Solvent-Based Pressure-Sensitive Adhesives for PVC Sign and Marking Films

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Received 21 March 2000; accepted 7 September 2000

ABSTRACT: This article shows the influence of parameters such as acrylic acid, initiator content, molecular mass, viscosity, content of methyl acrylate, content of ethyl acrylate, and content of *N*-vinyl caprolactam on such important parameters of pressure-sensitive adhesives as shrinkage, plasticity, adhesion to the steel, and deformation. Pressure-sensitive adhesives based on acrylic polymers and containing 2-ethylhexyl acrylate, methyl acrylate, acrylic acid, and *N*-vinyl caprolactam are used for production of self-adhesives containing polyvinyl chloride carrier. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 3212–3219, 2001

Key words: acrylic; pressure-sensitive adhesives; polyvinyl chloride; shrinkage; deformation

INTRODUCTION

The goal of this work was to develop a solvent-based (SB) pressure-sensitive adhesive for polyvinyl chloride (PVC) sign and marking films with high performance.[1] The exact specifications of this new pressure-sensitive adhesive (PSA) are the following parameters:[2]

- Low to very low shrinkage ($S \leq 0.5$ or $l_r \leq 0.5$ mm)
- Very good anchorage to the PVC
- Very good adhesion on steel and good adhesion on polyethylene
- Good deformation performance (0 or 0^+)
- Good aging performance

EXPERIMENTAL

The following experiments were conducted in order to study the influence of diverse parameters on other important performances. The synthesis of PSA was based on acrylic monomers polymerized in a typical organic solvent such as ethyl acetate.[3]

2-Ethylhexyl acrylate (2-EHA), methyl acrylate (MA), ethyl acrylate (EA), acrylic acid (AA), *N*-vinyl caprolactam (VC), ethyl acetate, heptane, and 2,2′-azo-diisobutyronitrile (AIBN) were purchased from Tokyo Chemical Industry Co. (Japan).

The synthesized pressure-sensitive adhesives were crosslinked with aluminium acetyl acetonate, and were purchased from Hüls AG (Marl, Germany).

Shrinkage (S or l_r): presents the percentage (S) or millimeter (l_r) change of dimensions of the foil covered with PSA and attached to the glass after keeping it 1 week in 70°C temperature.

Plasticity[2]: a parameter representing the resistance of a cylinder made of PSA with a diameter of 5 mm and a height of 1 cm under the pressure of 10*N* after 24 h.

Deformation: a parameter representing durability of adhesives. Durability is measured this way: a foil should be stuck to round holes of the surface of plates. If after 7 or 14 days the foil is still closely attached to the measured surface,

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Journal of Applied Polymer Science, Vol. 81, 3212–3219 (2001)

Table I Synthesized PSA Based on 2-EHA and AA

PSA	Monomeres (%) 2-EHA	AA	AIBN (%)	Solvent, Ethyl Acetate (%)	η (Pa · s)	AlACA (%)	Plasticity
1	97	3	0.1	100	0.6	0.25	216
2	96	4	0.1	100	1.5	0.25	273
3	95	5	0.1	100	3.2	0.25	286
4	94	6	0.1	100	4.8	0.25	300
5	93	7	0.1	100	8.5	0.25	313
6	92	8	0.1	100	12.8	0.25	330

Table II Important Properties of Synthesized Pressure-Sensitive Adhesives

PSA	Shrinkage S (%)	Shrinkage l_r (mm)	Adh (Steel) 20 min (N/25 mm)	Adh (Steel) 24 h (N/25 mm)	Adh (PE) 20 min (N/25 mm)	Anchorage on PVC	Deformation After 7 Days	Deformation After 14 Days
1	3.05	2.80	22.1	24.5	2.0	Very good	1	1
2	2.10	1.95	21.0	23.5	2.1	Very good	1	1
3	1.91	1.55	20.5	22.0	2.4	Very good	1	1
4	1.38	1.25	21.1	22.1	2.8	Very good	1	1
5	1.05	0.95	20.8	20.3	2.5	Very good	1	1
6	0.95	0.75	19.9	23.3	2.8	Very good	1	1

