

# HANDBOOK OF ADHESIVES

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# Ethylene Copolymer Based Hot Melt Adhesives

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For the purpose of this text hot melt adhesives will be defined as thermoplastic compounds, normally solid at room temperature, which become sufficiently fluid at elevated temperatures to "wet" substrates. Hot melt adhesives form bonds by resolidification upon cooling. They usually contain no water or volatile solvents as do emulsion or solution adhesives.

The use of hot melts as bonding and sealing agents dates back to antiquity when letters and legal documents were sealed with wax and marked with signature rings. Through the ages, hot melts based on a wide variety of both natural and synthetic raw materials have found use in many applications. However, the advent of low molecular weight polyethylene and ethylene copolymers has had a major influence on the expanded use of hot melts in the United States, particularly for packaging related end uses. This dramatic growth period started in the late 1960's and is presently in full swing. Market figures<sup>1</sup> indicate that the total United States consumption of hot melt adhesives grew from approximately 8 million pounds in 1964 to an estimated 100 million pounds in 1971.

The market by 1976 is expected to exceed 220 million pounds.

During the last 10 years, hot melts have made major inroads into certain application areas which had previously been dominated by water and solvent based adhesives. Carton and case sealing, laminating, bookbinding, and shoes are areas in which this trend toward hot melt adhesives has been particularly significant. Adhesive users have taken advantage of the quick setting feature of hot melts to increase production rates through the use of high speed, compact application equipment. Adhesive producers, on the other hand, have used the broad formulating latitude available with hot melts to design a myriad of compounds for specific end uses and substrates. In recent years, government and public concern over ecology has further stimulated both users and producers to place more emphasis on hot melt adhesives.

In this chapter, only ethylene copolymer based hot melt adhesives will be discussed in detail. However, no text on the subject of hot melt adhesives would be complete without at least a mention of the two other major polymer



classes which find use in hot melt adhesives today, namely polyethylene homopolymers and polyamides. Polyethylene hot melts probably have the largest share, by pound volume, of the market. These systems have relatively low cost and perform well on most porous, easy to bond substrates and in applications where flexibility, especially at low temperatures, is not required. Historically the major end uses for polyethylene systems have been with paper products such as carton and case sealing and adhesives for multiwall bags.

Polyamide hot melts are relatively high in cost. They are used in applications requiring good elevated temperature performance and/or solvent or detergent resistance. The shoe and furniture industries have been major users of polyamide systems. Polyamide hot melts are also becoming more important in the garment industry where they are used as label adhesives and for stitchless seaming.

Ethylene copolymers, particularly ethylene vinyl acetate copolymers (EVA) represent the third major class of hot melt adhesive polymers. While these copolymers are moderately more expensive than polyethylene homopolymers, their greater versatility has made them the polymer of choice for many of today's hot melt bonding applications.

Ethylene copolymer hot melts have better adhesion to a wider variety of substrates and better retention of properties at low temperatures than polyethylene systems. These copolymer systems are quick setting, require no cure or fusing nor water or solvent removal, and involve relatively low equipment, operating, and material costs. Ethylene copolymer based hot melts are more susceptible to cold flow and solvent attack than either polyethylene or polyamide systems. However, because of their superior adhesive properties, flexibility, and wider compatibility with modifier resins and plasticizers, these polymers offer the formu-

lating latitude required to perform a greater variety of jobs. EVA copolymers, for example, are used in soft, permanently tacky pressure-sensitive adhesives, also in tough rigid hot melt compositions used for semi-structural furniture and construction bonding applications. Table 1 lists the major advantages and limitations of EVA based hot melt adhesives.<sup>2</sup>

## HOT MELT ADHESIVE FORMULATING

Ethylene copolymer based hot melt adhesives are most often composed of two primary ingredients plus one or more secondary components. Primary ingredients are the *ethylene copolymer (s)* and one or more *modifier resins*. The copolymer functions as an elastomer and has a major influence on such important performance properties as cohesive strength, flexibility, low and elevated temperature performance, and melt viscosity. The modifier resins contribute specific adhesion and substrate wetting characteristics to the adhesive.

Secondary components include: *waxes*, *plasticizers*, *fillers*, and *antioxidants*. Wax functions as a non-volatile solvent for the hot melt and reduces melt viscosity. Plasticizers or liquid modifiers are used to a limited extent to formulate flexibility, specific wetting, and viscosity characteristics into hot melt compounds. Fillers are used for cost reduction, color control, and to improve cohesive properties. Antioxidants are used to retard oxidation of the hot melt during compounding and application.

