High Flow *Affinity*-Based Hot Melt Adhesives

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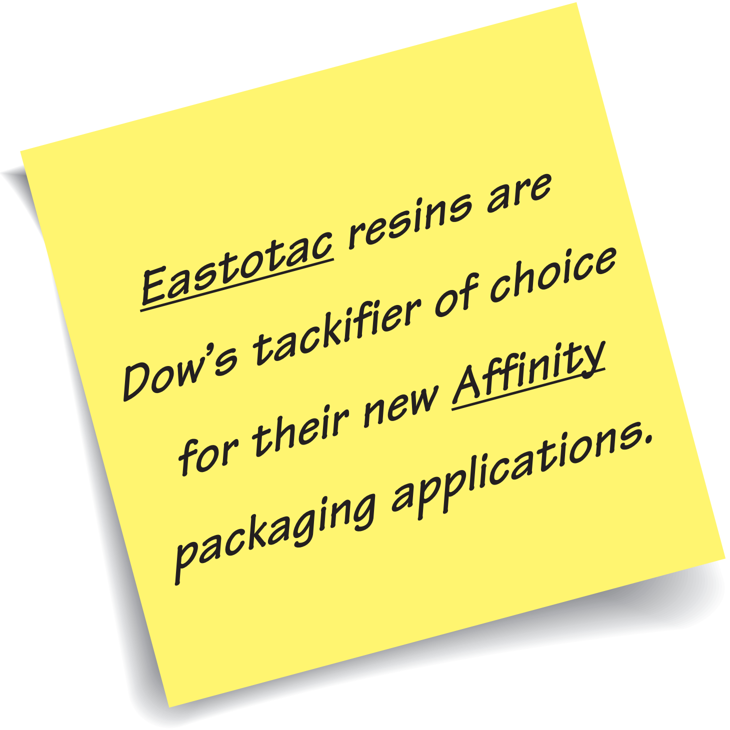
The introduction of high flow *Affinity*-based hot melt adhesives (HMAs) has been one of the most important events in the HMA market in the last 30 years. These novel polymers present an exceptional opportunity to formulate HMAs, which can deliver excellent adhesion at both low and high use temperatures, with unsurpassed processability, and excellent value for the end user.

This paper summarizes some of the important attributes of these polymers and HMAs made from these polymers and *Eastotac* tackifier resins.



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Introduction

High flow *Affinity*[1]-based HMAs combine impressive performance with customer demonstrated cost savings. These new products surpass their competition in processability, performance, cosmetic appearance, and most importantly they save money for end users. These HMAs offer high mileage due to aggressive bonding as well as lower density. They run clean and char-free resulting in savings in maintenance expenses such as filters and nozzles. As a result, end users experience much lower rates of line shut down and thus lost production. Additionally, the ease of cleaning the spilled or misfired beads from machinery and the lack of angel hairing or spider webs results in more savings in terms of reduced labor costs. Reduced wear and tear on the equipment, primarily due to the low acid content of the base polymer, have been documented. HMAs made from these polymers offer a wider service temperature than those of traditional ethylene vinyl acetate (EVA)-based hot melt adhesives. The clarity of the product in molten form and the much improved heat stability of the product as compared to competitive polymers results in better color and increased intervals between product changes in the melt tank. Finally, the lack of odor and smoke from the product improves workplace conditions. These attributes are summarized in Table 1. Use of these polymers in a wider variety of applications has been discussed in [1–2], and specifically as a flow modifier for thermoplastic polyolefins or TPO's in [3–4].

Affinity polymers are novel polyolefins manufactured using INSITE* Technology. The newly introduced polymers have unprecedented low density and low molecular weight combinations for a polyolefin. They are designed to be used in hot melt and hot melt pressure sensitive formulations in a variety of applications. These include:

1. Case and Carton Sealing
   a. Folding Carton Sealing
   b. Corrugated Container Closure
   c. Tray Forming
   d. Pallet Stabilization
2. General Packaging
3. Bottle Labeling
   a. Roll Feed
   b. Magazine Feed
4. Graphic Arts
   a. Lay-flat
   b. Hard Cover
   c. Soft Cover
5. Multi-wall and Specialty Bag
   a. Film Laminating
   b. Pinch Bottom
   c. Spot Paste
   d. Valve Assembly
   e. Longitudinal Seam and Bottom Paste
   f. Plastic Bags
   g. Vacuum Bags
   h. Security Bags
   i. Wax Bags
6. Nonwoven Hygienics
   a. Diaper Construction
   b. Core Stabilization

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[1] *Trademark of Dow Chemical Company.*

Table 1

Performance Attributes of High Flow *Affinity* Polymers

Performance Attribute	Observations
Increased mileage	Reduced adhesive usage, lowers cost as much as 15–30%, depending on application.
Reduced gel and char formation	No plugged filters and nozzles, reduced downtime and lost production.
No stringing and spider webbing	Enhanced package appearance, reduced labor cost, reduced downtime.
Improved thermal stability	Excellent control of viscosity resulting in precise control of bead size and bead placement.
Wide service temperature range	Final bonds resist extreme heat and cold, reducing waste, product returns, and replacement costs.
Color/clarity	Enhances package appearance.
Clean machining	Reduced wear and tear on the equipment, reduced downtime.
Odor free	Offers environmentally friendly workplace.