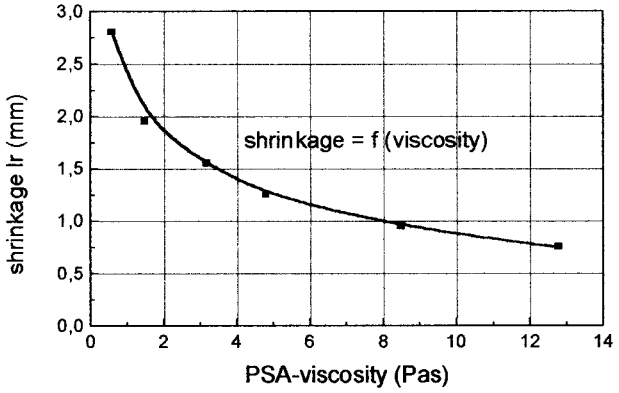

Figure 1 Viscosity influence on shrinkage.

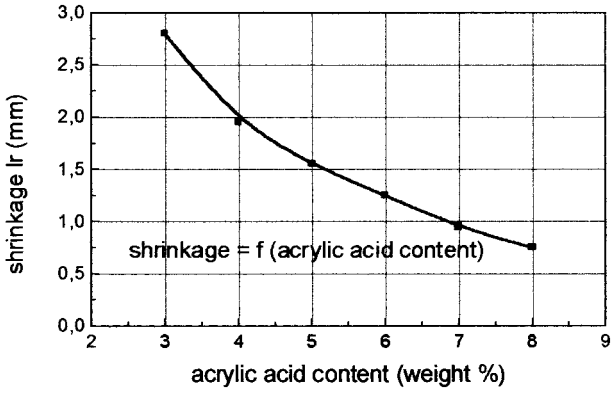

Figure 2 Shrinkage dependence of AA content.

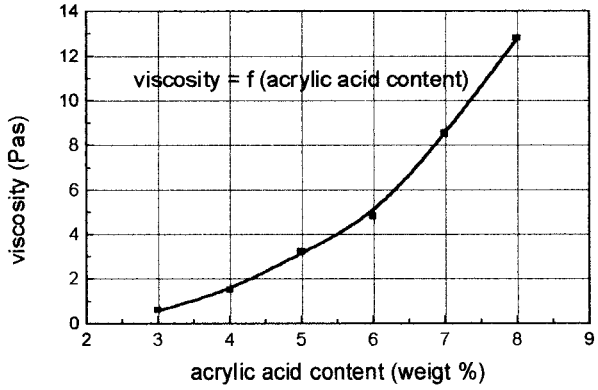

Figure 3 AA amount and influence on viscosity.

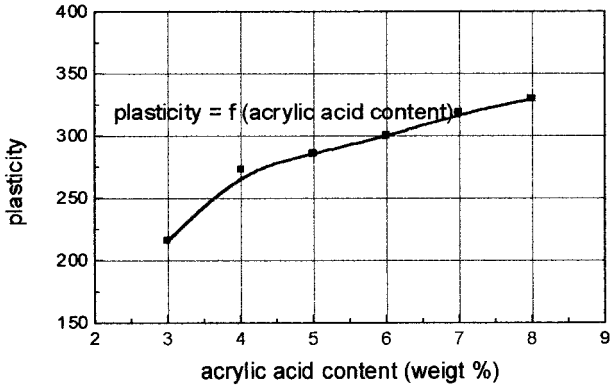

Figure 4 Plasticity dependence of AA content.

