

Curing hot melt adhesive systems

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ABSTRACT *Hot melt adhesives have come into wide use. Attempts have been made to improve their thermoplastic nature by curing with heat, oxygen, radiation, and moisture. The most effective methods are radiation and moisture. Electron beam curing of pressure-sensitive hot melts based on styrene-isoprene block polymers and moisture-cured urethane hot melts are reviewed. These new curing technologies are partially responsible for the trend away from solvent adhesives to 100% solids adhesives.*

KEYWORDS

Adhesives
Curing, Cross linking
Hot melts
Radiation
Thermoplastics
Urethanes

Since their appearance as a major factor in adhesive technology over 25 years ago, hot melts have been used in bottle labeling, case sealing, box fabrication, and other packaging and converting uses. Hot melt adhesives have also been widely used for pressure-sensitive labels and tapes, for edge banding in furniture fabrication, and for other purposes. The hot melts are fast, they require little energy, and their volatile emissions are low.

Hot melt adhesives are made of relatively low-molecular-weight, thermoplastic materials to ensure their melting and application at moderate temperatures of 150–200°C. Almost since their introduction, a way to cure or cross-link them has been sought, both to overcome their main limitation of heat sensitivity and to increase their strength. Remarkable progress in the technology has been made in the last five years.

Methods of cure

The methods that have been employed in curing are those of heat, oxidation, radiation, and moisture, as illustrated in Fig. 1.

Heat curing

Since the beginning of modern technology, heat has been used to cure or cross-link rubber, as in the vulcaniza-

tion process of Goodyear invented in the middle of the nineteenth century. The first cross-linked plastic was the heat-cured phenol-formaldehyde resin developed by Baekeland in the early twentieth century. However, since hot melt adhesives are materials applied and manufactured at elevated temperatures, the use of more heat to cure them becomes a risky proposition. The heat must be carefully controlled during both processing and application. This type of control, while theoretically possible, does not appear to be practical.

In spite of this limitation, the patent literature contains many examples of heat-curing hot melts. One such material consists of a combination of block polymer, a tackifier, oil, and a curing agent such as a heat-reactive phenolic resin or a capped isocyanate (1).

The problem with this type of system is that the heat used to cure the system is greater than the heat used in application. Since the boundary temperature is never as sharp as we would like, the chances of curing during manufacture or application are strong.

Oxygen curing

The use of an outside source of oxygen to cure a polymer is an old idea that goes back to the use of an unsaturated oil such as linseed oil in oil paints. Cross-linking by oxygen in the air,

assisted by organic metal dryers, is commonly known.

The patent literature shows attempts to make a curing hot melt by this method. One such example is a thermoplastic polyester resin containing unsaturated groups, capable of reacting with oxygen, to which peroxides and/or metallic organic dryers are added (2).

Like heat curing, oxygen curing is interesting from a theoretical and historical view, but the most practical methods are radiation curing and moisture curing.

Radiation curing

This method of cross-linking hot melts is not just a laboratory curiosity, but it is a method that has come into wide practice in the past decade. Pressure-sensitive adhesives are one of the main areas for radiation curing.

One organization has a novel material based on low-molecular-weight polyesters with pendant acrylic groups that can undergo rapid cross-linking with radiation (3). These materials must be heated to 50°C for coatings.

Another company has introduced a special grade of styrene-isoprene block polymer that can be formulated into a radiation-curable, pressure-sensitive hot melt using conventional hot melt equipment and formulation techniques. This company offers a

polymer that reportedly cures approximately four times faster than conventional styrene-isoprene block polymer. This polymer can be used in the same type of equipment as conventional pressure-sensitive hot melts and can be formulated for optimum peel, hold, and tack.

Electron beam is the preferred curing radiation method because of its ability to penetrate much deeper than ultraviolet radiation. With electron beam, the adhesive can be irradiated in-line as it is coated, even through a release paper. Radiation levels of from 2.5–7.0 Mrads are possible. The radiation greatly improves the holding power not only at room temperature but also at elevated temperatures (Fig. 2).

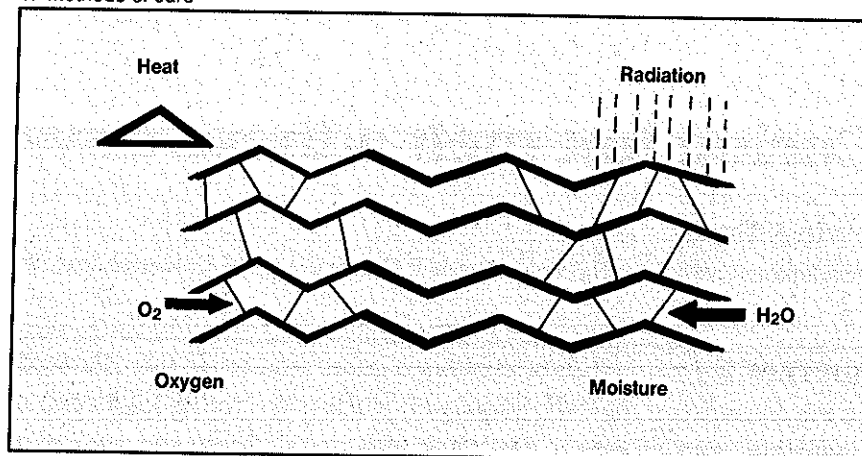
This technology has extended the use of hot melt, pressure-sensitive adhesives from uses requiring low performance levels to areas where solution adhesives that are more easily cured by heat or catalyst predominate. This development is one step further in the trend to replace organic solvent adhesives with 100% solids materials. Today, it is possible to produce such items as masking tapes that are able to withstand paint oven temperatures, tapes that are used in heat insulation, nonpenetrating labels of paper, and tapes and labels with holding abilities far in excess of the conventional hot melts that are presently available.

