

Developments in Ethylene-Based Hot Melt Adhesives

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Recent developments in hot melt adhesive technology have contributed substantially to the industry's phenomenal growth. Current research is producing new advances, in such areas as new ethylene polymers and fast-dissolving EVA resins, which are expected to become commercial in the near future and further expand the hot melt adhesives market.

Domestic consumption of hot melt adhesives has risen from less than 10 million pounds in 1964 to an estimated 130 million pounds in 1974. During this period, hot melts have been the fastest-growing segment of the adhesives market. They have numerous advantages; among the most important are fast processing speeds, relatively low raw material cost, and no solvents to produce pollutants or fire hazards. Hot melt adhesives are widely used in packaging, bookbinding, footwear, product assembly, and carpet backing applications.

The substantial growth already achieved by hot melt adhesives is expected to continue, stimulated by more widespread automation in the packaging industry, new polymers and other raw materials to meet applica-

tion demands, and new uses. Currently, there is a considerable expenditure in R&D efforts in hot melt technology.

These efforts may help realize a predicted 15 per cent annual growth rate for hot melt systems that could bring annual consumption to more than 300 million pounds by 1980 (see Figure 1).

Recent Developments

Although the history of hot melts, in the classical sense of the term, can be traced back to the Middle Ages when molten wax was used to seal documents, their modern history only goes back to the 1950s when ethylene copolymers were first used to modify paraffin wax. Most of the technology and commercial applications of these ethylene copolymer hot melt systems were geared to the coatings market because it was potentially much larger than the adhesives market. It wasn't until the mid 1960s that hot melt adhesives began to attract serious attention independent of coatings.

Since then, the technology associated with these systems has been in a state of rapid evolution. Independent

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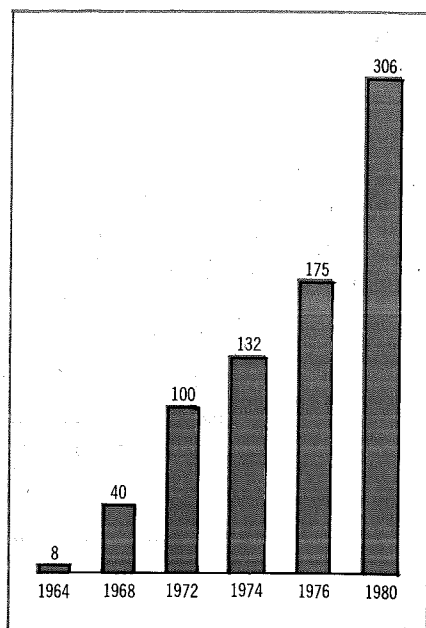


Figure 1 — Consumption of hot melt adhesives, in millions of pounds, with estimates to 1980.

formulating parameters had to be developed, because the work up to that time had been related to hot melt coatings. Specific formulations and compounding and application equipment were required to meet the specialized demands of the adhesives market.

Here, briefly reviewed, are some noteworthy developments of the past few years that have contributed to the rapid growth of hot melt adhesives.

Hot Melt Pressure-Sensitive Adhesives. Environmental and safety requirements have stimulated a major effort in the adhesives industry in general, and the pressure-sensitive industry in particular, to eliminate adhesive systems based on flammable and toxic solvents. In addition, hot melt pressure-sensitive adhesives provide attractive production economics due to the fast processing rate, small working area (no drying equipment), relatively low resin cost, and zero solvent cost.

A hot melt pressure-sensitive adhesive is a 100 per cent solids thermoplastic composition, which is applied in a molten condition and sets to a solid state with permanent tack when cooled. There are five basic formulation ingredients: 1) elastomers, 2) plasticizers, 3) tackifiers, 4) fillers, and 5) stabilizers.

The elastomer in a hot melt pressure-sensitive adhesive must meet a strict set of requirements: compatibility with modifying resins, good adhesion to a variety of substrates,

good melt stability, and low viscosity. The presence of a unique combination of these required properties make ethylene vinyl acetate copolymers (EVA resins) the choice as the base elastomer for many hot melt pressure-sensitive adhesive applications. Table I summarizes the effects of EVA resin variables on the adhesive properties of these systems.

In addition to the elastomer, the other components can play an important role in the formulation of hot melt pressure-sensitive adhesives. Table II summarizes the effects of each of these components in achieving the proper balance of properties required by an end-use application. A detailed discussion of hot melt pressure-sensitive adhesives can be found in an article published previously in *ADHESIVES AGE* (1).