Table III Synthesized PSA with Constant 2-EHA and AA Content and Different AIBN Content

PSA	Monomers (%) 2-EHA	Monomers (%) AA	AIBN (%)	Solvent, Ethyl Acetate (%)	η (Pa · s)	AIACA (%)	Plasticity
7	95	5	0.01	100	12.6	0.25	366
8	95	5	0.05	100	9.1	0.25	332
9	95	5	0.10	100	5.8	0.25	316
10	95	5	0.15	100	4.2	0.25	286
11	95	5	0.20	100	3.2	0.25	255
12	95	5	0.25	100	2.1	0.25	211
13	95	5	0.30	100	1.7	0.25	185

Table IV Important Properties of Synthesized Pressure-Sensitive Adhesives

PSA	Shrinkage S (%)	Shrinkage l_r (mm)	Adh (Steel) 20 min (N/25 mm)	Adh (Steel) 24 h (N/25 mm)	Molecular Mass ×1000 (g/mol)	Anchorage on PVC	Deformation After 7 Days	Deformation After 14 Days
7	0.55	0.45	20.5	23.5	830	Very good	1	11
8	0.80	0.80	20.0	23.0	650	Very good	1	1
9	0.95	0.95	18.5	21.8	585	Very good	1	1
10	1.10	1.15	18.0	21.5	505	Very good	1	1
11	1.25	1.35	17.4	20.5	426	Very good	1	1
12	1.35	1.40	16.4	19.7	380	Very good	1	1
13	1.55	1.50	15.9	17.7	265	Very good	1	1

deformation is marked as 0 (very good product). If after 7 or 14 days the foil attached to the surface is slightly deformed, the parameter is marked as 0^+(quality acceptable). If after 7 or 14 days the foil is strongly deformed, the parameter is marked as 1 (not acceptable).

RESULTS AND DISCUSSION

Influence of AA

The SB-PSA shown in Table I were synthesized based on soft monomer 2-EHA and AA for crosslink-

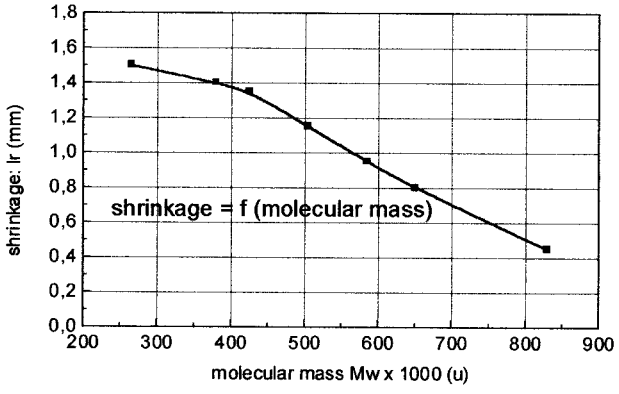

Figure 5 Effect of molecular mass on shrinkage.

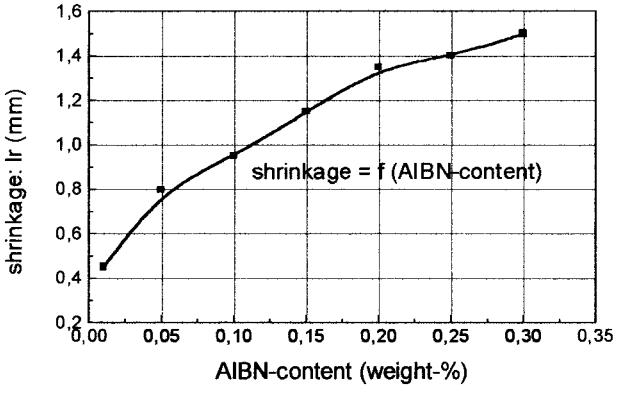

Figure 6 Effect of amount of AIBN on shrinkage.