Test Methods

Polymer Test Methods

The differential scanning calorimetry (DSC) data were gathered on a TA Q1000 using 5–8 mg of sample pressed into a thin film. The sample was heated to 180°C and kept isothermal for 3 minutes to ensure complete melting (first heat). The sample was then cooled at 10°C/min to –90°C and kept isothermal for 3 minutes. The sample was then heated to 150°C (second heat) at 10°C/min. The second heat curve and data are reported in this work. Additionally, from the cooling curve the crystallization temperature is reported.

The viscosity data were measured both by dynamical mechanical spectroscopy (DMS) and by capillary rheometry. The DMS data were gathered on a Rheometrics ARES with 50 mm parallel plates in a nitrogen purge at 150% strain. A separate sample was used at each temperature of 110, 150, and 190°C, with each frequency sweep being conducted from 0.1–100 rad/s. The capillary data were gathered on a Goettfert Rheograph 2003 with a 0.5 mm diameter die and 30 length-to-diameter die ratio from 100–10,000 s^{-1}. An overlay of the DMS and capillary data is presented in this work.

Density was measured according to ASTM D792 [5]. Brookfield viscosity was measured according to ASTM D3236 [6] on a Brookfield LVDVII+ with Thermosel. Data are reported at either 350°F (177°C), the conventional HMA testing temperature, or 250°F (121°C), the temperature commonly used for a low application temperature hot melt adhesives. The melt indexes [7] at 190°C with a 2.16 kg weight were estimated based upon the Brookfield viscosity.

HMA Methods

Gardner color was determined as a function of time at the application temperature for the HMA [8]. Approximately 25 grams of adhesive was placed in a 4-oz glass jar and loosely wrapped with aluminum foil. Several samples were prepared for each HMA and placed in a forced air oven. The HMA was removed from the oven at the desired time and immediately decanted into a Gardner color tube. The Gardner color was determined as described in [9] using a Gardner Delta Illuminator.

The peel adhesion fail temperature (PAFT) and shear adhesion fail temperatures (SAFT) were determined on 40 lb virgin Kraft paper coated at 350°F (177°C) for *Affinity* GA 1950 and 250°F (121°C) for *Affinity* GA 1900. The adhesive thickness was 25 + 5 mil and the bond configuration for the Kraft coupons was 1″ × 3″ with a 1″ × 1″ bond overlap. The samples were conditioned overnight at 73°F (23°C) and 50% relative humidity. The PAFT weight used was 100 grams and the SAFT weight was 500 grams as described in [10]. The starting temperature was 30°C with a ramp rate of 0.5°C/min.

Heat stress data were based on Jefferson Smurfit virgin and recycled corrugated cardboard with conditions similar to that for PAFT and SAFT; a weight of 500 grams was used. For fiber tear, a ⅛–¼″ bead was used on cardboard coupons of 2″ × 2.5″ overlapped crosswise with the bond formed by light finger pressure. The samples were conditioned overnight at 73°F (23°C) and 50% relative humidity, with those at freezer conditions being kept for 30 minutes at the desired temperature. The fiber tear assessment was based on samples which were pulled apart by hand.

For the PAFT, SAFT, and heat stress studies, ten samples were measured in order to report the standard deviations; for fiber tear, three samples were used. Error bars are reported as the product of the standard deviation and the *t* distribution or Student's *t* at the 95% confidence level or at an $\alpha = 0.025$ [11]. For the PAFT, SAFT, and heat stress studies where error bars are reported, the Student's *t* is 2.262.

Polymers

Dow Chemical has recently introduced two high flow *Affinity* polymers, namely *Affinity* GA 1950 and *Affinity* GA 1900. These two polymers are intended for use in hot melt adhesives for case and carton sealing and graphic arts and a third one, *Affinity* EG 8200, is a low melt index polymer suitable for use in diaper construction and graphic arts applications. The physical characteristics of these polymers are shown in Table 2.

DSC heating curves of *Affinity* GA 1950 and GA 1900 are shown in Figure 1. It should be noted that the low crystallinity of these polymers coupled with low molecular weight (low viscosity) are primarily responsible for their excellent performance in HMAs. Figure 2 shows the viscosity of these two polymers as a function of shear rate and temperature. It should be noted that these polymers exhibit Newtonian behavior up to about 1,000 sec^{-1}. Much more detailed structure/property relationships of this general class of polymers are discussed elsewhere [12].