These pressure-sensitive systems have made deep inroads into a market currently dominated by solvent systems, thereby contributing to the recent rapid growth of hot melts. There is still, however, tremendous opportunity for hot melts to attain a much greater share of the pressure-sensitive market.

"Rule 41" Hot Melt Adhesives. One of the most important reasons for the impressive growth of hot melts has been the ability of the formulators to meet the demanding requirements of diverse adhesive applications. A good example is the success achieved in conforming to the difficult standards of Rule 41.

Briefly, Rule 41 is a set of regulations issued by the Uniform Freight Classification Committee which governs the packaging requirements of all materials shipped by rail. Effective July 31, 1970, amended Section 7A permitted — for the first time — the use of hot melt adhesives in sealing corrugated containers up to a gross weight of 65 pounds.

The amendment also required that the hot melt be a 100 per cent solids thermoplastic material, and maintain a bond in temperatures between -20°F and $+165^{\circ}\text{F}$. Further modification of Rule 41 reduced the required flap coverage to 25 per cent (rather than 50 per cent coverage), allowing the hot melt to be applied in eight stripes (four on each side) of specified location and bead width.

In addition to these requirements, the formulators also had to consider the problem of the viscosity limitations of commercial application equipment.

A modern folding-carton-sealing line, for example, is generally equipped with a hot melt adhesive applicator whose practical upper viscosity limit is 10,000 cps.

To help solve the problem, prototype hot melt formulations were developed at the Union Carbide laboratories that meet Rule 41 requirements while maintaining sufficiently low viscosity for use with commercial application equipment. A typical formulation is described in Table III. This subject has been discussed in more detail in a prior *ADHESIVES AGE* article (2).

Ethylene Ethyl Acrylate (EEA) Copolymers. The introduction of new and improved polymers, tackifiers, and waxes by raw material suppliers has been a factor in the growth of hot melts. This is particularly true of materials which provide unique performance properties, such as ethylene ethyl acrylate resins.

EEA copolymers are amorphous, thermoplastic resins composed of a repeating sequence of nonpolar methylene groups and a moderately polar acrylate group. A unique combination of properties makes EEA an excellent choice as the base polymer for many hot melt adhesive applications.

In comparison with EVA, a number of improved properties are provided by EEA resins in hot melt systems. These properties include better flexibility, increased thermal stability, improved adhesion to olefinic substrates, and better wax compatibility.

A sample formulation for an EEA-based commercial hot melt adhesive system is illustrated in Table IV. A detailed discussion of EEA systems has been presented (3).

Compounding and Application Equipment. In addition to new raw materials and improved formulating know-how, the development of compounding and application equipment that can readily handle today's sophisticated hot melt adhesive systems has also contributed to the success of hot melts.

Initially, all the machinery for hot melts was designed to handle low-viscosity coating formulations. But as hot melt adhesives began to grow in industrial importance, equipment to handle higher viscosities had to be developed. During the past few years, equipment manufacturers have greatly accelerated the growth of hot melts by introducing application machinery that can apply adhesives with viscosities of 4 to 5 million cps. Recent refinements in

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high-speed dispensing equipment have improved the economics of hot melts and further contributed to their growth.

Improved compounding equipment has also helped. Recently introduced high-shear mixers, capable of blending materials at moderate temperatures and then extruding the finished product, have permitted many specialty hot melt adhesives to be commercially compounded for the first time.

This review of developments has covered a few of the many recent noteworthy contributions to the hot melt industry. If the predicted growth rate for hot melt adhesives is to be realized, however, developments like these must continue to be forthcoming from raw material suppliers, adhesive formulators, and equipment manufacturers.

New Advances

The numerous research programs currently in progress are geared to a multitude of end-use applications. It is still uncertain which of these programs will eventually become commercial and contribute significantly to the growth of hot melts. However, several of the R&D programs at the Union Carbide laboratories seem likely to meet some of the immediate and future needs of the hot melt industry.

New Ethylene Polymers. A series of experimental ethylene-based polymers has been developed for hot melt adhesive systems. The new resins can be used unmodified as directly applied hot melt adhesives, or used to alter existing hot melt adhesive systems. They can also be used with other raw materials to formulate new adhesive systems.

These new materials exhibit excellent adhesion to a wide variety of substrates and have the ability to bond dissimilar substrates. Compared to existing ethylene homopolymer and copolymer hot melts, the new polymers show better retention of adhesive properties at low and elevated temperatures. If used as a self-contained hot melt adhesive system, these resins may help reduce inventory and supply problems associated with the current raw material shortages.