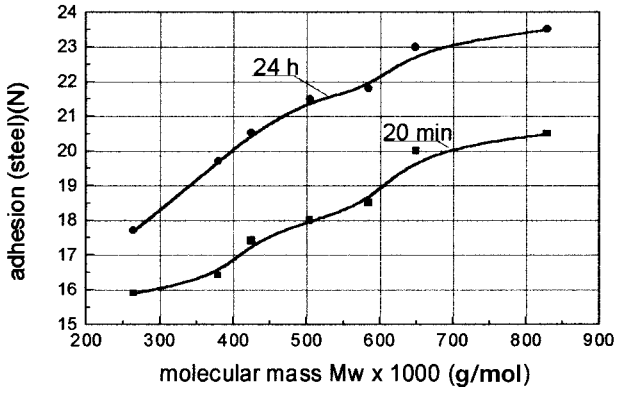

Figure 7 Effect of molecular mass on adhesion to steel.

ing with solid content (sc) on 50 wt %. The dosage time was 4 h. The synthesized PSA was crosslinked with aluminium acetyl acetonate.[4] The performance qualities of these PSA are described in Table II.

The greatest attention was attached to the shrinkage parameter. With shrinkage greater than 1.0%, other properties were neglected.

The influence of the AA content and the viscosity on the investigated properties such as shrinkage, plasticity, and viscosity are presented in Figures 1–4.

The following conclusions can be inferred from experimental results:

- The low viscosity has a negative influence on shrinkage
- The increase of the AA content corresponds with the increase of viscosity and influences shrinkage positively
- There is a direct proportional relation between AA content and the plasticity of PSA

All subsequent investigations were performed for PSA with an AA content of 5%. The dosage remained 2.5 h.

Influence of the Initiator Content on Molecular Mass, Viscosity and Exemplary Properties Such as Shrinkage

The SB-PSA shown in Table III were synthesized based on 2-EHA = 95% and AA = 5%. The solid content was 50%. Performance qualities of these synthesized products are presented in Table IV.

Table V PSA Based on 2-EHA, AA, EA, and MA

	Monomers (%)								
PSA	2-EHA	AA	EA	MA	AIBN (%)	Solvent, Ethyl Acetate (%)	η (Pa · s)	AlACA (%)	Plasticity
14	65	5	20	10	0.1	100	5.5	0.25	284
15	65	5	15	15	0.1	100	6.8	0.25	305
16	65	5	10	20	0.1	100	8.1	0.25	330
17	65	5	5	25	0.1	100	10.5	0.25	349
18	65	5	0	30	0.1	100	12.5	0.25	366

Table VI Important Properties of Synthesized Pressure-Sensitive Adhesives

	Shrinkage		Adh (Steel) 20 min	Adh (Steel) 24 h	Molecular Mass		Deformation	
PSA	S (%)	l_r (mm)	(N/25 mm)	(N/25 mm)	×1000 (g/mol)	Anchorage on PVC	After 7 Days	After 14 Days
14	1.20	1.15	21.0	21.5	330	Good	1	1
15	0.95	0.95	21.5	23.4	386	Very good	1	1
16	0.85	0.85	19.5	24.2	510	Very good	1	1
17	0.80	0.70	20.0	27.2	645	Very good	1	1
18	0.65	0.55	19.6	30.5	780	Very good	1	1

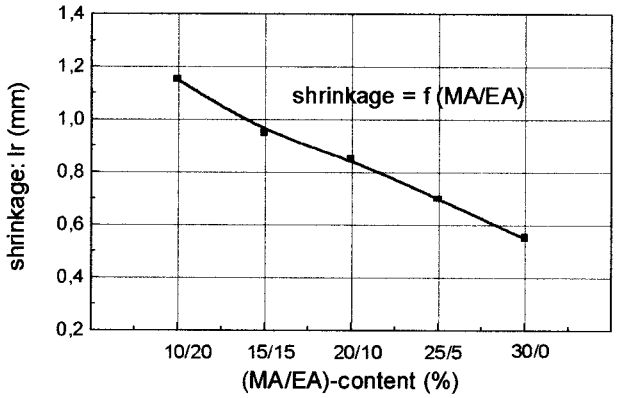

Figure 8 Effect of rate of MA to EA to shrinkage.

