Modified thermoplastic polymers

Jeff A. Jones
Research specialist, Quantum Chemical Corp., 3100 Golf Rd., Rolling Meadows, Ill. 60008.

Doug Wielinski
Market development coordinator, Quantum Chemical Corp., 1275 Section Rd., Cincinnati, Ohio 45237.

ABSTRACT *Adhesion of hot-melt adhesives containing ethylene vinyl acetate (EVA) polymers can be increased by modifying them with maleic anhydride (MAH). Test results indicate that modification does not detract from heat stability, color, or compatibility with other materials. The MAH-modified EVA polymers showed excellent adhesion to nonporous substrates such as aluminum and nylon.*

KEYWORDS
Adhesives
Adhesion
Ethylene vinyl acetate
Hot melts
Maleic anhydride

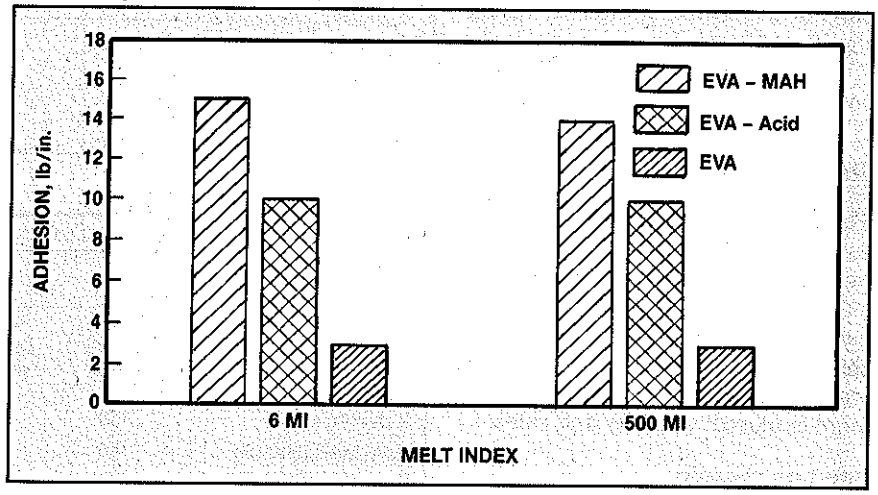
Ethylene-vinyl acetate (EVA) copolymers have been used extensively in adhesive applications since the 1960s[1]. In an effort to expand the range of use for these polymers, we investigated methods of improving their adhesion without sacrificing desirable properties such as heat stability and compatibility.

Anhydride functionality is commonly used to improve polymer adhesion[2]. We incorporated low levels of maleic anhydride (MAH) into commercial EVA copolymers containing 25% or 28% VA [weight/weight (w/w)] in an attempt to develop materials with superior adhesion. This article focuses on studies of two such polymers and compares their performance with nonfunctionalized as well as carboxylic acid functionalized EVAs.

Synthetic approach

The literature[2] indicates that significant improvements in adhesion can be obtained by incorporating maleic anhydride into the polymer matrix. Consequently, a variety of synthetic methods for "maleating" EVA were investigated in an effort to control the polymer's physical properties while optimizing its adhesion. These investigations led to the development of methods that incorporated MAH into the EVA polymer with no apparent loss in physical properties. **Table I** compares the physical properties of a 6-MI (melt index) EVA and a similar EVA-MAH polymer. (Both EVAs contained 28% VA.)

1. Adhesion of different EVAs (28% VA content) to aluminum [T-peel (Al to Al); ASTM D-1876-72 at 12 in./min.]



Adhesion to aluminum

A primary objective of this study was to increase the adhesion of the base EVA polymer to nonporous substrates. **Figure 1** shows the results of a T-peel (aluminum to aluminum) study comparing the adhesion of three EVAs at 6 MI and three in the 400–500-MI range. In each MI level, a maleated EVA (EVA-MAH) is com-

[1]Specialty Polyolefins—Ethylene Based, Vols. I & II, Townsends Marketing Associates, Inc., Houston, Tex., 1988.
[2]Trivedi, B. C. and Culbertson, B. M., Maleic Anhydride, Plenum, N.Y., 1982.

I. Physical properties of base EVA and EVA-MAH polymers

	EVA	EVA-MAH
Melt index *	6	6
Vinyl acetate content, % (w/w)	28	28
Acid no.	0	4-8
Density	0.95	0.95
1% SecMod, psi	1730	1720
Melting point, °C	71.9	73.3
Elongation, %	820	750
Break, psi	2200	2630
Shore A	83	84
R&B, °F	277	270
Mw	5.8×10^4	6.0×10^4
Mn	1.9×10^4	1.7×10^4
Mw/Mn	3.0	3.4

*Determined using ASTM D-1238. SecMod=secant modulus. Shore A=hardness, shore A. R&B=ring and ball softening point. Mw=molecular weight. Mn=number average molecular weight. Mw/Mn=polydispersity.