### Ethylene Copolymers

Ethylene vinyl acetate (EVA) copolymers represent, by a wide margin, the major class of ethylene copolymers used commercially in hot melt adhesives. Ethylene ethyl acrylate (EEA)

Table 1. EVA-Based Hot Melt Adhesives — Advantages and Limitations.

Advantages	Limitations
Broad formulating latitude necessary to develop adhesion to a wide variety of substrates	Melt at elevated temperatures
Retention of properties at low temperatures	Cold flow
Quick setting	High viscosity needed for maximum performance
No cure or fusing required	Attacked by some greases, oils, and solvents
No water or solvent to be removed	
Low equipment, operating and material costs	
Pressure-sensitive systems can be formulated	



and ethylene acrylic acid (EAA) copolymers are also used where the specific properties of these polymers are required.

EVA copolymers are commercially available at various vinyl acetate (VA) contents and melt indices\* (see Table 2) ranging from 18 to 40 wt % VA (82–60% ethylene) and 0.4 to 500 melt index (MI). These two parameters are the major variables affecting performance. Hot melt adhesives are based primarily on the 28 and 33 wt % VA copolymers. The 28 wt % VA copolymers are available over the widest range of MI (0.4 to 350 dg/min) and, therefore, offer the greatest formulating latitude to the compounder.

Table 3 indicates, qualitatively, the effect

Table 2. Commercial EVA Copolymers.

% VA by Weight	Melt Index	Commercial Product/Supplier
18	500	Elvax 410/DuPont
18	150	Elvax 420/DuPont
18	125	EVA-303/Union Carbide
18	2.5	EVA-308/Union Carbide
18	2.5	Elvax 460/DuPont
18	1.5	Ultrathene UE 630/USI
19	425	Ultrathene UE 640/USI
19	150	Ultrathene UE 612/USI
19	1.5	Ultrathene UE 631/USI
20	28	EVA-305/Union Carbide
25	350	EVA-401/Union Carbide
25	350	Elvax 310/DuPont
25	20	Elvax 350/DuPont
25	2	Elvax 360/DuPont
28	400	Elvax 210/DuPont
28	400	Ultrathene UE 653/USI
28	350	EVA-501/Union Carbide
28	150	Elvax 220/DuPont
28	43	Elvax 240/DuPont
28	24	Ultrathene UE 636/USI
28	20	EVA-505/Union Carbide
28	16	Ultrathene UE 646/USI
28	15	Elvax 250/DuPont
28	12	EVA-506/Union Carbide
28	6	Elvax 260/DuPont
28	5	EVA-507/Union Carbide
28	3	Elvax 265/DuPont
28	3	Ultrathene UE 634/USI
28	1.2	EVA-508/Union Carbide
28	1.2	Ultrathene UE 645/USI
28	0.4	EVA-509/Union Carbide
30	120	Ultrathene UE 639/USI
31	24	Ultrathene UE 638/USI
33	25	Elvax 150/DuPont
33	20	EVA-605/Union Carbide
33	5	EVA-607/Union Carbide
40	55	Elvax 40/DuPont

Table 3. Effect of Vinyl Acetate Content of an EVA Resin on Adhesion.

Substrate	Vinyl Acetate Content	
	18% VA	33% VA
Kraft paper	—	Little effect
Glassine paper	—	Little effect
Wood	—	Little effect
ABS	—	Slight trend
Aluminum	—	Major improvement
Steel	—	Major improvement
Plasticized vinyl	—	Major improvement
Rigid vinyl	—	Major improvement
Polypropylene	—	Major improvement
High density polyethylene	—	Major improvement

that the VA content has on the adhesion of typical hot melt formulations to a number of substrates. The higher VA copolymers give better adhesion to polar substrates such as vinyl, aluminum, and steel, while the lower VA resins yield improved adhesion to olefinic materials such as polyethylene and polypropylene. VA content has little effect on adhesion to certain substrates such as paper and wood where mechanical adhesion and modifier resin selection are more important. However, VA content does influence elevated temperature properties, especially creep resistance (e.g., cold flow and compression set). At equivalent melt indices lower VA copolymers will have better elevated temperature properties. VA content has only a minor effect on other hot melt properties, such as cohesive strength, melt viscosity, and flexibility. Copolymer melt index is the primary variable influencing these important properties.

