Hot-melt adhesive development and the proliferation of raw materials

Henry L. Buccigross and Jay H. Cheney

A key factor for the continued advancement of hot-melt adhesives will be the effective utilization of available raw materials.

The manufacturing world is driven by a need to produce products in a timely, cost effective, and environmentally safe manner. Because hot-melt adhesives fulfill these requirements, they are arguably the most desirable adhesives for use in manufacturing applications. The potential utilization of hot-melt adhesives is limited primarily by their ability to meet performance requirements. The hot-melt adhesive industry has recognized this fact. Over the past several decades, substantial improvements have been and continue to be made in the overall performance of hot-melt adhesives. This progress is largely the result of advances in raw materials and formulation techniques.

Although hot melts have many desirable qualities, there are also shortcomings. Some of the properties which have limited the use of hot-melt adhesives are poor elevated-temperature performance, a tendency to cold flow, thermal instability, dark color, and, perhaps most importantly, the strength/viscosity relationship. That is, the stronger adhesives are so viscous that specialized equipment is required for their application.

As a result of the continuous advancements of hot melts, the number of suitable end-use applications has grown significantly. Initially, hot-melt adhesives were limited to use in very low performance applications such as paper bonding. As their performance improved, hot-melt adhesives were used in more demanding and more visible end-use applications. The industry segments that currently utilize hot-melt adhesives include converting/packaging, disposables, furniture, footwear, automotive, construction, electronics, textile, and appliance. The specific applications for hot melts vary from tapes and labels to product assembly.

Coincidental with the development of new end-use applications has been the growth of adherends with which hot-melt adhesives can be used. Developments in specific adhesion have given rise to advocating their use with a wide variety of materials, including metals, plastics, ceramics, and wood products. As the strength and durability of hot-melt adhesives has improved, utilization has grown to include bonding of heavier gauge materials in applications demanding semi-structural strength and long life. As lighter color raw materials have become available, hot-melt applications have broadened to applications where aesthetics are important.

With the increasing use of new composite and other high-strength materials and the desire of manufacturers to identify faster, environmentally safe adhesive systems, there are still many new opportunities for hot-melt adhesives—provided they can meet performance requirements.

Finally, perhaps the strongest driving forces of all for suppliers to consider are volume and growth. We estimate that hot-melt adhesives represent a $700-900 million business at the compounder level, while real growth is about 5-6%.

With the continued development of thermoplastic systems and the relatively recent introduction and growth of reactive hot-melt systems, the hot-melt industry is situated to satisfy even more demanding end-use applications. A key factor for the continued advancement of hot-melt adhesives will be the effective utilization of available raw materials. A list of some common types of raw materials is provided in Table I.

The evolution of hot-melt adhesive raw materials

We have somewhat arbitrarily divided hot-melt adhesive evolution into three eras—Early, Second Generation, and Current. Obviously there were no sharp dividing lines between eras, and it is likely that some of the ingredients that were used 50 years ago are still being used today.

The earliest hot-melt adhesives were formulated from natural products. The very first hot-melt adhesive was likely compounded from a pitch of some sort. Certain vegetable waxes (e.g., castor-wax), natural resins (e.g., rosin), some mineral waxes (e.g., microcrystalline types), and mineral resins (e.g., coal tar or fossil) were also used as early hot melts. The applications for these earliest adhesives were generally low-performance ones. For example, they were used in laminating building papers, in nonfood paper-to-paper packaging applications, and as can label pickup adhesives.

Later, blends of some of the above materials with low

Buccigross and Cheney are director and senior engineer, respectively, of the Adhesives, Coatings, and Sealants Unit at Arthur D. Little, Inc., 15 Acorn Park, Cambridge, Mass. 02140-2390.

I. *Common types of raw materials utilized in hot melt adhesives*

Base polymers				
Thermoplastic systems	*Reactive systems*	*Tackifier resins*	*Waxes*	*Miscellaneous*
Acid copolymers	Epoxy	Styrene resins	Paraffins	Antioxidants
Amorphous polyolefins	Polyester	Styrene copolymer resins	Microcrystallines	Plasticizers—liquid and solid
Olefin/butyl rubbers	Polyurethane	α-Pinene resins	Oxidized microcrystallines	Fillers
Ethylene/acrylic copolymers		β-Pinene resins	Synthetics	Foaming agents
Ethylene/vinyl acetate copolymers		Dipentene resins	Oxidized synthetics	
Ethylene terpolymers		Hydrogenated rosins	Ester waxes	
Polyacrylic		Esterified rosins	Polyethylene wax	
Polyamide		C-5 Hydrocarbon resins		
Polyisobutylene		C-9 Hydrocarbon resins		
Polyester		Phenolic resins		
Polystyrene		Aromatic (coal tar) resins		
Polyvinyl acetate		Terpene phenolic resins		
Polyvinyl butyral		Paraffinic oils		
Polyethylene		Naphththenic oils		
Styrene block copolymers		Coumarone indene resins		
		Polybutenes		

molecular weight polymers became more common. The low molecular weight polymers of choice included materials such as ethyl cellulose and polymerized rosin. These were combined with compatible waxes—vegetable types in the case of ethyl cellulose, mineral waxes in the case of the polymerized rosins. The uses for these early blends were generally similar to those described previously. However, the resulting lighter-colored, better-performing adhesives allowed these blends to be used in applications where aesthetics were more important and the applications were somewhat more demanding.

