HOT-MELT ADHESIVES

High-performance hot melts for bonding polar and nonpolar substrates

REIMAR HEUCHER AND RÜDIGER BUTTERBACH

ABSTRACT

Hot-melt adhesives have been developed to bond polar and nonpolar materials. This paper describes adhesives based on polyamide resins and on polypropylene resins. Applications in the cable industry are presented to illustrate the potential utility of the newly developed hot melts. Additional laboratory data suggest that the new series of products can bond a variety of difficult substrates and resist degradation in acidic or basic environments.

Application:

New polyamide- and polypropylene-based hot melts for bonding polar and nonpolar materials.

THE DEMAND FOR NEW AND BETTER hot-melt adhesives continues to grow each year. Environmental regulations limiting emissions of volatile compounds have boosted the market for hot melts in favor of solvent-based adhesives. Furthermore, new nonpolar substrates such as polyethylene and especially polypropylene are being introduced to different markets (automotive industry, cable industry, general industry).

Polyamide resins based on dimer fatty acid have very good universal bonding characteristics, but their application is limited to polar substrates or pretreated substrates. Polypropylene resins based on atactic polypropylene also show excellent adhesion on nonpolar substrates like polyethylene and polypropylene, but conventional polypropylene resins typically show poor adhesion to polar substrates.

This paper describes recently developed high-performance hot-melt adhesives based on:

- Polyamide (PA) resins and blends
- Polypropylene (PP) resins and blends.

These new adhesives can bond both polar and nonpolar substrates with or without pretreatment. Examples are presented to illustrate the performance of these adhesives in terms of low-temperature flexibility, temperature creep resistance, and peel-strength with a range of substrates.

NEW PA HOT MELTS

PA chemistry and characterization

The polycondensation of a diacid and a diamine yields a PA resin, as seen in **Fig. 1**. A large variety of dicarboxylic acids and diamines are available as precursors, which makes it possible to tailor a PA resin for specific properties. The key raw material for our PA resin is the dimerized fatty acid, which has a tremendous influence on the structure of the PA *(1, 2)*. **Figure 2** shows one possible structure of the dimer.

Introduction of diols produces polyester amides, which show good adhesion to metal substrates. Subsequent incorporation of polyether chains produces materials with extraordinary low-temperature flexibility and excellent adhesion on metals and plastics. **Figure 3** shows these three structural elements.

The test methods that were used to characterize the PA hot-melt adhesives are given in **Table I**.

Polymer blends based on PA

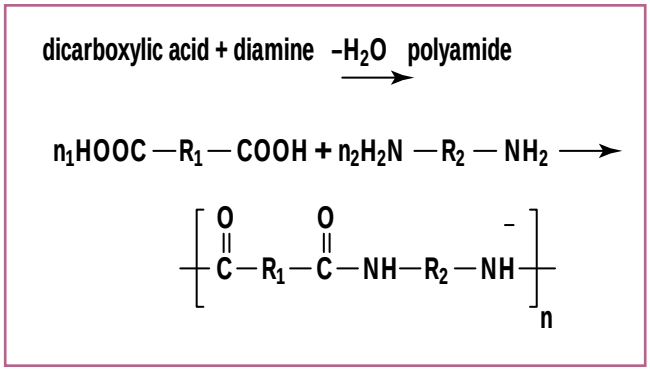
Limitations in the adhesion properties of PA hot melts make it necessary to combine this base with other polymers. Our main resins have dimerized fatty acid PAs. Blending of these resins with other resins and materials has produced a new generation of adhesives that show good adhesion to problematic substrates. For example, it is possible to bond X-ray-crosslinked polyethylene without any pretreatment. The new hot melts also show good adhesion to metals.

The utility of PA-based hot melts is illustrated in the following section with an example from the cable industry *(3)*, where changes in materials and production technology prompted development of new adhesives.

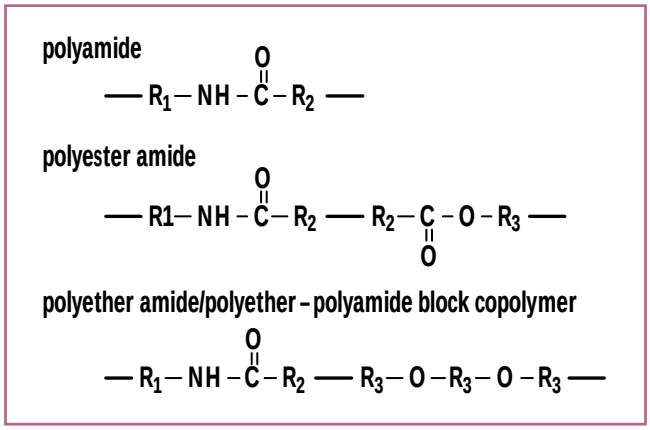
Products for coating heat-shrink articles. When a telecommunications cable is spliced to provide a new line to a customer, the splice has to be sealed to prevent moisture from penetrating. There are many techniques for splice repair, including the use of so-called heat-shrink articles.