If these materials become commercial, they are expected to find use in a wide variety of applications that include adhesives for the automotive, footwear, and wood and metal furniture markets. There may be formulations for product assembly systems, laminating, and bonding dissimilar substrates, and general purpose adhe-

Table I—Effects of VA Content and Melt Index of EVA Resins on Properties of Hot Melt Pressure-Sensitive Adhesives

Vinyl acetate content	Adhesive property	Melt index
18% 33%	increased	0.4 350
Little effect	Creep resistance	←
Slight → trend	Peel strength	→
→	Quick tack	→
Little effect	Melt viscosity ^a	←
Slight ← trend	Melt stability	Slight → trend

(a) Only adhesive property on chart for which an increase does not indicate an improvement.

Table II—Effects of Components on Property Balance of Hot Melt Pressure-Sensitive Adhesives

Hot melt component	Pressure-sensitive adhesive property				
	Creep resistance	Peel strength	Quick tack	Melt viscosity ^a	Melt stability
EVA resin	+	—	—	+	
Plasticizer	—	—	+	—	
Tackifier	—	+ ^b	+ ^b	—	—
Filler	+	—	—	+	
Stabilizer					+ ^c

+ Indicates the property will increase.

— Indicates the property will decrease.

(a) Only adhesive property on chart for which an increase does not indicate an improvement. A decrease usually indicates an improvement.

(b) Tackifiers increase the property. However, a maximum amount is reached beyond which an excess rapidly decreases the property.

(c) Antioxidants and UV stabilizers.

Table III—"Rule 41" EVA Hot Melt Formulation

	Parts by weight
EVA-305 ^a (ethylene copolymer)	40
CKM-2400 ^a (phenolic resin tackifier)	15
Piccolyte A-115 ^b (polyterpene tackifier)	12.5
Super Sta Tac ^c (synthetic polyterpene)	12.5
Polywax 1000 ^d (wax for lowering viscosity)	10
Castorwax ^e (wax for lowering viscosity)	10
Antioxidant 330 ^f	0.1

Test data

Peel (165°F.)	passes
Shear (165°F.)	passes
Fiber tear (40°F., 80% R.H.)	passes
Fiber tear (-20°F.)	passes
Viscosity at 350°F.	7,440 cps

^a Union Carbide Corp.

^b Pennsylvania Industrial Chemical Corp.

^c Reichhold Chemicals, Inc.

^d Bareco Div. of Petrolite Corp.

^e Baker Castor Oil Co.

^f Ethyl Corp.

Table IV—EEA Hot Melt Adhesive Formulation for Heat Sealable Tape

	Parts by weight
DPD-6169 ^a (EEA copolymer)	45
Dymex ^b (tackifier)	20
Piccolyte S-115 ^c (tackifier)	20
Cellolyn 21 ^b (plasticizer/tackifier)	5
Be Square 190/195 ^d (microcrystalline wax)	10
Antioxidant 330 ^e (stabilizer)	0.1

^a Union Carbide Corp.

^b Hercules, Inc.

^c Pennsylvania Industrial Chemical Corp.

^d Bareco Div. of Petrolite Corp.

^e Ethyl Corp.