Moisture-cured hot melts

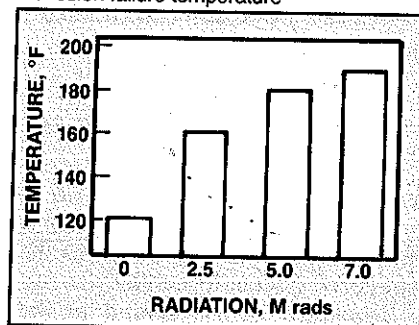
Moisture curing is the area that shows the most promise for growth in curing hot melts. The essential element is the exposure to moisture to cure the material. Since moisture is present everywhere (in the air, occluded on substrates, and in all cellulosic product substrates), this technique eliminates the need for expensive and powerful radiation sources. The moisture-cure hot melt carries with it its own curing mechanism. It does not necessitate special application and dispensing equipment that protects the adhesive from any contact with moisture until the point of use.

The two systems that utilize a moisture cure are the silane-type silicone polymers and the isocyanates. The low-molecular-weight polymers that cure by silanol condensation are used in moisture curing silicone sealants and gasketing materials.

1. Methods of cure



2. The effect of radiation on the shear adhesion failure temperature



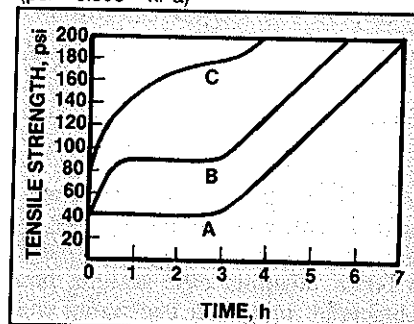
Since the silane cure is slow and does not give a strong bond, we will concentrate on the isocyanate or urethane-reactive hot melts that are making rapid progress in the market today.

The urethanes are based on the reaction product of a polyol and MDI (methylene bis-diisocyanate). MDI is the preferred isocyanate because of its low volatility at elevated temperature. An excess of MDI is used to create a polymer with terminal NCO groups. Their use as laminating adhesives is not new. Dissolved in solvents, they have been used as laminants for flexible packaging for over 20 years and also as structural adhesives.

What is relatively new is their use as reactive hot melts. Because of recent advances in adhesive technology, reactive urethane hot melts are available that can be applied at relatively low temperatures of 120°C. These hot melts are continuing to be used for new applications in many diverse fields, such as:

1. Nonsolvent, one-side-contact adhesives with moderate load-bearing

3. The development of shear tensile strength (psi $\times 6.895 = \text{kPa}$)



properties and moderate heat resistance

2. Laminating materials for polyvinyl chloride (PVC) films that are applied at low enough temperatures not to affect the texture of the vinyl and cure to give a high, plasticizer-resistant bond.
3. Use as bookbinding adhesives that are ink solvent resistant and for use in high heat and mechanical stress conditions.

These applications have been made possible by the following advances:

1. Development of adhesives that can be applied at 120°C but when cooled have enough cohesive strength or green strength to hold a joint or lamination together until final cure takes place.
2. Special spray equipment that prevents contact with moisture during application.
3. Formulations of adhesives that allow controlled, open time. Available are (a) fast-set types that allow for high-speed operations such as bookbinding and (b) slow set and

I. Comparison of curing vs. thermoplastic hot melts

Characteristic	Reactive	Thermoplastic
Application temp., °F	250	325
Application method	spray, slot	spray, slot, die, wheel
Heat resistance, °F	350	225
Solvent resistance	very good	poor
Structure	cross-linked	thermoplastic
Cost, \$/lb	3.50	1.00-2.50
Adhesion		
Polyvinyl chloride	excellent-good	fair-poor
Polycarbonate	excellent-good	poor
Polyolefins	fair-poor	good-fair

long open-time types for operations that require hand fabrication of large sections.

Figure 3 shows how shear strength develops with time for these variants. The long open products (A) have tack for up to 15 min and are used for hand assembly of large panels. The shorter open time materials (B) are required for holding down warped substrates, while the fast-set products (C) would work well for in-line operations like bookbinding.

A comparison of a reactive urethane hot melt and a thermoplastic hot melt are shown in Table I. The reactive hot melt adhesives provide better heat and solvent resistance, as well as somewhat better adhesive, but do in fact cost more money.

Summary

Curing hot melts are being introduced into the market. Both radiation-cured and moisture-cured products are commercially available and are extending the use of hot melt adhesives into areas that were thought impossible to serve several years ago. This trend is in keeping with the general trend of growth of the hot melt segment of the adhesive market. There is no doubt that hot melt adhesives will dominate the market of the future because of their low pollution, high production speed, their efficiency, and their low use of energy. Curing hot melts will make a major contribution in bringing about this dominance.

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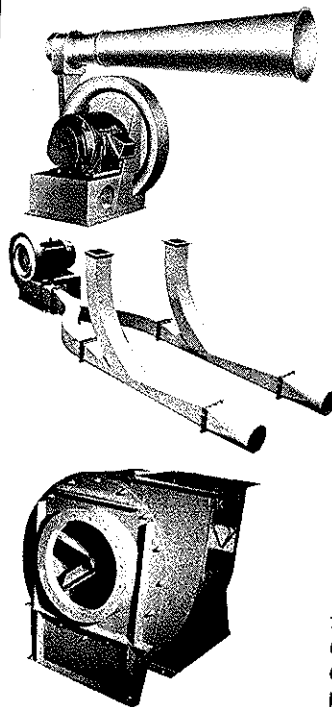
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