Solving plasticizer migration problems

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ABSTRACT *Whether plasticizer migrates into or out of the hot melt upon aging, hot-melt adhesives and sealants can be adversely affected. Certain low-molecular-weight polyethylenes are extremely useful additives for controlling the adverse effects of plasticizer migration. These polyethylenes were evaluated in butyl-rubber-based, hot-melt sealants containing a plasticizing oil. They were also evaluated in (a) rubber-block-copolymer-based, hot-melt, pressure-sensitive adhesives and (b) EVA-copolymer-based, hot-melt, laminating adhesives for bonding to plasticized PVC films and sheeting.*

KEYWORDS
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Plasticizer migration can adversely affect hot-melt adhesives and sealants, whether the plasticizer migrates into or out of the hot melt upon aging. For example, paraffinic oil or phthalate plasticizers in hot-melt sealants can migrate from the sealant mass. This migration causes the loss of adhesion and flexibility and could be the cause of fogging or substrate staining. On the other hand, when plasticizers migrate from PVC (polyvinyl chloride) films or sheeting into either pressure-sensitive or laminating types of adhesives, bond strength is diminished.

Select low-molecular-weight (LMW) polyethylene homopolymers and copolymers have the ability to efficiently gel organic liquids, including plasticizers. Consequently, we evaluated these polymers in sealants to determine how well they relieve plasticizer migration from the sealant.

Furthermore, certain LMW polyethylenes exhibit excellent barrier properties to many organic liquids, including various plasticizers. Therefore, we evaluated these polymers in adhesives to determine their ability to diminish the adverse effects of plasticizer migration from a PVC film into the adhesives.

Gelling of organic liquids

LMW polyethylenes can gel organic liquids effectively because of a unique structure. Of relatively low molecular weight, they have a fairly narrow molecular weight distribution and a semi-crystalline nature. **Table I** shows the molecular weight range of these polyethylenes compared to other components in adhesive formulas. They are higher in molecular weight than paraffin or microcrystalline waxes, but lower in molecular weight than standard types of base polymers such as LDPE or EVA copolymers.

Table II presents the properties of various LMW polyethylenes evaluated. These products include ethylene homopolymers, copolymers, terpolymers, and ionomers. The variety of these polyethylenes that are available makes it easier to select products having proper compatibility with the organic liquid to be gelled.

A LMW polyethylene gel is a distribution of small polyethylene particles in an organic liquid. The polyethylene gel is useful as a means of distributing polyethylene in a finely divided state into many systems. These gels are viscous, highly thixotropic liquids, or semi-solids. The gels are prepared by heating the LMW polyethylene in an organic liquid and then cooling. During cooling, the polyethylene is precipitated as minute particles with a size of 0.5–20 μm. On standing, the particles form a three-dimensional lattice network structure.

Table III shows the viscosities of 10% concentration gels of various LMW polyethylenes in toluene. **Table IV** lists the cloud points of 10% concentrations of some LMW polyethylenes in selected solvents. Generally, the cloud point is a good indication of how readily the polyethylene dissolves in a solvent. A high cloud point indicates that the polyethylene is more difficult to dissolve.

Plasticizer migration into and out of sealants and adhesives

Plasticizer bleed-out

We evaluated LMW polyethylenes in a butyl-rubber-based, hot-melt, sealant-type formulation, as shown in **Table V.** In this evaluation, we sought to minimize the amount of migration of the paraffinic oil plasticizer. A preliminary screening of various LMW polyethylenes was undertaken to determine which were the most effective gellants for the paraffinic oil; gel characteristics are given in **Table VI.**

Based on their ability to efficiently

I. Molecular weights

Wax or polymer	Mol. wt. range
Paraffin wax	350-540
Microcrystalline wax	450-700
LMW polyethylene	700-3350
LDPE	>8000
EVA copolymer	>8000