Table 4 gives a qualitative assessment of the effect of melt index on a number of important hot melt adhesive properties. Melt index has little effect on specific adhesion to various substrates. However, as indicated, high and low temperature adhesion is increased by the use of a lower melt index (i.e., higher molecular weight) copolymer. Room temperature adhesion is better, initially, with high melt index polymers, possibly because of their better substrate wetting characteristics. However, after the bonds are allowed to age, particularly at

\* A measured mass flow of material through a standard capillary die under standard temperature and pressure conditions in a given time. For EVA resins ASTM D-1238 is used grams/10 min @ 44 psi, 190°C). High melt index corresponds with low melt viscosity.



Table 4. Effect of Melt Index of an EVA Resin on Adhesive Performance.

Property	Melt Index	
	0.4	350
Adhesion @ -20°F	←—Major improvement—→	
Adhesion @ 73°F	←—Improvement—→	
Adhesion @ 140°F	←—Major improvement—→	
Adhesion @ 73°F After aging 2 weeks @ 140°F	←—Improvement—→	
Cohesive strength	←—Major improvement—→	
Elevated temperature strength	←—Major improvement—→	
Flexibility	←—Major improvement—→	
Melt viscosity	←—Major increase—→	

elevated temperatures, these differences in room temperature adhesion disappear and the positive effects of high molecular weight are again reflected. Cohesive strength, elevated temperature strength, and flexibility all show a major improvement with decreasing melt index.

Unfortunately, melt viscosity also increases with decreasing melt index. Since most commercial applications carry restrictions with regards to allowable melt viscosity, compromises in performance are often necessary to achieve a proper balance of properties. However, it is important to note that polymer blends employing both high and low melt index EVA resins often yield better properties than can be obtained through the use of a single intermediate melt index resin. For example, an adhesive formulation prepared with a blend of a 20 and a 0.4 melt index EVA resin may have better elevated temperature properties and low temperature flexibility than a comparable adhesive having the same melt viscosity and copolymer content but based entirely on a 15 melt index copolymer.

#### Other Copolymers

**EEA copolymers.** The formulating latitude available with EVA copolymers does not exist in the case of EEA copolymers. Commercial products are available only at the 18% ethyl acrylate, 82% ethylene level and only at 6 and

20 melt index.\* EEA copolymers, therefore, find use only where their unique properties fit an end use application. These properties, compared with those of EVA copolymers are: (1) better adhesion to olefinic substrates, particularly polypropylene, (2) improved thermal stability. The lower cost of EEA copolymers also contributes to their use in certain types of hot melt adhesives.

**EAA copolymers.** The use of EAA copolymers in hot melt adhesives has been limited up to this time by a number of factors including high price and poorer thermal stability, compared with EVA. However, the EAA copolymers do offer a number of positive performance advantages including excellent adhesion to metals and glass. They are also alkali dispersible. These properties should be of greater significance in the future as hot melt adhesives move into more of the metal bonding applications now dominated by solvent adhesives. Alkali dispersibility will be a major attraction of EAA for paper bonding applications demanding repulpability.

#### Modifier Resins

As mentioned previously, modifier resins represent the second major class of ingredients used in most commercial ethylene copolymer based hot melt adhesives. Most modifiers are relatively low molecular weight solid resins and may be either natural or synthetic products. They are used to supplement the flexibility, toughness, and cohesive strength of the elastomer. Primary contributions of the modifier resin are: specific adhesion, substrate wetting, open "tack" time and in some cases, improved elevated temperature strength. The basic classes of modifiers most often used in hot melts are:

**Wood rosin and wood rosin derivatives,** mainly esters, have, for many years, been used in hot melt adhesives and coatings to improve properties such as adhesion and heat seal strength. When treated properly, these resins are easily handled, however, they cannot withstand high temperatures (260–300°F) for long periods of time due to susceptibility to degradation and oxidation.

Wood rosin and its derivatives have low to medium viscosities and have a wide range of softening points. Due to their resinous makeup, which causes them to act as tackifiers, these materials are subject to blocking at temperatures below their softening points. For some

\* Union Carbide DPD-6169 and DPD-9169, respectively.