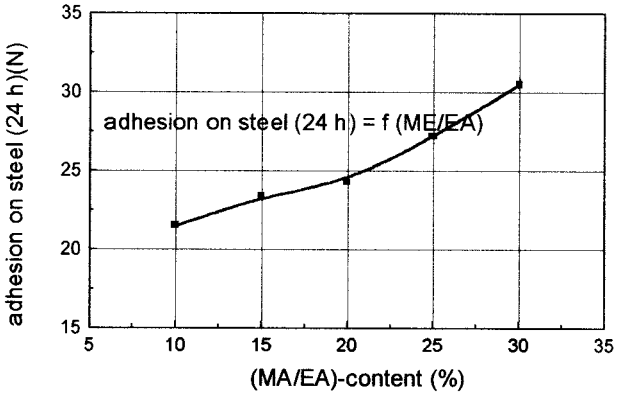

Figure 9 Effect of rate of MA to EA to adhesion on steel.

The results showing the influence of the molecular mass and the viscosity on shrinkage are shown in Figures 5–7.

An increase of the molecular mass leads to reduction of shrinkage. The increase of both viscosity and the molecular mass (and so minimiza-

Table VII PSA Based on 2-EHA, MA, and AA, Synthesized in a Solvent Blend of Ethyl Acetate and Heptane

	Monomers (%)			AIBN	Solvent (%)		η	AlACA	
PSA	2-EHA	MA	AA	(%)	Ethyl Acetate	Heptane	(Pa · s)	(%)	Plasticity
19	65	30	5	0.1	95	5	16.1	0.25	385
20	65	30	5	0.1	90	10	12.1	0.25	386
21	65	30	5	0.1	85	15	9.5	0.25	372
22	65	30	5	0.1	80	20	5.4	0.25	363
23	65	30	5	0.1	75	25	5.1	0.25	351
24	65	30	5	0.1	70	30	3.8	0.25	369
25	65	30	5	0.1	65	35	2.9	0.25	350
26	65	30	5	0.1	60	40	2.2	0.25	333
27	65	30	5	0.1	55	45	1.5	0.25	311

Table VIII Important Properties of Synthesized Pressure-Sensitive Adhesives

	Shrinkage		Adh (Steel) 20 min	Adh (Steel) 24 h	Molecular Mass	Anchorage	Deformation	
PSA	S (%)	l_r (mm)	(N/25 mm)	(N/25 mm)	×1000 (g/mol)	on PVC	After 7 Days	After 14 Days
19	0.40	0.45	17.5	19.1	865	Very good	0^+	0^+
20	0.46	0.50	16.9	18.6	780	Very good	1	1
21	0.55	0.55	16.4	18.2	695	Very good	1	1
22	0.65	0.65	17.2	20.1	605	Very good	1	1
23	0.95	0.85	21.3	22.2	460	Very good	1	1
24	1.05	1.00	20.4	22.1	374	Very good	1	1
25	1.30	1.25	18.2	18.9	325	Very good	1	1
26	1.55	1.50	17.3	18.1	266	Very good	1	1
27	2.00	1.90	16.6	18.0	214	Very good	1	1

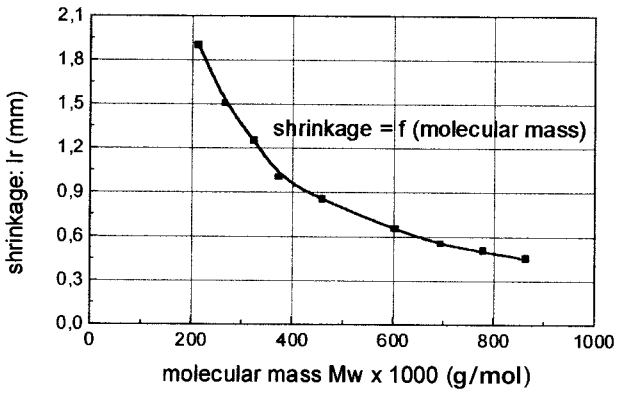

Figure 10 Shrinkage dependence of molecular mass.