II. Typical properties of some LMW polyethylenes

Grade	Description	Viscosity at 140°C, mPa·s	Mettler drop point,[a] °C	Penetrometer hardness,[b] dmm
6	Homopolymer	350	106	4.0
8	Homopolymer	400	116	1.0
9	Homopolymer	450	117	0.5
617	Homopolymer	180	102	7.0
405T	6% EVA copolymer	600	103	4.0
400	13% EVA copolymer	340	95	9.5
520[c]	2.5% EAA copolymer	500	107	1.9
540	5% EAA copolymer	350	108	2.0
580	10% EAA copolymer	185	102	4.0
656	Oxidized PE	2500[d]	100	9.0
392	Oxidized HDPE	240	138	<0.5
A87	E-acrylate copolymer[e]	480	96	10.0
B136	E—VA—AA terpolymer[f]	900	104	3.7
290	EAA Zn ionomer	900[g]	99[h]	1.7
291	EAA Zn ionomer	5500.0[g]	102[h]	1.1

[a]ASTM D-3954. [b]ASTM D-5. [c]Experimental product. [d]At 150°C. [e]Experimental 10% E-2 ethylhexylacrylate copolymer. [f]Experimental 5% VA, 5% AA terpolymer. [g]At 190°C. [h]Melting point via DSC. dmm = decimillimeters. DSC = differential scanning calorimetry.

III. Viscosity of 10% gels of various LMW polyethylenes in toluene

Polyethylene grade	Brookfield viscosity,[a] mPa·s
6	Approx. 20,000
8	Over 20,000
392	Approx. 600
400	Approx. 4
405T	Approx. 6

[a]At 30°C.

IV. Cloud point (°C) of 10% LMW polyethylenes in selected solvents

Solvent	Grade 6	Grade 8	Grade 400
Linseed oil	100	108	88
Mineral oil[a]	80	88	64
V.M. and P. naphtha[b]	73	80	58
Xylene	67	74	51

[a]Boiling point range = 121°C to 177°C.
[b]V.M. and P. = Varnish Maker's and Painter's Naphtha, boiling point range = 110°C to 149°C.

V. General hot melt sealant formulation

Component	Weight percent
Crosslinked butyl rubber (55 Mooney viscosity*)	20.0
Calcium carbonate, fine ground	19.7
Aliphatic/aromatic resin (92°C S.P.)	40.0-30.0
Paraffinic oil (avg. molecular wt. = 440)	20.0
Butyl zimate	0.3
LMW polyethylene	0-10.0

*ML 1 + 3 at 127°C. M = Mooney. L = large rotor.

VI. Gels of LMW polyethylene (8%) and paraffinic oil[a] (92%)

Polyethylene grade	Firmness	Oil separation[b]
6	Firm	None
617	Med. firm	None
400	Very thin	...
405T	Med. firm	None
520	Med. firm	None
656	Soft	Some

[a]Avg. molecular wt. = 440.
[b]One week at ambient conditions.

gel the oil, Grades 6 and 405T were chosen for evaluation in the sealant compound. **Table VII** gives the results. The control sealant formulation exhibited severe oil bleed-through, whereas the polyethylene containing compounds showed significantly less bleed-through. The best results were obtained with a 10% concentration of Grade 6.

In other testing, the control sealant formula showed excessive flow or slump after aging for one week at 70°C, whereas the 5% and 10% Grade 6 formulations showed no flow and the 5% Grade 405T compound exhibited minimal flow. This improvement in resistance to slump caused by elevated temperature is due to the gelation properties of the polyethylenes. Furthermore, sealants modified with Grades 6 and 405T were less tacky at ambient conditions than the control.

Bonding to plasticized PVC

Our next objective was to diminish the adverse effects of plasticizer migration from flexible PVC films and sheeting into an adhesive. We performed evaluations to determine the benefits of adding select types of LMW polyethylene because of their excellent barrier properties.

