produce network polymer and isobutanol.⁶ The high-temperature requirement is generally necessary if one is to start with a linear polymer and build the whole network after film formation and heating. However, as will be shown later, IBMA reactions can occur at a significantly lower temperature such as 121°C if all that is needed is to connect the microgels by forming grafting with the linear polymer provided that the molecular weight of the linear polymer is sufficiently high to

Table II Network Formation in the Film: Case 1

Sample	Drying Condition	Gel (%)	M_w (g/mol)	M_n (g/mol)	M_e (g/mol)	M_c (g/mol)	Loss Tack SS (N/m)	Loss Tack HDPE (N/m)	90° Peel SS (N/m)	90° Peel HDPE (N/m)	Shear $4.9 \text{ N} \times 1.27 \text{ cm}$ (min)
1	Room temperature	3	209K	50K	50K	—	965	298	631	211	1.3
1	121°C, 10 min										
	150°C, 10 min	68	153K	50K	43K	144K	298	281	140	105	140
2	Room temperature	1	169K	31K	62K	—	824	702	351	351	0.3
2	121°C, 10 min										
	150°C, 10 min	54	120K	30K	60K	77K	211	175	88	88	117
3	121°C, 10 min	78	148K	32K	42K	54K	368	228	228	105	27

1: 2EHA/AA/IBMA/DDM 96.9/2.5/0.5/0.1 initiated by WAKO V-50 at 60°C. 2: 2EHA/AA/IBMA/DDM 96.3/2.5/1/0.2 initiated by WAKO V-50 at 60°C. 3: Control (microgels formed during polymerization and no additional crosslinking after drying), 2EHA/AA 97.5/2.5, initiated by KPS at 80°C.

Table III Network Formation in the Film: Case 2

Sample	Drying Condition	Gel (%)	M_w (g/mol)	M_n (g/mol)	M_e (g/mol)	M_c (g/mol)	Loss Tack SS (N/m)	Loss Tack HDPE (N/m)	90° Peel SS (N/m)	90° Peel HDPE (N/m)	Shear $4.9 \text{ N} \times 1.27 \text{ cm}$ (min)
1	Room temperature	54	124K	31.7K	56K	80K	368	316	256	105	8.4
1	121°C, 10 min	67	118K	36K	50K	72K	211	228	123	88	383
2	Room temperature	65	245K	32K	40K	117K	351	211	163	70	20
2	121°C, 10 min	75	210K	25K	43K	61K	351	228	165	123	400
3	121°C, 10 min	73	210K	25K	57K	61K	509	316	235	123	250
4	121°C, 10 min	78	148K	32K	42K	54K	368	228	205	88	27
5	121°C, 10 min	78	148K	32K	61K	54K	439	316	237	116	15

1: 2EHA/AA/IBMA/DDM 96.4/2.5/1/0.1 initiated by KPS at 80°C. 2: 2EHA/AA/IBMA 97/2.5/0.5 initiated by Wako V-50 at 60°C. 3: Same as (2) with 15 wt % tackifier. Only M_w of the polymer reported. 4: Control (microgels formed during polymerization and no additional crosslinking after drying), 2EHA/AA 97.5/2.5, KPS initiated at 80°C. 5: Control with 15% tackifier.

form entanglements with the microgels. As will be shown later, this is very effective in increasing the shear-holding power without an adverse effect in peel and loop tack. The IBMA level used in this study was between 0.5 and 1 wt % of the total monomer in order not to increase the crosslink density significantly.

Figure 1 shows the schematic morphology of network formation in the emulsion film as a result of IBMA reactions due to heating the film. In case 1, uncrosslinked acrylic polymer with an IBMA functionality was heated and the result was a continuous network with lower molecular weight species trapped inside as a plasticizer and outside the network. In case 2, a microgel-containing acrylic polymer with IBMA functionality

was heated and the result was the interconnection of these microgels by the linear polymer provided that $M_w \geq 2M_e$ for the linear polymer and $M_c > M_e$ for the microgel. In case 3, these microgels were not interconnected by the linear polymer because $M_w < 2M_e$. An example of case 3 would be the tackified system where tackifier addition increased M_e so that the linear polymer now was too short to entangle with the microgels. In case 4, again, these microgels were not interconnected by the linear polymer because $M_w > 20M_e$. Due to the dense entanglement, the linear polymer would kinetically be hindered from diffusing and forming interconnection with the microgels when heated. Hypothetically, the linear polymer chains with such a high molecular

Table IV Network Formation in the Film: Case 2 (Continued)