Table 2

Physical Properties of Adhesive Grade *Affinity* Polymers

Polymer	Density (g/cc)	Melt Index, g/10 min (190°C, 2.16 kg weight)	Viscosity, cP @ 177°C (350°F)	T_m (°C)[1]	T_c (°C)[2]	% Crystallinity[3]	T_g[4] (°C)
Affinity GA 1900	0.87	1,000[5]	8,200	69.4	54.3	15.8	–58
Affinity GA 1950	0.874	500[5]	17,000	71.4	53.1	18.3	–57
Affinity EG 8200	0.87	5	—	63.0	46.0	15.9	–53

[1] *T_m: Melting Temperature* [2] *T_c: Crystallization Temperature* [3] *(Heat of Fusion in J/g)/(292 J/g) × 100* [4] *Glass Transition Temperature* [5] *Apparent Melt Index*

Figure 1

DSC Heating Curves of High Flow *Affinity* Polymers

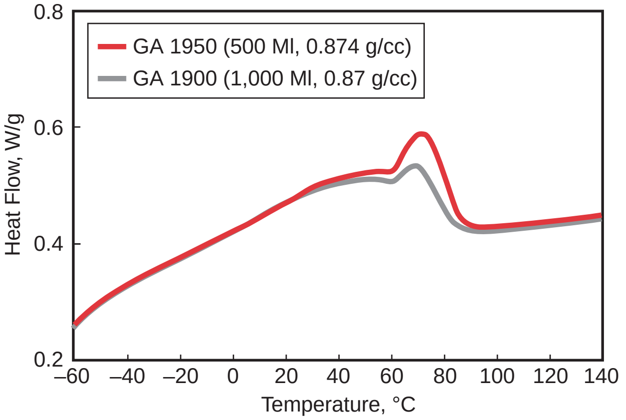
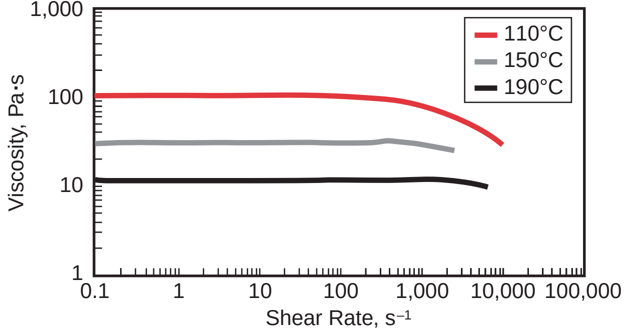


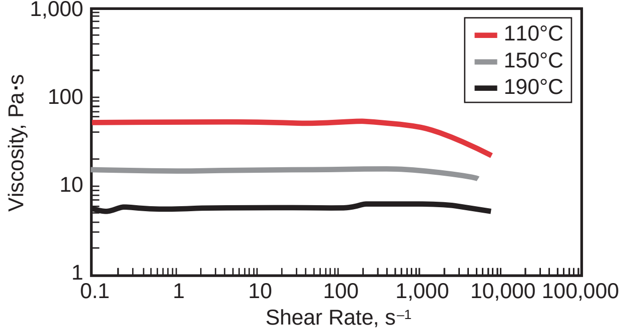
Figure 2

Viscosity of High Flow *Affinity* Polymers

GA 1950 (500 MI, 0.874 g/cc)



GA 1900 (1,000 MI, 0.87 g/cc)



HMA Performance

Table 3 shows HMA formulations prepared using *Affinity* GA 1950 and GA 1900 with different tackifying resins. The attributes and properties of these formulations will be discussed in this section.

Cost Savings

High flow *Affinity*-based HMAs offer lower overall cost as compared with EVA or ethylene-n-butyl acrylate (EnBA)-based HMAs. In one case study a pound of *Affinity*-based HMA sealed significantly more cases than a pound of incumbent HMA. Mileage advantage in this case study resulted in savings of 15 to 30%. These savings resulted from aggressive bonding, improved thermal stability, and lower density. Additional savings were achieved due to the ability to bond to a wide range of substrates, reduction in waste, reduction in maintenance, and lower inventory due to a wide service temperature.

In another case study, a Dow plant, which used to change filters and nozzles on a monthly basis and, therefore, experienced significant downtime, switched from an EVA based HMA to an *Affinity* GA 1950-based HMA, and operated with no downtime and no need to change nozzles and filters for a period of 18 straight months.

Gardner Color and Color Change

High flow *Affinity*-based formulations produce exceptionally clear and odor-free hot melt adhesives. This is attributed partly to the polymer component and partly to the hydrocarbon tackifiers used in the formulations. Figure 3 shows color change for two high flow *Affinity*- and EVA-based HMAs at 350°F (177°C) for up to 7 days. Table 4 shows the Gardner color as a function of temperature for the HMA formulations of Table 3, including one EVA-based HMA. As can be seen, both the initial and aged color is substantially improved for the *Affinity*-based HMA. These properties make high flow *Affinity*-based HMAs a preferred product when improvement in cosmetic aspects of the packaged goods and the work environment conditions are needed.

Table 3

Hot Melt Adhesive Formulations of *Affinity* GA 150 and GA 1900 and Three Different Tackifying Resins From Eastman Chemical Company
(The experimental tackifier resin is intended to be available in Europe.)