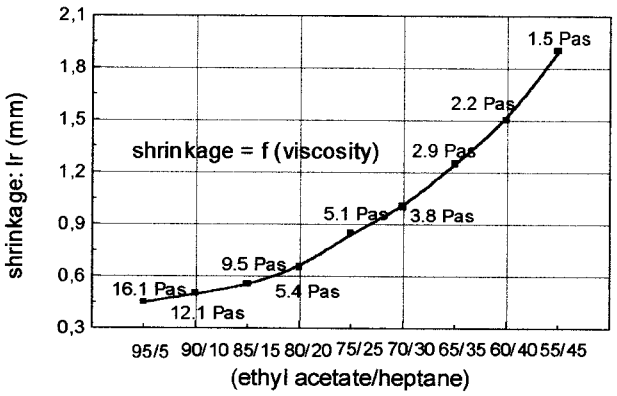

Figure 11 Progress in rate of ethyl acetate/heptane on shrinkage.

tion of the AIBN content) leads to the reduction of shrinkage. PSA with high molecular mass exhibits better adhesion on steel.

Influence of the Content of MA and EA on Shrinkage

The SB-PSA shown in Table V were synthesized based on 2-EHA, AA, MA, and/or EA. Performance qualities of these synthesized products are presented in Table VI. The results of the influence of the AA content on shrinkage and adhesion on steel (after 24 h) are presented in Figures 8 and 9.

As expected, the increase of MA/EA-content affects positively the adhesiveness of PSA on the steel surface (after 24 h).

Influence of the Various Solvent Composition (Molecular Mass/Viscosity) on Shrinkage

The SB-PSA shown in Table VII were synthesized based on 2-EHA, MA, and AA by the same concen-

Table IX PSA Based on 2-EHA, MA, and AA with Different VC Contents

	Monomers (%)								
PSA	2-EHA	MA	AA	VC	AIBN (%)	Solvent, Ethyl Acetate (%)	η (Pa · s)	AlACA (%)	Plasticity
28	64	30	5	1	0.1	100	6.2	0.25	288
29	63	30	5	2	0.1	100	6.3	0.25	295
30	62	30	5	3	0.1	100	6.5	0.25	303
31	61	30	5	4	0.1	100	7.1	0.25	31
32	60	30	5	5	0.1	100	7.4	0.25	334
33	59	30	5	6	0.1	100	8.2	0.25	352

Table X Important Properties of Synthesized Pressure-Sensitive Adhesives

	Shrinkage		Adh (Steel) 20 min	Adh (Steel) 24 h	Molecular Mass		Deformation	
PSA	S (%)	l_r (mm)	(N/25 mm)	(N/25 mm)	×1000 (g/mol)	Anchorage on PVC	After 7 Days	After 14 Days
28	0.75	0.65	16.3	22.8	485	Very good	1	1
29	0.55	0.5	16.7	23.1	508	Very good	0^+	0^+
30	0.45	0.4	17.8	24.8	535	Very good	0^+	0^+
31	0.45	0.35	18.4	24.9	610	Very good	$0/0^+$	$0/0^+$
32	0.4	0.35	19.1	25.1	667	Very good	0^+	0^+
33	0.4	0.3	19.5	25.3	733	Very good	0^+	0^+

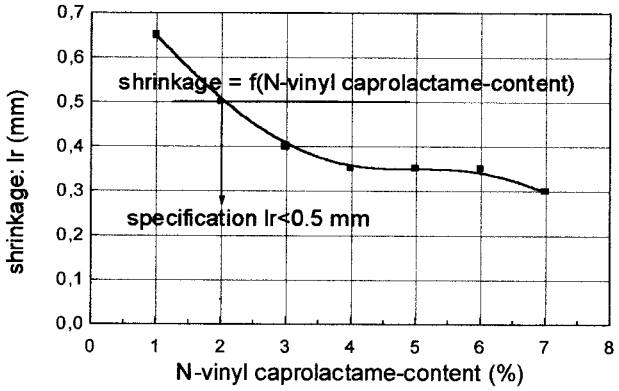

Figure 12 Effect of amount of VC on shrinkage.