Sample	Drying Condition	Gel (%)	M_w (g/mol)	M_n (g/mol)	M_e (g/mol)	M_c (g/mol)	Loss Tack SS (N/m)	Loss Tack HDPE (N/m)	90° Peel SS (N/m)	90° Peel HDPE (N/m)	Shear $4.9 \text{ N} \times 1.27 \text{ cm}$ (min)
1	Room temperature	45	188K	36K	25K	143K	193	70	246	53	50
1	121°C, 10 min	77	100K	30K	23K	76K	211	88	123	70	1100
2	Room temperature	45	188K	36K	36K	143K	316	175	316	123	23
2	121°C, 10 min	77	100K	30K	40K	90K	386	281	211	105	995
3	121°C, 10 min	79	257K	45K	21K	80K	316	175	158	70	70
4	121°C, 10 min	79	257K	45K	31K	80K	433	228	211	88	55

1: BA/AA/IBMA/DDM 96.4/2.5/1/0.1, KPS initiated at 80°C. 2: Same as (1) with 15 wt % tackifier. MWD is bimodal. Only M_w of the polymer reported. 3: Control (microgels formed during polymerization and no additional crosslinking after drying), BA/AA 97.5/2.5, KPS initiated at 80°C. 4: Control with 15% tackifier. Only M_w of the polymer is reported.

Table V Network Formation in the Film: Case 3

Sample	Drying Condition	Gel (%)	M_w (g/mol)	M_n (g/mol)	M_e (g/mol)	M_c (g/mol)	Loss Tack	Loss Tack	90° Peel	90° Peel	Shear
							SS (N/m)	HDPE (N/m)	SS (N/m)	HDPE (N/m)	4.9 N × 1.27 cm × 1.27 cm (min)
1	Room temperature	54	124K	31.7K	81K	80K	596	386	403	172	7
1	121°C, 10 min	67	118K	36K	70K	58K	386	281	281	160	48
2	121°C, 10 min	78	148K	32K	61K	54K	439	316	246	105	15

1: 2EHA/AA/IBMA/DDM 96.4/2.5/1/0.1, KPS initiated with 15 wt % tackifier. Only M_w of the polymer reported. 2: Control (2EHA/AA 97.5/2.5, KPS initiated) with 15 wt % tackifier. Microgels formed during polymerization. Only M_w of polymer reported.

weight would effectively form their own network (“phantom network”) instead.

Tables II–VI show examples of the four cases mentioned above. In each case, control examples were given by showing the molecular properties and adhesive performance of acrylic PSAs having the same compositions, but without IBMA. The purpose is to show the impact of various types of network morphology on adhesive performance.

In case 1, heating the gel-free acrylic PSAs at 121°C for 10 min followed by 150°C for 10 min was necessary to make a network. Heating at 121°C for 10 min alone was not sufficient to form a network. As shown in Table II, the shear-holding power of samples 1 and 2 were significantly increased upon heating and loop tack and peel were decreased. The loop tack and peel were lower than those of the control (sample 3) although the gel content was lower. This means that a continuous network morphology was more rigid than were microgels which lowered the viscoelastic energy dissipation during debonding.

The finding is further collaborated by the result shown previously¹ (Table VII) where solvent-borne acrylics with a high gel content (70–80%) had a lower loop tack and peel compared to those of emulsions. As discussed previously, a solvent-borne acrylic mechanism of crosslinking by AAA led to a continuous network in the film.

In case 2, IBMA was present both in the microgels and in the linear polymers. Examples of both P(2EHA-*stat*-AA) and P(BA-*stat*-AA) are shown in Tables III and IV, respectively. In all examples, the linear polymers were able to form an interconnection with the microgels because their $M_w \geq 2M_e$. A significant increase in the shear-holding power was obtained after heating the film at 121°C for 10 min. Table III shows the molecular properties and adhesive performance of P(2EHA-*stat*-AA)-based polymers while those of P(BA-*stat*-AA)-based polymers are shown in Table IV. A closer examination reveals that a minimal impact on peel reduction was obtained when the PSA had a small increase in the gel content after heating

Table VI Network Formation in the Film: Case 4

Sample	Drying Condition	Gel (%)	M_w (g/mol)	M_n (g/mol)	M_e (g/mol)	M_c (g/mol)	Loss Tack	Loss Tack	90° Peel	90° Peel	Shear
							SS (N/m)	HDPE (N/m)	SS (N/m)	HDPE (N/m)	4.9 N × 1.27 cm × 1.27 cm (min)
1	Room temperature	54	604K	151K	20K	136K	49	47	74	39	10
1	121°C, 10 min	80	267K	35K	21K	50K	109	47	89	40	420
2	121°C, 10 min	80	267K	35K	30K	50K	280	160	130	81	107
3	121°C, 10 min	79	257K	45K	21K	80K	316	175	160	70	70
4	121°C, 10 min	79	257K	45K	31K	80K	433	228	211	88	55

1: BA/AA/IBMA 97/2.5/0.5 initiated by Wako V-50 at 60°C. 2: Same as (1) with 15 wt % tackifier. 3: Control, BA/AA 97.5/2.5, initiated by KPS at 80°C. Microgels formed during polymerization. No additional crosslinking after drying. 4: Same as (3) with 15 wt % tackifier. Only M_w of the polymer reported.