	***Affinity*[1] GA 1950**				***Affinity* GA 1900**		
Component, wt %	***Eastotac*[2] H-130R**	***Eastotac* H-142R**	**Experimental Tackifier**	**Component, wt %**	***Eastotac* H-130R**	***Eastotac* H-142R**	**Experimental Tackifier**
Affinity GA 1950	34.5	34.5	34.5	*Affinity* GA 1900	29.5	29.5	29.5
Eastotac H-130R	35.0	—	—	*Eastotac* H-130R	35.0	—	—
Eastotac H-142W	—	35.0	—	*Eastotac* H-142W	—	35.0	—
Experimental Tackifier	—	—	40.0	Experimental Tackifier	—	—	35.0
Paraflint[3] H2	30.0	30.0	25.0	*Paraflint* H2	35.0	35.0	35.0
Irganox[4] 1010	0.5	0.5	0.5	*Irganox* 1010	0.5	0.5	0.5
Total	100.0	100.0	100.0	Total	100.0	100.0	100.0

[1] *Trademark of Dow Chemical Company*
[2] *Trademark of Eastman Chemical Company*
[3] *Trademark of Sasol (now under Sasolwax trademark)*
[4] *Trademark of Ciba Specialty Chemicals Inc.*

Figure 3

Color Change at 350°F (177°C) Over 168 Hours (7 Days) for HMAs Based on (A) *Affinity* GA 1950 and on (B) EVA

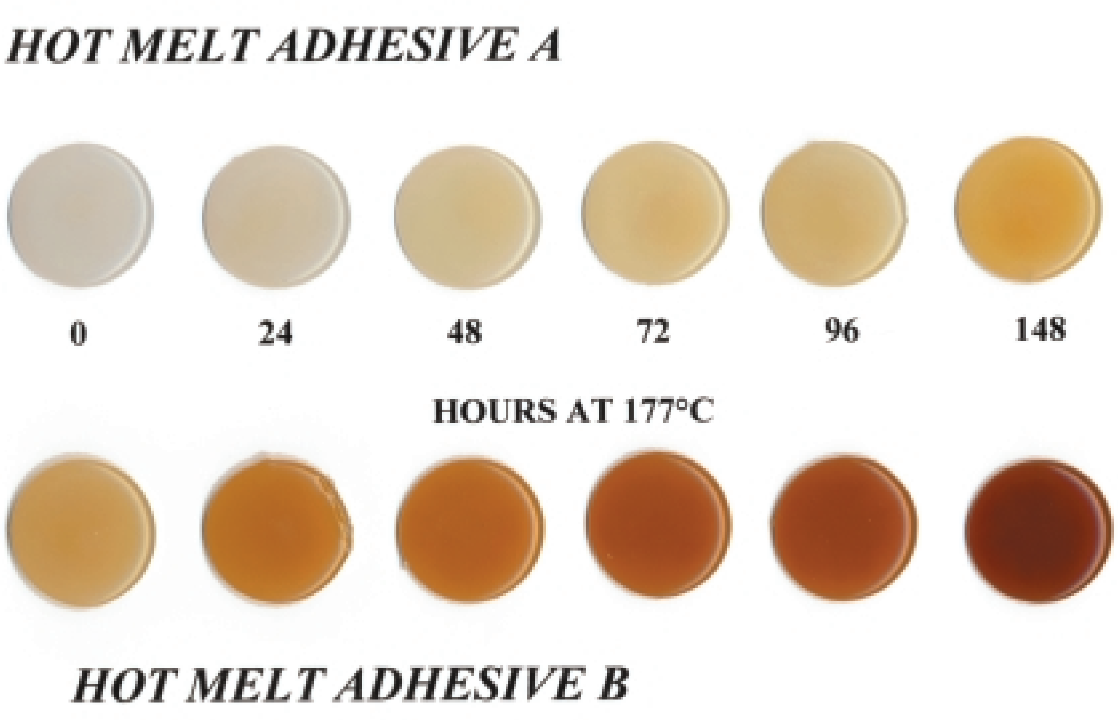


Table 4

Gardner Color as a Function of Time at the Application Temperature for the HMAs of Table 3 Along With an EVA-Based Low Application Temperature HMA

	***Affinity*[1] GA 1950 Conventional (350°F) HMA**			***Affinity* GA 1900 Low Application Temp. (250°F) HMA**			
	***Eastotac*[2] H-130R**	***Eastotac* H-142R**	**Experimental Tackifier**	***Eastotac* H-130R**	***Eastotac* H-142R**	**Experimental Tackifier**	**EVA-Based LATHMA**
Gardner Color, Initial	3	3	2	1	2	2	5
Gardner Color @ 12 hrs	4	4	5	3	3	5	8
Gardner Color @ 24 hrs	5	4	5	3	3	5	11
Gardner Color @ 36 hrs	6	5	6	5	3	5	11
Gardner Color @ 48 hrs	5	6	6	5	3	5	12
Gardner Color @ 96 hrs	11	8	11	6	3	6	13
Gardner Color @ 200 hrs	13	13	11	9	4	7	14