A heat-shrink article is made of polyethylene, which is then crosslinked, expanded, corona-treated, coated with an adhesive, and frozen. When the polyethylene is reheated, it shrinks to its normal dimensions (memory effect) to form a tight seal. **Figure 4** shows three types of heat-shrink articles: wraparound sleeves, end caps, and tubes.

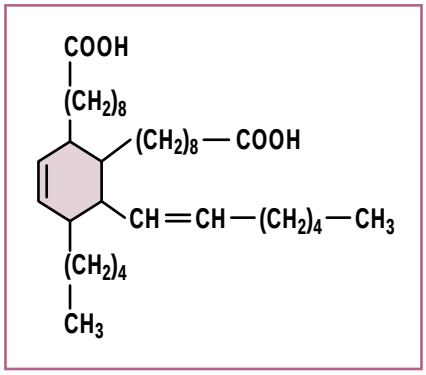
Wraparounds are used to seal splices in telecommunications cable. When the polyethylene is reheated, the adhesive must have an excellent flow behavior so that it seals all small areas and fills the larger cavities. Adhesives are formulated to provide good adhesion to all of the exposed



1. Polyamide synthesis by polycondensation



3. Structural elements for polyamide adhesives



2. Dimerized fatty acid

Property	Measurement method
Softening point, °C	ASTM E 28, in glycerine
Viscosity, mPa·s	ASTM D 3236, system RVT, spindle 27
Temperature creep resistance, °C	Henkel test instruction SKE 10-05
Low-temperature flexibility, °C	Henkel test instruction SKE 10-04 (similar to ASTM D 3111)
T-peel strength, N/cm	DIN 53282 and DIN 53539 C*

*Specimen width 25 mm, crosshead speed 50 mm/min

1. Test methods

cable components within the application's temperature range, typically 110–160°C. In the case of thermoplastic polyethylene, the cable insulation material is flame-pretreated to obtain good adhesion.

The characteristics of three hot melts designed for different heat-shrink applications are given in **Table II**.

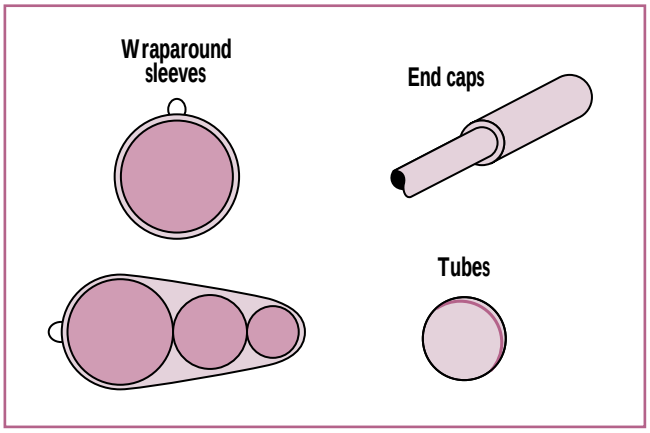
Coextrusion technology. The technique for producing heat-shrink articles has changed tremendously in recent years. In the original method of production, the polyethylene substrate was crosslinked, expanded, and corona-treated. The tube was then coated with adhesive. The length of heat-shrink tubes produced using this technique was limited to about 1 m. The current technique provides greater flexibility by allowing continuous production of coated heat-shrink tubes. Adhesive coating is applied immediately after extrusion of the polyethylene tube, in essence a coextrusion of tube and adhesive. The coextruded tube is then crosslinked and expanded to the desired size, as seen in **Fig. 5**.

Clearly, this production technique created new demands for the adhesive coating. First, any adhesive designed for use in this application would have to show good adhesion to the freshly extruded, untreated polyethylene substrate. Pretreatment is not possible. Furthermore, because the polyethylene is crosslinked after the coating with hot melt, the adhesive must be able to withstand the stresses imposed by the various crosslinking methods (e.g., electron beam or peroxide). An adhesive that also crosslinked at this point would be unsuitable.