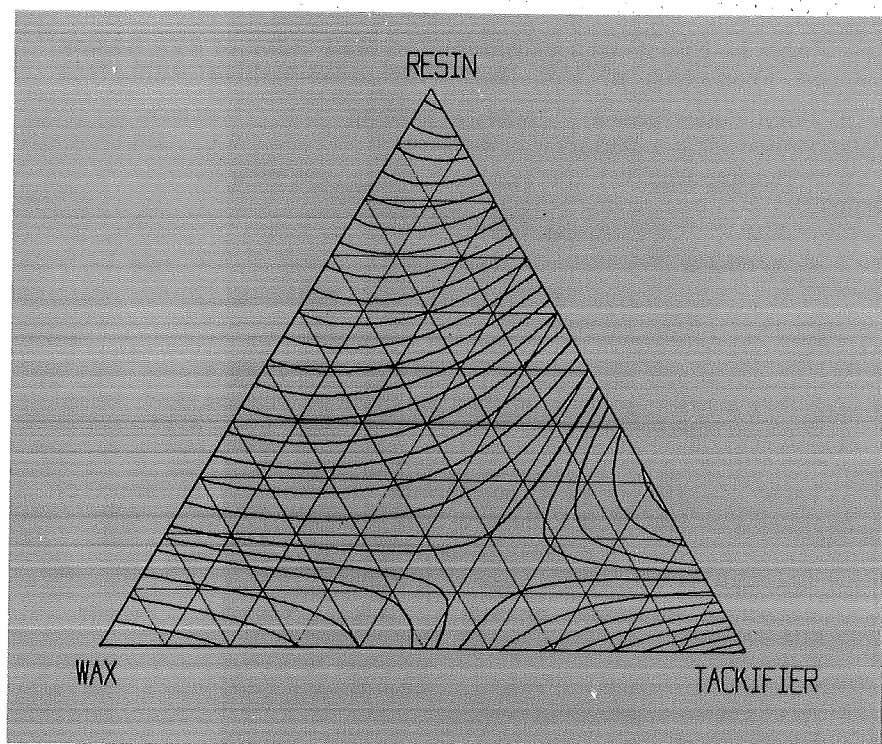


Figure 2 — Computer-developed viscosity-composition profile for tertiary hot melt adhesive systems.

sives for use in temperature extremes. Obviously, the versatility of the new ethylene polymers offers potential for further growth of hot melt adhesives.

Fast-Dissolving EVA Resins. One of the problems with high molecular weight EVA has been the difficulty of dissolving these resins in wax. This has precluded the use of many of these low melt index materials in commercial hot melt formulations.

Development work is underway on a new patented process that will enable the copolymer to be dissolved in wax in a much shorter time and at a lower temperature. This new process is expected to be a boon to the growth of hot melts because it will decrease the time needed for producing the adhesive (or coating) and the cost. It will also eliminate the problems of thermal and mechanical degradation of the components. And many hot melt adhesive and coating compositions containing high molecular weight (low melt index) copolymers will be commercially producible for the first time.

Repulpable Hot Melt Adhesives. One particular area where hot melt adhesives have enjoyed phenomenal growth is bookbinding. Today almost every paperback book manufactured in the United States is bound with a hot melt adhesive. The attractive economics associated with fast processing

rates have enabled hot melts to replace animal glues in this operation.

The major limitation to the further use of EVA hot melts in bookbinding is the inability to reuse the paper trimmed from the pages after binding. This is particularly crucial in light of current paper shortages.

Development programs to alleviate this problem and to encourage further use of hot melts in bookbinding are underway. Commercial and experimental ethylene polymers are being evaluated in an effort to develop a primerless repulpable (alkali dispersible) system that will provide improved adhesion to a wide variety of papers, and good low temperature flexibility.

Hot Melt Sealants. A sealant often can be considered a gap-filling adhesive because in many cases it performs two primary functions — holding parts together and sealing out dirt, water and fumes.

Historically, the sealant business has been dominated by oil-based products, with solvent and latex systems having a minor share of the market. Lately, however, the two largest consumers of sealants — the automotive and construction industries — have shown considerable interest in hot melts. These systems provide properties not available with other sealants, particu-

larly 100 per cent solids and no significant shrinkage.

Currently being investigated is the usefulness of different ethylene copolymers in conjunction with other materials in hot melt sealant formulations. Potential sales for these sealant systems are estimated at several hundred million pounds per year.

Formulating with Computers. Perhaps the most exciting development on the horizon for hot melts is the use of computers to determine the performance characteristics and physical properties of innumerable compositions. The computer could be used to develop a hot melt adhesive formulation, then optimize the system according to required performance parameters. Proper programming will also enable the formulator to determine replacements for raw materials with a minimal effect on performance.

An example of the virtually limitless versatility of the computer is illustrated in Figure 2. Any tertiary hot melt adhesive system is selected. The viscosity of each of the three components is determined individually, and at several intermediate compositions. The computer can then map out the melt viscosity at any composition of the given polymer, tackifier, and wax.

It should be pointed out that work involving the computer in hot melt formulating and raw material selection has only scratched the surface. Its potential to assist the formulator and encourage the rapid growth of hot melts is, of course, tremendous.

Hot melts have made great strides in the last ten years. The recent developments that have been reviewed contributed significantly to this growth. The new advances that have been described along with others coming out of research programs will certainly continue that growth in the future. Continued efforts by raw material suppliers, equipment manufacturers, and formulators should maintain the position of hot melts as the fastest growing and most attractive segment of the adhesive industry.

References

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- (2) Litz, R. J., "EVA Systems for New Hot Melt Adhesives to Meet Rule 41 and Packagers' Requirements," *Ibid*, Vol. 15, No. 8, August 1972, pp. 44-46.
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