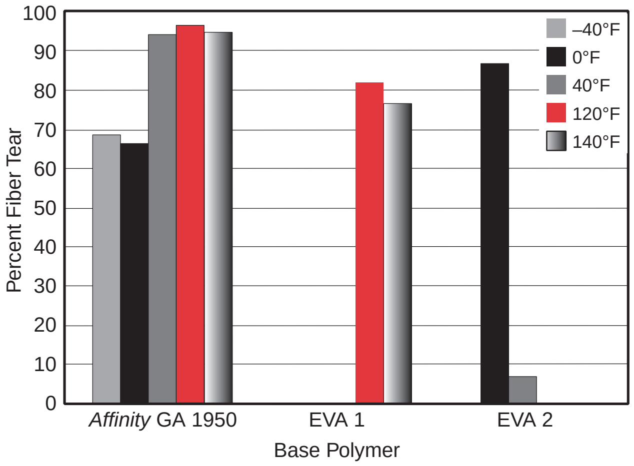
[1] *Trademark of Dow Chemical Company*
[2] *Trademark of Eastman Chemical Company*

Percent Fiber Tear

Hot melt adhesives formulated with high flow *Affinity* polymers provide excellent adhesion to a wide variety of substrates due to the low crystallinity and the very low molecular weight of these polymers. These include the many difficult-to-bond coatings used in the production of folding cartons. This aggressive bonding is maintained over a wide temperature range. HMAs based on EVA polymers and other competitive HMAs are not comparable to the performance of high flow *Affinity*-based HMAs. Typical percent fiber tear results for three different HMAs are shown in Figure 4.

Figure 4

Percent Fiber Tear at Five Different Temperatures of HMAs Formulated With Different Base Polymers, With Two EVA Formulations Designed to Perform at Low and High Temperatures

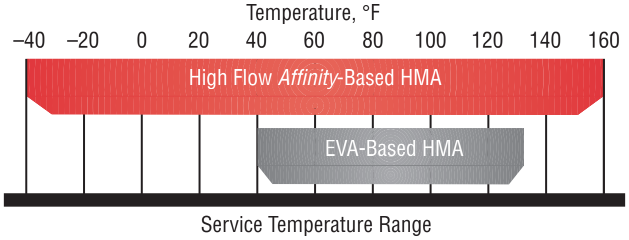


Service Temperature Range

Hot melt adhesives formulated with high flow *Affinity* polymers exhibit exceptional performance at both ends of the temperature scale, due to the very low glass transition temperature of the polymer and the heat resistance offered by the optimum tackifier. These polymers are the ideal choice when the packaging needs call for freezer-to-microwave exposure. Formulations prepared with high flow *Affinity* polymers save money for both the formulator and the end-user as the number of HMAs kept in the inventory and the plant floor will be reduced. One HMA can solve both the low temperature and the high temperature needs of the line operator. Frequent changes from one HMA grade to another will no longer be necessary. The service temperature range for *Affinity*- and EVA-based HMAs is shown in Figure 5.

Figure 5

Service Temperature Range for an *Affinity*-Based HMA and an EVA-Based HMA



PAFT, SAFT, and Heat Stress

High upper service temperature, as measured by PAFT, is very important for warehouse storage purposes, especially in warm climates. *Affinity*-based HMAs offer superior PAFT performance when compared with competitive samples. Formulations that offer PAFT values in excess of 160°F have been prepared. Use of high performance HMAs based on *Affinity* polymers will reduce the failure rate in cases sealed with these HMAs, thus reducing returned boxes and associated expenses.

Table 5 shows the PAFT, shear adhesion fail temperature (SAFT), heat stress, and onset and full fiber tear temperatures for both conventional and low application temperature hot melt adhesives (LATHMAs) measured on the samples of Table 3. The last column in Table 5 summarizes the results of a commercially available EVA-based low application temperature HMA. These results for PAFT, SAFT, heat stress, and fiber tear are shown pictorially in Figures 6–9 along with the error bars of the measurements. The average PAFTs of the *Affinity*-based HMAs were 150°–169°F as compared to 132°F for the EVA-based HMA. Similarly, the SAFTs were much improved for the *Affinity*-based HMAs at 188°–208°F as compared to 165°F for the EVA-based HMA. Onset of and full fiber tear was impressive for the conventional application temperature *Affinity*-based HMAs at –40° to –50°F and 0°F, respectively, and at 10° to –20°F and 10° to 20°F, respectively for the *Affinity*-based LATHMA. In comparison, the fiber tears for the EVA-based HMA were all poor at >35°F. Heat stress results were comparable for the LATHMAs at 177°–187°F for *Affinity*-based HMAs and 187°F for the EVA. The conventional HMA heat stress results were substantially higher for those based on *Affinity* at 196°–202°F.