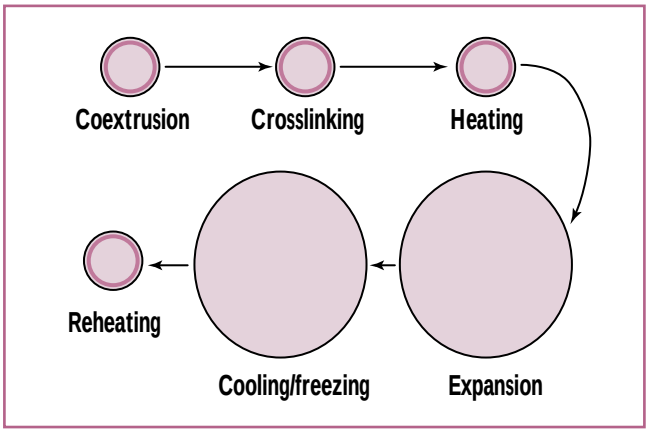
A crosslinked adhesive would have extremely high viscosity, which would show poor flow behavior in the end application and therefore would not form an adequate seal. Nevertheless, the adhesive's viscosity profile has to be adjusted to accommodate the new production technique. In this case, it generally means that the viscosity is significantly higher than for normal hot-melt systems. The flow behavior is extremely important in achieving a constant, uniform thickness of the adhesive layer. The layer of coated adhesive must be uniformly distributed, and it must maintain the same thickness before and after the crosslinking of the tube. If it does not, the heat-shrink tube will fail.

Table III compares the adhesive requirements for conventional heat-shrink articles and those produced using the new coextrusion technology. **Table IV** shows the properties of four PA adhesives designed for coextrusion applications.

Products for pressurized systems. Overpressurization of telecommunication cables is a new technique for detecting leakage. The hot-melt adhesive must be able to bond, seal, and fill in a repaired splice while resisting the force applied during overpressurization of the cable.



4. Heat-shrink articles



5. Coextrusion of polyethylene heat-shrink tubes and polyamide adhesive

Products with very good adhesion at room temperature and higher are necessary.

Figure 6 shows T-peel values over the range 20–70°C for the newly developed adhesives that are being used in cable-splicing applications. **Table V** shows other important properties of this new generation of adhesives. **Figure 7** shows the relationship between temperature creep resistance and viscosity for ten predescribed PA-based adhesives. Clearly, the viscosity and the temperature creep resistance of the new generation of PA-based adhesives (SKE-8–10) have improved.

The products discussed here were developed specifically for heat-shrink articles in the cable industry. However, there are many other product-assembly applications where such adhesives should prove useful.

Property	ADHESIVES SKE-1	SKE-2	SKE-3
Field of application	Tubes	End caps	Wraparound sleeves
Softening point, °C	86	140	100
Viscosity at 160°C, mPa·s	11,000	35,000	30,000
Low-temperature flexibility, °C	–25	–30	–30
Temperature creep resistance, °C	60	90	85
T-peel strength, N/cm			
PE-X–PE-X at 20°C	90	110	90
PE-X–PE-X at 60°C	…	20	16

II. Polyamide hot melts for heat-shrink articles

	Conventional	Coextrusion
Bonding	Polyethylene substrate pretreated to enhance bond with adhesive	Adhesive must bond to untreated polyethylene
Crosslinking	Adhesive not resistant to crosslinking treatment	Adhesive must resist crosslinking treatment
Profile expansion	Tube expanded before adhesive application	Tube expanded after adhesive application
Viscosity	Normal viscosity range	High viscosity to achieve constant thickness

III. Comparison of polyamide-adhesive properties for conventionally produced heat-shrink tubes and for coextrusion of heat-shrink tubes and adhesive