Second-generation hot-melt adhesive formulation involved the utilization of higher molecular weight polymers in combination with chemical plasticizers. Such materials as polyvinyl butyral were combined with plasticizers such as liquid phosphates. Polyvinyl acetate polymers gained widespread use during this period. Formulations based on polyvinyl acetate polymers also utilized solid plasticizers like dicyclohexyl phthalate and diphenyl phthalate, along with certain of the resins described above, i.e., rosins and fossil resins. With the continued development of formulations of this sort, the applications for hot-melt adhesives grew markedly. The light-colored adhesives made application in the label area practical for the first time, and uses in food packaging grew rapidly. Case and carton sealing, bag heading, and certain bookbinding applications were satisfied by hot melts of this type.

Currently, we find that high molecular weight polymers, which have been more or less specifically cultivated for hot-melt use, form the basis for most hot-melt adhesive formulations. Some common types are listed in Table I under the heading "Base Polymers." Such polymers are used alone or are combined with waxes, synthetic tackifier resins, plasticizers, antioxidants, and other ingredients, as listed in the remainder of the table.

The polyamide and polyester base polymer types are normally used with little or no modification—that is, uncompounded. Atactic or amorphous polypropylene (APP) has historically been used with little modification. However, this is changing as amorphous polypropylene manufacturers have begun to understand the value of producing polymers which are useful in compounded adhesives. Polyethylene-based hot melts are often compounded with other polymers and tackifier resins.

The workhorses of this group of high molecular weight polymers are the ethylene copolymers, especially the ethylene vinyl acetate copolymers (EVAs). These polymers are most often compounded with waxes, many sorts of tackifier resins (petroleum hydrocarbon, terpenes, etc.), and sometimes with various plasticizers.

It is important to note that these current waxes and tackifiers are vastly different from those used only a decade or so ago. The waxes tend to be narrower cuts (more compatible) and in many cases exhibit higher melting points. The resins are cleaner, lighter colored, exhibit much improved heat stability, and are designed to provide very specific compatibility with base polymers.

Another class of polymers that are highly compounded are the thermoplastic elastomers of the diblock and the triblock type. These are block copolymers containing a rigid domain (styrene) and an elastomeric domain (isoprene, butadiene, etc.). The elastomeric domain may be saturated or unsaturated. These materials dominate the hot-melt pressure-sensitive area. Proper formulation is critical to the performance of block copolymer-based adhesives. The resins and plasticizers (including oils) used with these polymers are selected to associate either with the styrenic block (reinforcing function) or with the elastomeric block (tackification function). Seldom, if ever, is it desirable for any one ingredient to associate broadly with both blocks. Thus, the co-ingredients must be identified according to the block with which they will associate.

With the advancement and expansion of formulation technology, applications for hot melts have broadened considerably. They are widely used in product assembly for applications such as shoe fabrication, structural wood bonding, high-quality bookbinding, and edge banding of high-pressure laminates. In just a decade or so, hot melts have become the most common form of adhesive for pressure-sensitive applications.

If we look at trends, we find that the applications have gone from nondemanding low-end ones to high-performance ones; the compositions, from low-cost, low-margin products to high value-added ones; the type, from instantaneous to pressure sensitive; and the end uses, from paper converting toward structural bonding. In terms of polymers, the trends are toward ethylene-vinyl acetates, amorphous polypropylenes, block copolymers, inherently pressure-sensitive polymers, wax-compatible high molecular weight polymers, tailored polyesters, tailored polyamides, and cross-linkable or reactive types.

The raw material situation

We are now beginning to see just how complicated the raw material picture has become. Table I lists some of today's commonly used raw materials. When one realizes that most of the polymers and tackifiers are produced in several configurations (e.g., different comonomer content, molecular weight, softening point, etc.) and by numerous manufacturers, it is easy to understand that there are literally thousands of materials available for compounding hot-melt adhesives. This fact creates problems for the compounder, who is faced with selecting and combining the best "four or five" ingredients to satisfy a specific formulation need.

Moreover, if one includes the raw materials for reactive hot-melt adhesives (which are significantly different from the traditional ingredients for thermoplastic systems), the situation becomes even more complex and confusing.

It is likely, with so many raw materials being available, that even experienced formulators may not be aware of the best raw material for satisfying a particular need. Thus, in an effort to assist all formulators of hot melts in the selection of the most suitable ingredients, we believe a categorization of hot-melt adhesive raw materials is needed. It is time to analyze and organize our raw materials base.

A second reason for this categorization is to remind formulators of all of the available raw materials. As time goes on and our raw material base becomes larger, it becomes more likely that potentially useful raw materials may be overlooked in the compounding of an adhesive.

Proposed approach

It seems to us that there are three steps to this categorization. The first is to identify and acquire information on all raw materials. This will require the cooperation of raw material suppliers and perhaps compounders.

The second step is to develop a basic listing and classification of the raw materials—the initial form of a "Hot Melt Adhesives Raw Materials Guide." We recommend that materials be classified by function (base polymer, tackifier, wax, etc.) and general chemical composition, and that key physical properties also be included. Such a task has been previously undertaken on two occasions by the TAPPI Hot Melt Committee. CA Reports Nos. 37 and 55, entitled "Raw Materials for Hot Melts," were published in 1971 and 1975, respectively. We believe that an update is appropriate.

The final step would be the development of a more detailed characterization of the various raw materials. This may include a description of each type of raw material, its function, general compatibility, end-use areas, etc. We believe that such a guide would be very beneficial to the continued evolution of hot-melt adhesive technology.

Conclusions

Over the last 30 years, the development of hot-melt adhesive technology has been considerable and impressive. Along with this development, the industry has identified an overwhelming number of raw materials—most of which are of significant value to the compounder. To allow the continued effective development of hot-melt adhesives over the upcoming decades, we, as members of the industry, must make an effort to organize and define our resources.□

Received for review March 19, 1991.

Accepted April 18, 1991.

Presented at the TAPPI 1991 Hot Melt Conference.