Table 5

PAFT, SAFT, Heat Stress, and Onset and Full Fiber Tear of the Formulations Shown in Table 3 Along With an EVA-Based Low Application Temperature HMA

	***Affinity*[1] GA 1950 Conventional (350°F) HMA**			***Affinity* GA 1900 Low Application Temp. (250°F) HMA**			
	***Eastotac*[2] H-130R**	***Eastotac* H-142R**	**Experimental Tackifier**	***Eastotac* H-130R**	***Eastotac* H-142R**	**Experimental Tackifier**	**EVA-Based LATHMA**
Avg. PAFT, °F	158	169	150	161	158	151	132
St. Dev., °F	8.8	4.9	6.3	7.3	7.5	4.4	7.5
Avg. SAFT, °F	208	204	210	188	205	198	165
St. Dev., °F	5.0	4.5	2.6	7.7	5.2	3.1	3.7
Avg. Heat Stress, °F	200	196	202	177	183	188	187
St. Dev., °F	23.4	7.2	16.2	11.7	9.3	8.9	6.7
Onset of Fiber Tear, °F Virgin Corrugated	–50	–40	–50	–20	10–15	10–15	>35
Full Fiber Tear, °F Virgin Corrugated	0	0	0	10–15	20	20	>35
Onset of Fiber Tear, °F Fiber Tear Recycled	–50	–40	–50	–20	10–15	10–15	>35
Full Fiber Tear, °F Fiber Tear Recycled	0	0	0	10–15	20	20	>35

[1] *Trademark of Dow Chemical Company*

[2] *Trademark of Eastman Chemical Company*

Figure 6

Peel Adhesion Fail Temperature (PAFT) for High and Low Application Temperature *Affinity*-Based HMAs and an EVA-Based HMA

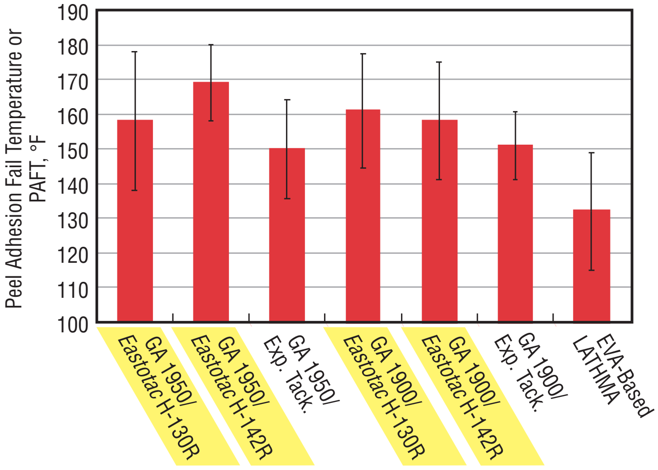


Figure 7

Shear Adhesion Fail Temperature (SAFT) for High and Low Application Temperature *Affinity*-Based HMAs and an EVA-Based HMA

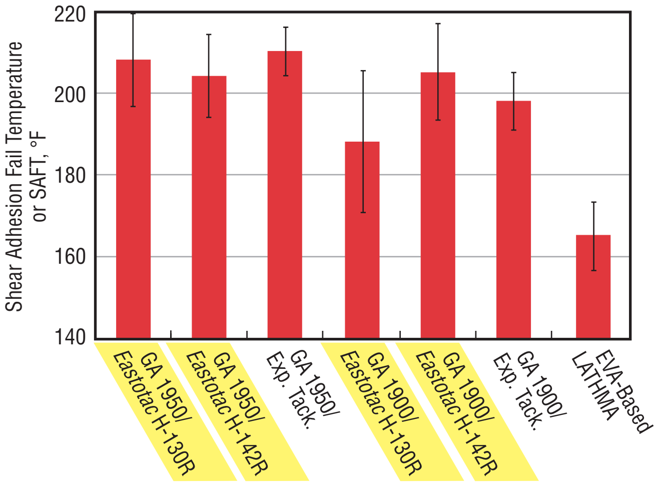


Figure 8

Heat Stress Data for High and Low Application Temperature *Affinity*-Based HMAs and an EVA-Based HMA

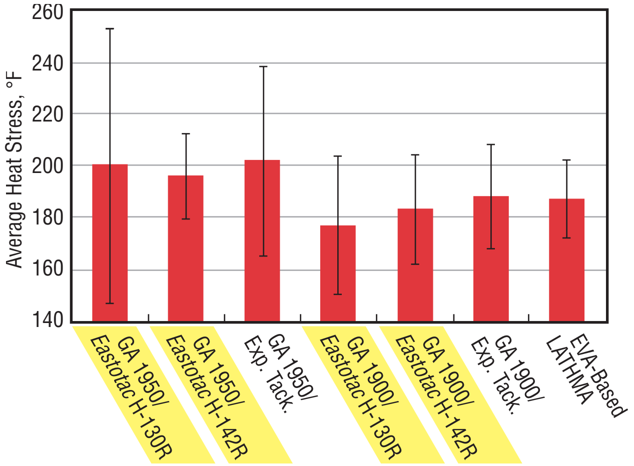
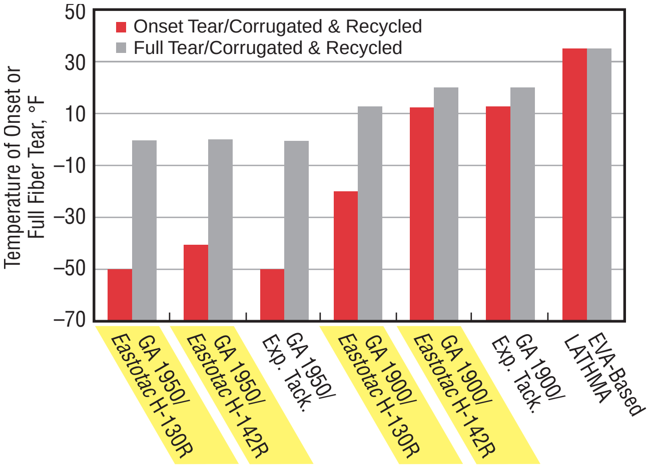