First, the LMW polyethylenes were tested in the pressure-sensitive adhesive formulation given in **Table VIII.** This evaluation was performed to determine the peel adhesion, before and after aging, to a 0.089-mm, pigmented, polymeric plasticizer containing PVC film. The test results in **Table IX** show that, after aging for one week at 70°C or one day at 82°C, only slight reductions in adhesion were observed in the test and control

VII. Oil bleed-out from butyl-based hot melt sealants

Formulation no.	Polyethylene grade	Polyethylene, %	Bleed-out
A1	...	...	Severe
A2	6	5	Moderate
A3	6	10	Light
A4	405T	5	Moderate

VIII. General hot melt pressure-sensitive adhesive formulation for bonding to plasticized polyvinyl choride

Component	Weight percent
S-I-S block copolymer (14% S, 86% I)	23.5
S-B-S block copolymer (28% S, 72% I)	8.0
Fully hydrogenated rosin ester (85°C S.P.)	61.5
Polybutene (avg. mol. wt. = 2060)	6.0
Hindered phenolic A.O.	0.5
Butyl zimate	0.5
Subtotal	100.0
LMW polyethylene	0-5.0

A.O. = Anti-oxidant. S-I-S = styrene-isoprene-styrene. S-B-S = styrene-butadiene-styrene.

IX. Adhesion of modified hot-melt pressure-sensitive adhesives to plasticized PVC*

	B1	B2	B3	B4	B5	B6
Polyethylene grade						
Grade	...	9	617	316	540	580
Amount, %	...	1	5	1	5	5
180° peel adhesion, N/m						
Initial	1505	1488	1278	1610	1558	1733
7 days at 70°C	1278	1225	1278	1050	1155	1278
1 days at 82°C	1295	1225	1208	1313	1365	1208
7 days at 82°C	193	1173	1488	1260	1243	1050

*0.089 mm, pigmented, polymeric plasticized.

X. Adhesion of modified hot-melt pressure-sensitive adhesives to plasticized PVC*

	D1	D2	D3	D4
Polyethylene grade				
Grade	...	540	580	B136
Amount, %	...	5	5	5
180° peel adhesion, N/m				
Initial	1610	1138	1628	1278
75 days at ambient temp.	805	1173	1470	1138
1 day at 70°C	35	788	910	963

*0.076 mm, clear, epoxidized soybean oil/DOA plasticized. DOA = dioctyladipate.

formulas. After aging for one week at 82°C, however, the control adhesive exhibited a soft, gummy texture and demonstrated a dramatic decrease in adhesion, while the polyethylene-containing formulas exhibited a minimal change in peel strength. The loss of cohesive strength in the control formulation was the result of the attack of the polymeric plasticizer from the PVC substrate.

In the second evaluation, we utilized a PVC that is more flexible: a 0.076-mm, clear PVC, plasticized with a combination of epoxidized soybean oil and dioctyladipate. As indicated in **Table X**, after aging 75 days at ambient conditions, the control adhesive exhibited a 50% decrease in peel strength, whereas the three LMW polyethylene-containing formulas showed essentially no decrease in adhesion. After accelerated aging for one day at 70°C, all of the tested adhesives exhibited a decrease in peel strength. However, the polyethylene containing formulations were reduced 35%, on average, whereas the control had a peel strength reduction of nearly 100%.

The third evaluation was performed using an 0.203-mm, clear PVC, plasticized with a linear phthalate. The test results shown in **Table XI** indicate that initially and after aging for either 60 days at ambient conditions or one day at 52°C, the polyethylene-containing adhesive showed higher adhesion than the control. However, after aging for seven days at 52°C, all adhesives showed a significant loss in adhesive strength as a result of the migration of the monomeric type of plasticizer.

Using the same linear phthalate plasticized PVC, other LMW polyethylenes were evaluated. As the results in **Table XII** show, these polyethylene-containing adhesives exhibited initial adhesion that was either similar to or better than the control.

After aging one day at 52°C, the control lost nearly all of its initial adhesion, while the polyethylene-modified adhesives showed no loss in peel strength. However, after aging for seven days at 52°C, the polyethylene-containing adhesives exhibited significant losses in adhesion, while the control adhesive exhibited almost total loss of adhesion. Furthermore, after aging 60 days at

ambient conditions, all adhesives showed a decrease in peel strength; the control exhibited the least adhesion, at 49 N/m, while the adhesive containing Grade 290 showed the highest adhesion, at 569 N/m.