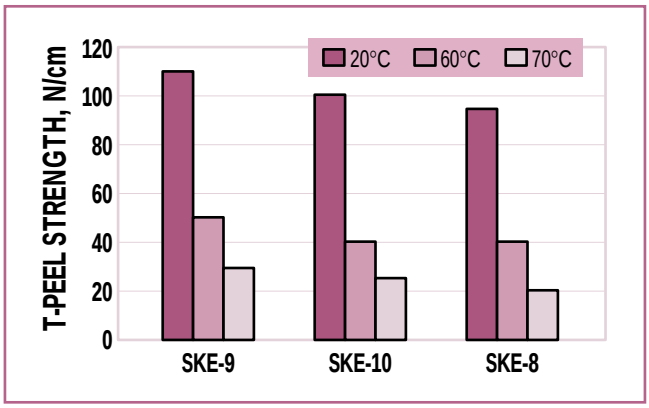
NEW PP HOT MELTS

PP chemistry and characterization

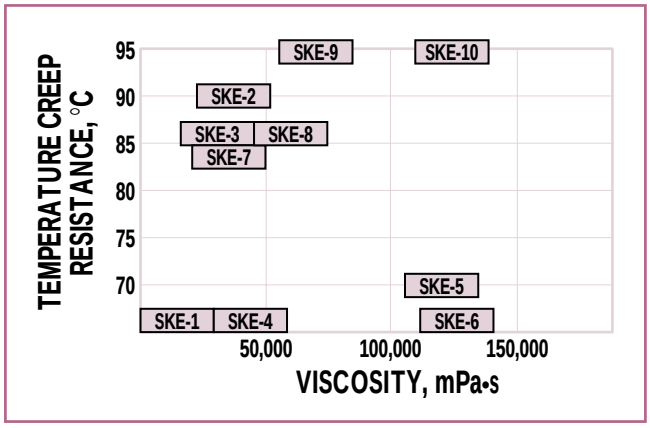
Polymerization of propylene yields either an atactic or an isotactic conformation of PP, depending on the catalyst used. Isotactic PP shows good mechanical and chemical properties and maintains them at higher temperatures. At lower temperatures, this material shows poor low-temperature flexibility and impact strength. Atactic PP in low-molecular-weight versions has very good adhesion properties and low-temperature flexibility. At higher temperatures, this material softens dramatically and loses all mechanical properties. The limitations in adhesive properties of hot melts are obvious.

Polymer blends based on PP: Advantages and disadvantages

Given the requirements for hot melts, it is necessary to develop polymer blends based on atactic PP. These hot-melt resins have good adhesion on different substrates and are especially suitable for bonding nonpolar substrates like polyethylene and (of course) PP without any pretreatment. The new generation of products provides many advantages over traditional atactic PP-based hot melts. Recently developed hot melts show low-temperature flexibility, good impact strength at lower tem-



6. T-peel strength of three polyamide adhesives on polyethylene substrate at three levels of temperature



7. Temperature creep resistance vs. viscosity (at 100°C) for ten polyamide adhesives

Property	ADHESIVES SKE-4	SKE-5	SKE-6	SKE-7
Softening point, °C	95	110	101	126
Viscosity at 160°C, mPa·s	35,000	120,000	125,000	33,000
Low-temperature flexibility, °C	–5	–5	–5	–20
Temperature creep resistance, °C	60	70	65	85
T-peel strength, N/cm				
PE-X–PE-X at 20°C	90	110	70	60
PE-X–PE-X at 60°C	…	…	…	8
PVC–PVC at 20°C	…	…	…	45

IV. Polyamide hot melts for coextrusion with heat-shrink tubes

Property	ADHESIVES SKE-8	SKE-9	SKE-10
Field of application	Wraparound sleeves	Wraparound sleeves	Wraparound sleeves
Softening point, °C	100	114	117
Viscosity at 100°C, mPa·s	47,000	67,000	125,000
Low-temperature flexibility, °C	–20	–25	–25
Temperature creep resistance, °C	85	95	95
T-peel strength, N/cm			
PE-X–PE-X at 20°C	95	>110	100
PE-X–PE-X at 60°C	40	50	40
PE-X–PE-X at 70°C	20	30	25

V. Polyamide hot melts for pressurized systems

KEYWORDS

Addition polymers, adhesives, bonding strength, cables, hot melts, mechanical properties, physical properties, polyamides, polycondensates, polyhydrocarbons, polyolefins, polypropylene, properties, thermoplastics.

peratures, and high-temperature creep resistance. **Table VI** shows the main characteristics of five products. Their thermal and adhesion properties are illustrated in **Figs. 8 and 9**, respectively.

Products for general assembly

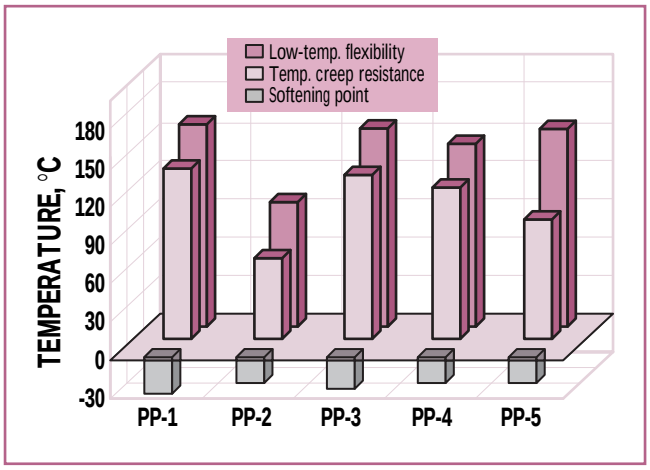
The newly developed PP-based products show excellent adhesion to polar substrates in consideration to the chemical base. There are many potential applications for these adhesives in energy and telecommunications cables or in the electronics industry. Because of the nature of PP, these resins also provide good chemical resistance against water-based systems. **Table VII** shows the chemical properties of these materials. Clearly, these products would be suitable for use in assembling materials that come into direct contact with acids and bases.