Figure 9

Fiber Tear Data for High and Low Application Temperature *Affinity*-Based HMAs and an EVA-Based HMA



Viscosity and Thermal Stability

Viscosity values of the HMAs of Table 3 measured at application temperature as a function of time are shown in Table 6. The thermal stability of *Affinity* GA 1950- and GA 1900-based HMAs is clearly outstanding. These formulations owe their stability to both the pure hydrocarbon nature of the backbone (no double bonds or oxygen atoms as in the case of styrenic block copolymers or EVA) and the type of tackifying resins used in the preparation. As shown in Table 7, most of these formulations were comparable in terms of the percent change in viscosity, with a maximum of a 3%–9% at 350°F and 0%–4% at 250°F. Note in most of these cases that the viscosity at over 8 days was less than these maximum values, indicating that much of this change was due to the experimental error of the test. In this study, one EVA was tested at only the low application temperature of 250°F and showed comparable results with a maximum viscosity change of 3%.

In another study, the viscosity change as a function of time was measured at the 350°F application temperature for both an EVA-based and an *Affinity* GA 1950-based HMA. These results are shown in Figure 10. The outstanding performance of the *Affinity*-based HMA over that of the EVA is clearly evident at this conventional application temperature. The *Affinity*-based HMA showed essentially no change in viscosity over 7 days, while the EVA-based system showed substantial changes after 1 day and a change of 65% over 7 days.

Figure 10

Viscosity Change as a Function of Time for an *Affinity* GA and an EVA-Based HMA

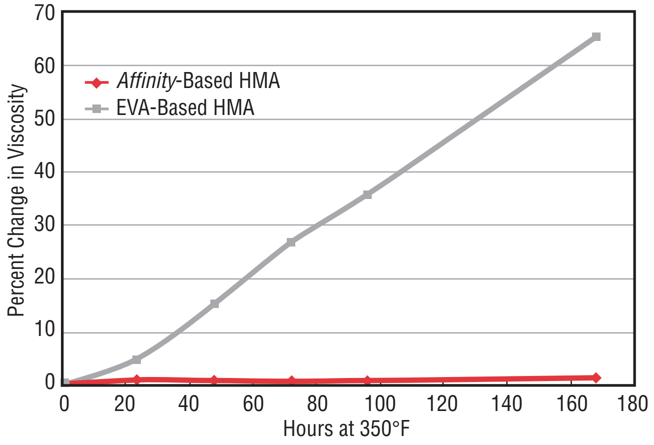


Table 6

Viscosity Change in cP as a Function of Time at the Application Temperature of 350°F for Conventional HMAs and 250°F for Low Application Temperature HMAs

	***Affinity*[1] GA 1950** **Conventional (350°F) HMA**			***Affinity* GA 1900** **Low Application Temp. (250°F) HMA**			
	***Eastotac*[2] H-130R**	***Eastotac* H-142R**	**Experimental Tackifier**	***Eastotac* H-130R**	***Eastotac* H-142R**	**Experimental Tackifier**	**EVA-Based LATHMA**
Viscosity (cP), Initial	597	772	538	1,092	1,127	1,037	1,055
Viscosity (cP), 12 hrs	610	765	587	1,102	1,132	1,030	1,050
Viscosity (cP), 24 hrs	620	740	577	1,102	1,147	1,025	1,055
Viscosity (cP), 36 hrs	607	750	570	1,105	1,150	1,035	1,065
Viscosity (cP), 48 hrs	607	763	567	1,102	1,175	1,025	1,052
Viscosity (cP), 96 hrs	597	795	580	1,117	1,175	1,025	1,055
Viscosity (cP), 200 hrs	602	790	570	1,110	1,135	1,035	1,085

[1] *Trademark of Dow Chemical Company*

[2] *Trademark of Eastman Chemical Company*

Table 7

Percent Change in Viscosity as a Function of Time at the Application Temperature of 350°F for Conventional HMAs and 250°F for Low Application Temperature HMAs