Finally, LMW polyethylenes were tested in the EVA-copolymer-based, hot-melt, laminating adhesive formulation shown in **Table XIII**. Here, two sheets of 0.203-mm, clear, linear, phthalate, plasticized PVC were bonded together. As the results in **Table XIV** show, the polyethylene containing adhesives exhibited initial adhesion that was similar to or better than that of the control. After aging one day at 52°C, the polyethylene-containing formulations showed an average of 57% better peel adhesion than the control. However, after aging seven days at 52°C, all of the adhesives exhibited a significant decrease in adhesion as a result of the migration of the monomeric, phthalate plasticizer.

These evaluations indicate that incorporating LMW polyethylenes in a hot-melt adhesive contributes significantly toward obtaining a stable adhesive bond to plasticized PVC. The polyethylenes demonstrate effective control of the migration of relatively high-molecular-weight plasticizers, such as polymeric types and epoxidized soybean oil. With monomeric plasticizers, the polyethylenes showed positive indications of controlling migration under relatively mild aging conditions. Under more stringent aging, the polyethylenes were not as successful. We are planning further work regarding the bonding of PVC films and sheeting containing monomeric plasticizers.

Conclusions and recommendations

Certain LMW polyethylenes are extremely useful additives for controlling the adverse effects of plasticizer migration into or out of adhesives and sealants. One of the most important of the potential uses of these LMW polyethylenes is in pressure-sensitive or laminating type adhesive applications involving plasticized PVC films or sheeting.

If such polyethylene modification allows wider use of hot-melt adhesive for adhering to plasticized PVC, manufacturers of PVC tapes, labels, and laminates may be able to realize the benefits of using hot-melts. These benefits include faster coating speeds and shorter production lines. Furthermore, LMW polyethylene-modified, hot-melt adhesives or sealants should be considered for adhering to surfaces contaminated with various organic liquids, such as oily metal substrates.

In addition, our evaluations have shown that LMW polyethylene modification can enable hot-melt sealants to incorporate high concentrations of plasticizing and extender oils to enhance properties or to reduce raw material costs.□

XI. Adhesion of modified hot-melt pressure-sensitive adhesives to plasticized PVC*

	E1	*E2*	*E3*	*E4*
Polyethylene grade				
Grade	...	540	580	B136
Amount, %	...	5	5	5
180° peel adhesion, N/m				
Initial	770	1523	2100	1103
60 days at ambient temp.	9	630	578	630
1 day at 52°C	18	945	508	473
7 days at 52°C	5	39	11	79

*0.203 mm, clear, linear phthalate plasticized.

XII. Adhesion of modified hot-melt pressure-sensitive adhesives to plasticized PVC*

	F1	*F2*	*F3*
Polyethylene grade			
Grade	...	290	A87
Amount, %	...	1	3
180° peel adhesion, N/m			
Initial	805	1225	805
60 days at ambient temp.	49	569	193
1 day at 52°C	35	1260	1208
7 days at 52°C	7	68	263

*0.203 mm, clear, linear phthalate plasticized.

XIV. Adhesion of modified hot-melt laminating adhesives to plasticized PVC*

	G1	*G2*	*G3*
Polyethylene			
Grade	...	290	316
Amount, %	...	3	1
180° peel adhesion, N/m			
Initial	1628	2380	1593
1 day at 52°C	613	893	1033
7 days at 52°C	21	135	25

*0.203 mm, clear, linear phthalate plasticized.

XIII. General hot-melt laminating adhesive formulation for bonding to plasticized PVC

Component	*Weight percent*
EVA copolymer (33% Vinyl acetate, 43 M.I.*)	40.0
Aliphatic/aromatic resin (95°C S.P.)	40.0–37.0
Microcrystalline wax (85° C M.P.)	19.7
Hindered phenolic A.O.	0.3
LMW polyethylene	0–3.0

*M.I. = melt index.

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