II. Viscosity of polymers over time at 350°F

Time held at 350°F	Viscosity (Brookfield LVT), cP EVA (400 MI)	EVA-MAH (500 MI)	EVA-Acid (500 MI)
0	28,250	22,250	22,250
24 h	29,250	22,800	24,250
48 h	32,000	26,250	42,250
72 h	35,250	32,300	>>100,000

III. Color of polymers after 24 h at high temperature

Temperature held for 24 h	EVA (400 MI)	EVA-MAH (500 MI)	EVA-Acid (500 MI)
250°F	Clear	Clear	Clear
300°F	Clear	Clear	Faint yellow
350°F	Light yellow Slight "skin"	Light yellow Slight "skin"	Light yellow Large "skin"

pared with a similar nonfunctionalized EVA and with an EVA functionalized with carboxylic acid[3] (EVA-Acid). It is apparent from Fig. 1 that at both MI levels, the EVA-MAH polymers yielded adhesion values significantly higher than both the EVA-Acid terpolymer and EVA base polymer.

Heat stability

The pot life of an adhesive is a measure of how long the material can be held at high temperature without suffering any deterioration in physical properties. In order to investigate this parameter, two areas of thermal stability of the EVA-MAH polymers were explored: viscosity and color.

Effect on viscosity

Thermal effects on viscosity were studied by comparing the performance of the three polymers (EVA, EVA-MAH, EVA-Acid) having MIs of 400-500. Each resin contained less than 1000 ppm of butylated hydroxytoluene (BHT) and no additional stabilizer. The change in viscosity was measured over time at 350°F. The results of this study are listed in **Table II**. The EVA-MAH polymer and the EVA control proved similarly resistant to thermal degradation, with little change in viscosity after 48 h. In the same time frame, however, the viscosity of the EVA-Acid terpolymer nearly doubled. Similarly, after 72 h, the EVA-MAH and EVA control proved to have good thermal stability, whereas the viscosity of the EVA-Acid increased to above 100,000 cP.

Effect on color stability

Another concern related to long pot life is a polymer's color stability. Thermal effects on color were studied by exposing the three 400-500-MI polymers to an air atmosphere at 250°F, 300°F, and 350°F for 24 h. (Again, no additional stabilizer was added during this test.) The qualitative results of this study are listed in

IV. Compatibility of polymers (6 MI) in paraffin wax

	Cloud point, °F 10% polymer in wax	20% polymer in wax	30% polymer in wax
EVA (6 MI)	159	162	163
EVA-MAH (6 MI)	161	160	163
EVA-Acid (6 MI)	211	195	163

V. Compatibility of polymers (400-500 MI) in paraffin wax

	Cloud point, °F 10% polymer in wax	20% polymer in wax	30% polymer in wax	40% polymer in wax	50% polymer in wax
EVA (400 MI)	158	157	158	157	158
EVA-MAH (500 MI)	156	157	162	164	164
EVA-Acid (500 MI)	157	162	161	162	159

[3]Mitsutani, A. and Morimoto, O., Functional Polymers by Graft-Polymerization, Research and Development Review Report No. 33, Nippon Chemtec Consulting, 1986.

VI. Compatibility of polymers in microcrystalline wax containing 10% polymer

	Cloud point, °F
EVA (6 MI)	187
EVA-MAH (6 MI)	186
EVA-Acid (6 MI)	>300
EVA (400 MI)	185
EVA-MAH (500 MI)	185
EVA-Acid (500 MI)	185

VII. Cloud points of different EVAs in 50:50 tackifier blends

Tackifier	Cloud point, °F EVA (28% VA, 400 MI)	EVA-MAH (25% VA, 500 MI)	EVA-Acid (25% VA, 500 MI)
Wingtack 95 (Goodyear)	>320	>320	>320
Wingtack extra (Goodyear)	>320	>320	>320
Zonatac 105 Lite (Arizona)	115	135	125
Regalrez 6108 (Hercules)	230	231	264
Permalyn 305 (Hercules)	108	122	114
Zonester 85 (Arizona)	109	124	113
Hercotac LA 95 (Hercules)	109	124	114
Nirez V2040 (Reichhold)	< 80	106	105
Nevex 100 (Neville)	287	310	303

VIII. Adhesion of various EVAs to different substrates [a]

	Adhesion, lb/in. Al[b]	EVOH[c]	Nylon[c]	Mylar™[c]
EVA (6 MI)	3	< 1	< 1	< 1
EVA-Acid (6 MI)	8	< 1	< 1	< 1
EVA-MAH (6 MI)	14	< 1	> 6 (CNS)	< 1
EVA-MAH_{exp} (6 MI)	14	5.4	> 6 (CNS)	< 1
EVA (400 MI)	3	< 1	< 1	< 1
EVA-Acid (500 MI)	8	< 1	1.4	< 1
EVA-MAH (500 MI)	14	1.2	< 1	< 1
EVA-MAH_{exp} (500 MI)	16	7.0	3.4	6.4

[a] Determined using ASTM D-1876-72 at 12 in./min.
[b] Test conducted at 300°F, 20 lb/in.², 4-s dwell.
[c] Tests of 6-MI materials conducted at 450°F, 100 lb/in.², 4-s dwell. Tests of 400-500-MI materials conducted at same pressure and dwell but at 300°F.