	***Affinity*[1] GA 1950** **Conventional (350°F) HMA**			***Affinity* GA 1900** **Low Application Temp. (250°F) HMA**			
	***Eastotac*[2] H-130R**	***Eastotac* H-142R**	**Experimental Tackifier**	***Eastotac* H-130R**	***Eastotac* H-142R**	**Experimental Tackifier**	**EVA-Based LATHMA**
Viscosity (cP), Initial	0	0	0	0	0	0	0
Viscosity (cP), 12 hrs	2	–1	9	1	0	–1	0
Viscosity (cP), 24 hrs	4	–4	7	1	2	–1	0
Viscosity (cP), 36 hrs	2	–3	6	1	2	0	1
Viscosity (cP), 48 hrs	2	–1	5	1	4	–1	0
Viscosity (cP), 96 hrs	0	3	8	2	4	–1	0
Viscosity (cP), 200 hrs	1	2	6	2	1	0	3
Minimum	0	–4	0	0	0	–1	0
Maximum	4	3	9	2	4	0	3

[1] *Trademark of Dow Chemical Company*

[2] *Trademark of Eastman Chemical Company*

Tackifier Selection

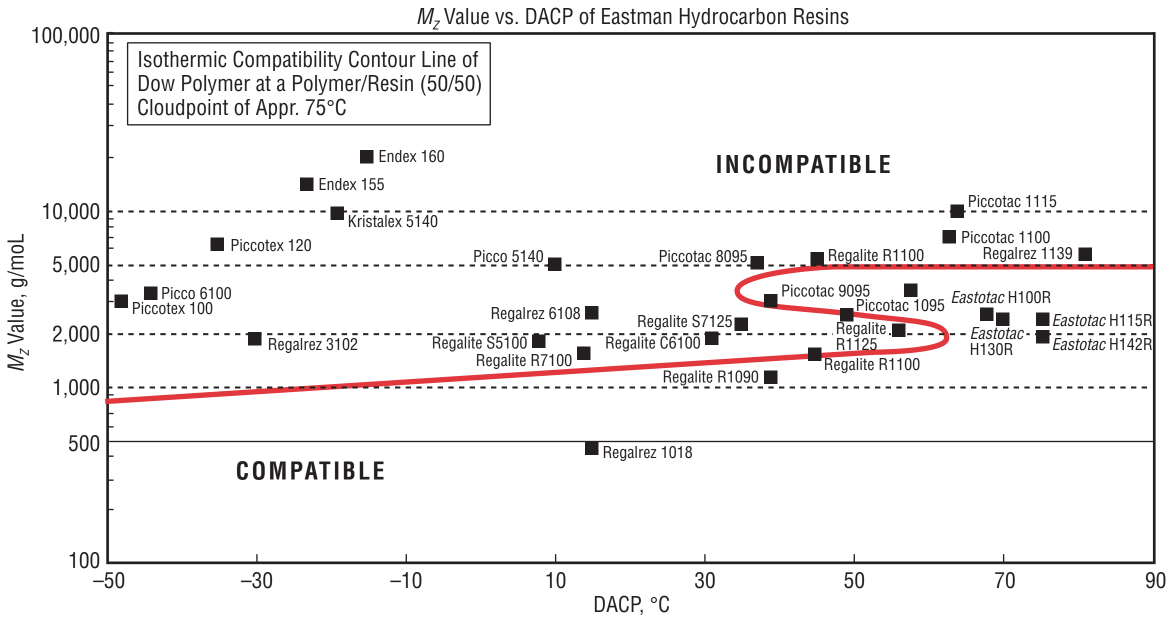
The performance of a hot melt adhesive is highly related to the compatibility of its components. As the tackifier is one of these critical components, studies were undertaken to assess the compatibility of *Affinity* polymers with several types of tackifiers. The compatibility of a resin with a given polymer depends mainly on its polarity and to a lesser extent on its molecular weight. The high molecular weight fraction of the resin, measured by its M_z value, may lead to symptoms of incompatibility such as turbid melts or migration upon aging. Therefore, it is customary to measure the compatibility of a hot melt adhesive by determining its cloudpoint. There are, however, several problems with this method among these being that it is time consuming and that the wax component can often obscure the cloudpoint.

To avoid these issues, the dual polymer/resin (1:1) cloudpoint measurements or the Hercules modified diacetone (MDA) alcohol method was used [13–14]. An isothermal compatibility contour for the *Affinity* GA polymers is shown in Figure 11. In this plot, the logarithm of the molecular weight (M_z) is plotted as a function of the resin polarity (lower DACP or diacetone alcohol cloudpoint value corresponds to increasing polarity) for several types of tackifiers.

Fully or partially hydrogenated C5 and C9 tackifiers are shown to be compatible with *Affinity* polymers. In particular, *Eastotac* tackifier resins show excellent compatibility with *Affinity* GA polymers.

Figure 11

Isothermal Compatibility Contour for *Affinity* GA Polymers



Summary

Novel high flow *Affinity* polymers offer unique properties which deliver outstanding performance in hot melt adhesives (HMAs). Designed to be used in both conventional and low application temperature HMAs, these polymers save money for both the HMA manufacturer as well as the end user.

References

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