Table VII Novel Emulsion versus Solvent-borne Acrylic PSAs

Adhesive	Loop Tack SS (N/m)	Loop Tack HDPE (N/m)	90° Peel SS (N/m)	90° Peel HDPE (N/m)	4.9N × 1.27 × 1.27 cm Shear (min)
1. P(2EHA- <i>stat</i> -AA) 97.5/2.5, 75% gel					
Neat					
Emulsion	396	230	165	128	400
Solvent	221	184	105	58	761
Tackified with 15% Snowtack® 920					
Emulsion	516	321	235	123	250
Solvent	491	300	210	98	250
2. P(BA- <i>stat</i> -AA) 97.5/2.5, 80% gel					
Neat					
Emulsion	211	91	119	84	1100
Solvent	249	121	107	46	5000
Tackified with 15% Snowtack® 920					
Emulsion	386	281	205	112	995
Solvent	368	253	228	123	386

at 121°C for 10 min compared to that dried at room temperature (e.g., sample 2). This might be because grafting the microgels by the linear polymer took place without forming a continuous network as described in case 1. There are two interesting features shown from the data of Tables III and IV. First, reactions of IBMA could take place at a lower temperature compared to that in case 1. It is hypothesized that linking the microgels only needed a few crosslink points in contrast to building the whole network that needed many crosslink points. Second, for both P(2EHA-*stat*-AA) and P(BA-*stat*-AA), the addition of a 15 wt % tackifier still shows a high shear-holding power with an increase in loop tack and peel, that is, that the tackifier did not interfere with the ability of the linear polymer to interlink the microgels as long as $M_w \geq 2M_e$ prior to heating the film.

In contrast to case 2, case 3 shows an example where the linear polymer was unable to link the microgels because $M_w < 2M_e$. Table V shows an example where the addition of the tackifier causes $M_w < 2M_e$ for the linear polymer. In this case, as expected, the improvement in shear-holding power was small.

The opposite from case 3 is when the linear polymer was too long, that is, $M_w > 20M_e$. Table VI shows examples of case 4. Since the molecular weight was very high, loop tack and peel were

significantly lower than were those shown in Table IV for similar compositions. Surprisingly, such a very high molecular weight linear polymer, although after heating showed an increase in shear, showed an increase that was still smaller than that given by linear polymers having a medium molecular weight such as those shown in Table IV. It is postulated that formation of a phantom network was the result of self-crosslinking of the linear polymer without interlinking the microgels. It is possible that due to dense entanglement the linear polymer would tend to stay together and formed crosslinking rather than diffusing and reacting with the microgels because it was kinetically more favorable.

Finally, the adhesive performance of selected IBMA-functionalized acrylic emulsion PSAs in both neat and tackified compositions was compared against that of solvent-borne acrylic PSAs as shown in Table VII. It is clear that by interconnecting the microgels chemically via IBMA reactions in the film after heating brought a similar performance in tack, peel, and shear between the emulsion and the solvent-borne. In contrast, a conventional acrylic emulsion as shown previously,¹ where the discrete microgels were connected only by entanglements, suffered from a low shear-holding power.

CONCLUSIONS

Novel acrylic emulsion PSAs which contained a low level of the IBMA copolymer showed a significant increase in the shear-holding power because of crosslinking reactions in the film when the film was heated. These reactions in the film caused chemical interconnection of the microgels provided that the M_w of the linear polymer was at least twice that of the M_e and that the M_c of the microgels was at least equal to the M_e .

REFERENCES

1. Tobing, S.; Klein, A. *J Appl Polym Sci* 2001, 79, 2230.
2. Anderson, C. U.S. Patent 3 769 254 (1973).
3. Lovell, P. A.; El-Aasser, M. S. *Emulsion Polymerization and Emulsion Polymers*; Wiley: New York, 1997; Chapter 15.
4. Bernard, M. U.S. Patent 5 278 227 (1994).
5. Keskey, W.; Schuetz, J.; Lee, D. I.; Schwartz, J. U.S. Patent 4 474 923 (1984).
6. CYLINK® IBMA Technical Information, CYTEC Industries.