These products are also qualified for use in pipe constructions, especially PP–PE multilayer pipes in heating or wastewater equipment. **Table VIII** shows the range of substrates that can be bonded with these adhesives during general assembly.

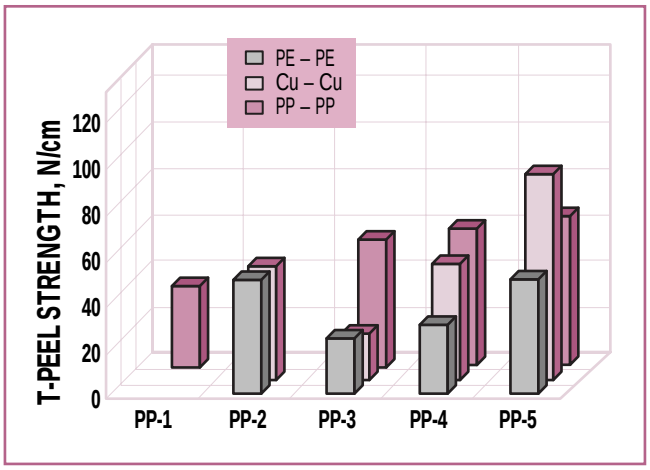
CONCLUSION

New polymeric materials are continually being introduced to the market. The task of adhesives suppliers will be to develop high-performance hot melts to bond these new materials.

One of the recent challenges was to develop adhesives that can bond polar and nonpolar substrates for a range of applications. The adhesives described in this paper were developed using polyamide resin or polypropylene resin as the base materials for new polymer blends. These new products can bond challenging substrates while maintaining excellent thermal and mechanical properties. Both systems have their



8. Thermal properties of five polypropylene adhesives



9. T-peel strength of five polypropylene adhesives on three substrates at 20°C

Property	ADHESIVES PP-1	PP-2	PP-3	PP-4	PP-5
Field of application	Furniture industry	Telecom. cable	Product assembly	Product assembly	Product assembly
Softening point, °C	158	97	158	142	155
Viscosity at 130°C, mPa·s	9,000	7,500	10,000	7,500	17,000
Low-temperature flexibility, °C	–30	–25	–25	–25	–25
Temperature creep resistance, °C	136	66	130	120	96
T-peel strength, N/cm					
PP–PP at 28°C	36	…	55	60	65
PE-X–PE-X at 20°C	…	50	25	30	50
Cu–Cu at 20°C	…	50	20	50	90

VI. Atactic polypropylene-based hot melts for general assembly

Property	ADHESIVES PP-1	PP-2	PP-3	PP-4	PP-5
Water absorption, %	0.06	0.1	0.1	0.1	0.06
WVTR*, g/m²·day	1.35	2.35	1.45	1.3	1.1
Resistance					
Alcohols	Excellent	Excellent	Excellent	Excellent	Excellent
Aliphatic CH	Fair	Poor	Good	Fair	Poor
Aromatic CH	Fair	Fair	Good	Fair	Poor
Ketones	Good	Very poor	Good	Poor	Poor
Weak acids	Excellent	Excellent	Excellent	Excellent	Excellent
Weak bases	Excellent	Excellent	Excellent	Excellent	Excellent

*Water vapor transmission rate

VII. Chemical properties of atactic polypropylene hot melts

Substrates	ADHESIVES PP-1	PP-2	PP-3	PP-4	PP-5
PP	X	…	X	X	X
PE	…	X	…	…	X
Wood	X	…	…	…	…
Copper	…	X	X	X	X
Aluminum	…	X	…	…	…
EPDM	…	X	X	X	X
Polyester	…	X	…	…	X

VIII. Atactic polypropylene hot melts for general assembly on selected substrates

advantages and disadvantages, and they need to be matched to appropriate applications. **TJ**

Heucher is a technical director at Henkel Corp., 5325 S. 9th Ave., La Grange, IL 60525. Butterbach is a senior development engineer with Henkel KGaA, D-40191 Düsseldorf, Germany.

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