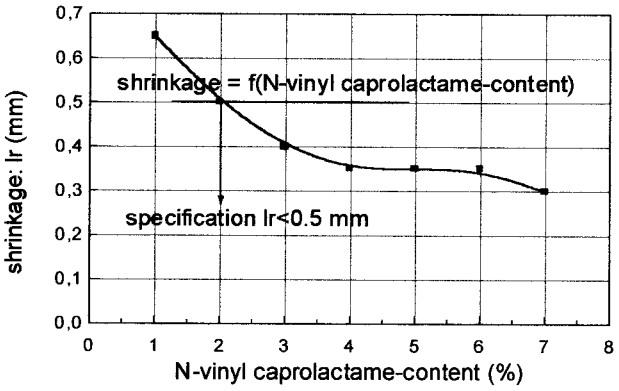

Figure 13 Effect of amount of VC on adhesion on steel.

tration of monomers (sc = 50%). Performance qualities of these synthesized products are presented in Table VIII. The results of influence of different solvent compositions (molecular mass/viscosity) on shrinkage are presented in Figures 10 and 11.

The investigated PSA with high molecular mass and high viscosity generally gives the PSA the lower level of shrinkage. The increase of molecular mass leads to the reduction of the shrinkage. A low viscosity has a negative influence on shrinkage. As shown in Figure 11, the increase of viscosity above 5.5 Pas (molecular mass greater than 600,000 g/mol) results in a high shrinkage.

Influence of Polar Monomer VC on Shrinkage, Anchorage on PVC, and Deformation

The SB-PSA shown in Table IX were synthesized based on 2-EHA, MA, AA, and VC. The sc was

Table XI PSA Based on 2-EHA, MA, AA, and VC with Different MA Contents

	Monomers (%)								
PSA	2-EHA	MA	AA	VC	AIBN (%)	Solvent, Ethyl Acetate (%)	η (Pa · s)	AlACA (%)	Plasticity
34	63	28	5	4	0.1	100	6.6	0.25	298
35	61	30	5	4	0.1	100	7.1	0.25	314
36	59	32	5	4	0.1	100	7.3	0.25	315
37	57	34	5	4	0.1	100	8.3	0.25	333
38	55	36	5	4	0.1	100	8.8	0.25	345
39	53	38	5	4	0.1	100	9.5	0.25	361
40	51	40	5	4	0.1	100	10.1	0.25	380

Table XII Important Properties of Synthesized Pressure-Sensitive Adhesives

	Shrinkage		Adh (Steel) 20 min	Adh (Steel) 24 h	Molecular Mass	Anchorage on PVC	Deformation	
PSA	S (%)	l_r (mm)	(N/25 mm)	(N/25 mm)	×1000 (g/mol)		After 7 Days	After 14 Days
34	0.70	0.65	22.5	26.0	485	Very good	0^+	0^+
35	0.55	0.55	22.1	25.5	610	Very good	0^+	0^+
36	0.45	0.40	22.8	26.6	687	Very good	0^+	0^+
37	0.40	0.35	22.5	26.4	735	Very good	$0/0^+$	$0/0^+$
38	0.40	0.35	20.8	23.2	761	Very good	$0/0^+$	$0/0^+$
39	0.35	0.30	17.4	23.1	809	Very good	$0/0^+$	$0/0^+$
40	0.30	0.25	15.1	20.2	855	Very good	$0/0^+$	$0/0^+$

50%. Performance qualities of this synthesized product are presented in Table X.