IX. Viscosity of EVA/Polyamide blends*

	Viscosity, cP
EVA (400 MI)	66,000
EVA-MAH (500 MI)	222,500
EVA-Acid (500 MI)	48,000

*75 parts EVA to 25 parts polyamide and 0.2 parts antioxidant

Table III. The EVA-MAH and the EVA control were equally resistant to discoloration, while the EVA-Acid polymer tended to yellow more quickly and to form a considerable quantity of degraded "skin."

Compatibility

The compatibility of a polymer in a specific blend is an important criterion for the hot-melt formulator. A material's cloud point is a measure of compatibility. The cloud points for EVA, EVA-MAH, and EVA-Acid polymers with both paraffin and microcrystalline waxes are reported as well as the cloud points obtained with various tackifiers.

Wax compatibility

Wax compatibility was evaluated for paraffin wax and for microcrystalline wax.

Paraffin wax. Table IV lists the cloud points for the 6-MI EVA, EVA-MAH, and EVA-Acid polymers with paraffin wax. At polymer levels of 30% (w/w), all three materials have similar compatibility. However, at 10% and 20% polymer, the EVA-MAH and EVA polymers are significantly more compatible (lower cloud point) than the EVA-Acid polymer. **Table V** shows the reported cloud points for the same three EVA types at 500 MI. In all cases, excellent compatibility was observed at blend ratios from 10% to 50% polymer.

Microcrystalline wax. Table VI lists the cloud points for the three EVAs at both the 6MI and 400-500 MI range with microcrystalline wax. At 10% loading the compatibilities were similar for all polymers, with the exception of the 6-MI EVA-Acid polymer. In this case, a cloud point >300°F was observed, indicating poor compatibility with microcrystalline wax.

Tackifier compatibility

The cloud points for the 500-MI series of EVA, EVA-MAH, and EVA-Acid with different tackifiers are reported in **Table VII.** At 50% polymer, similar compatibilities were observed for all three EVAs. Generally, the aliphatic hydrocarbon tackifiers proved least compatible with all three samples.

Adhesion to different substrates

Table VIII summarizes the values obtained in a brief, unoptimized survey of adhesion to different substrates for EVA, EVA-MAH, EVA-Acid, and a second experimental EVA-MAH (EVA-MAH_{exp}) at both the 6-MI and 400-500-MI levels. The substrates surveyed were aluminum, nylon, EVOH (ethylene vinyl alcohol), and Mylar™. The EVA-MAH polymers yielded significantly higher adhesion to aluminum than the EVA-Acid terpolymers or EVA controls. With nylon, both of the 6-MI EVA-MAH polymers gave excellent adhesion. Interestingly, only the EVA-

MAH_{exp} materials gave significant adhesion to EVOH and Mylar.

It is hypothesized that the maleic functionality of the EVA-MAH polymers provides a site for potential reaction with nucleophilic substrates (such as the free amine ends of nylon or the hydroxy functionality of EVOH) to yield strong, interchain adhesive bonds. The variations observed in adhesion between the two EVA-MAH materials are thought to be due to structural differences. This phenomenon is being studied.

Interaction with polyamides

In some cases, the cohesive strength of a hot-melt adhesive can be increased by blending in low-molecular-weight polyamides. **Table IX** lists the viscosities of EVA, EVA-MAH, and EVA-Acid polymers after being blended with a short-chain polyamide (amine no. 6). A significant increase in viscosity was observed only in the case of blended EVA-MAH. These data support the theory that the EVA-MAH polymer provides a reactive site capable of forming an interchain graft, in this case yielding a higher molecular weight adduct with polyamide.

Summary

Adhesion of EVA (ethylene vinyl acetate) polymers can be increased by modifying them with MAH (maleic anhydride). The heat stability and compatibility of MAH-modified EVA polymers are not diminished by modification. Modified EVA polymers showed excellent adhesion to aluminum and nylon, indicating that they are suitable for use in applications that require bonding between nonporous substrates.

Possible end-use applications for the EVA-MAH polymers include hot-melt adhesives for packaging, hot-melt sealant, carpet coating, carpet tape adhesives, aqueous dispersion coatings, wax-based coatings, and polymer modification.□

Received for review May 19, 1989.

Accepted May 19, 1989.

Presented at the TAPPI 1989 Hot Melt Conference.