The results of influence of the content of polar monomers on shrinkage and adhesion on steel are presented in Figures 12 and 13.

The increase of VC content generally has a positive influence on shrinkage. The increase of VC content generally has a positive influence on adhesion to steel under the following conditions: 20 min and 24 h.

Influence of the MA Content on Shrinkage and Other Important Properties

The SB-PSA shown in Table XI were synthesized based on 2-EHA, MA, AA, and VC. Performance qualities of these synthesized products are presented in Table XII. The experimental results which show the influence of the MA on shrinkage and other important properties are presented in Figures 14 and 15.

The best shrinkage values, the best adhesion on steel and the best deformation were observed at the MA content of 34%. The PSA with more than 34% MA were too dry, the adhesion on steel was too low.

The molecular mass generally has a beneficial effect on the shrinkage of PSA. Above a molecular mass of about 630,000 g/mol, the PSA has shrinkage below 0.5 mm.

CONCLUSIONS

The following conclusions are derived from the trials:

- AA (amount ≥5%) has a beneficial effect on PVC anchorage

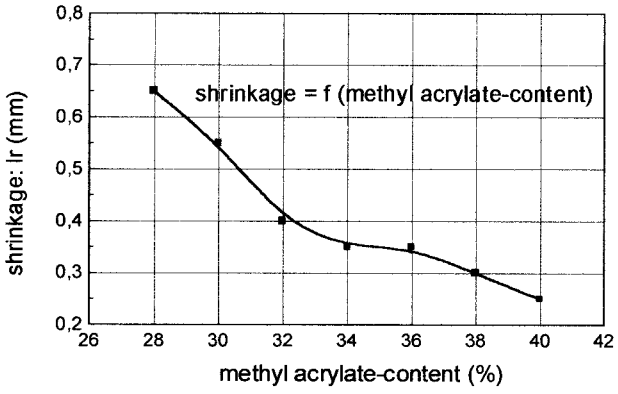

Figure 14 Effect of amount of MA on shrinkage.

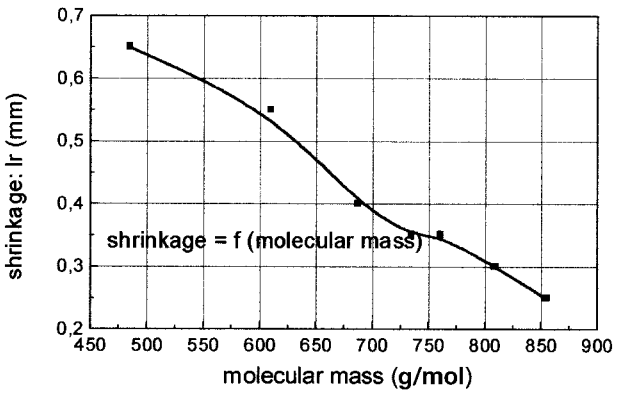

Figure 15 Effect of molecular mass on shrinkage.

- Increase of AA content increases the viscosity, decreases the mol mass, and as a result, decreases the shrinkage
- Decrease of AIBN concentration increases the molecular mass/viscosity, hence a decrease diminishes the shrinkage
- Influence of MA or EA on shrinkage: the best results were obtained with MA
- Increase of the AA content influences low shrinkage positively
- VC amount influences anchorage on PVC positively
- Influence of the solvent balance: ethyl acetate (good solvent for PSA acrylics)/heptane (poor solvent for PSA acrylics): the best properties are observed with ethyl acetate. The increasing of viscosity and molecular mass decreases shrinkage
- VC increases the anchorage to PVC

The best results of shrinkage, adhesion on steel, and of deformation were achieved with PSA 37 synthesized with 57% 2-EHA, 34% MA, 5% AA, and 4% VC.

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