UV-Curable Hotmelt Adhesives for Self-Adhesive Insulation Materials in Automotive Applications

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UV-curable pressure sensitive hotmelt adhesives (HMPSAs) have been successfully used for label, tape and self-adhesive insulation materials for several years.

Introduction

Although there is only a limited range of crosslinkable raw materials available, formulation of these materials has opened a wide range of new adhesives. Adhesive formulation is needed to tailor a product to specific application or customer requirements. Besides conventional formulation with non-reactive tackyfier resins, additional routes have been discovered.

The combination of UV-curable additives and tackyfier resins results in excellent adhesion and cohesion properties.

Compounding with UV-reactive additives result in changed viscosity and adhesion properties. In the presence of a UV-curable base resin, these additives do not require a further photoinitiator system and establish a covalent bond to the base polymer. The chemical bond between additive and base polymer results in low outgassing or fogging values.

The combination of UV-curable additives and tackyfier resins results in excellent adhesion and cohesion properties. A typical application area for such pressure sensitive adhesives is for self-adhesive insulation materials in the automotive industry.

This novel formulation technique adds another dimension to satisfy the market needs with UV-curable pressure sensitive adhesives and helps to further develop an environmentally safe adhesive technology.

Formulation Techniques

Today two polymer systems are the base for UV-curable pressure sensitive hotmelt adhesives:

- Acrylic polymers with a co-polymerized photoreactive group.
- Styrene-block-copolymers with free vinyl groups.

The acrylic systems available today already contain a photoreactive group polymerized into the acrylic backbone. Systems based on styrene-block-copolymers require an additional photoinitiator system.

From the adhesive formulators, the converters and the end-users point of view there is a multitude of differences, which are summarized in Table 1.

Table 1 shows that none of the technologies deliver superior performance in every aspect. UV-curable adhesives based on the

Table 1

Comparison of different polymer systems for UV-curable HMPSAs

Polymer base	Acrylic	Styrene-block-copolymer
Adhesion to polar surfaces	Very good	Moderate
Adhesion to non-polar surfaces	Moderate	Very good
Cohesive properties	Very good	Exceptional
Chemical resistance	Very good	Poor
UV light resistance	Very good	Poor
Odor (Photoinitiator)	Exceptional	Poor
Transparency	Exceptional	Moderate
Formulation window	Moderate	Very good
Reactivity of formulated systems	Very good	Exceptional

acrylic polymer have a higher significance in the market place than their styrene-block-copolymer counterparts. The following work will concentrate on the formulation of acrylic UV-curable materials.

Originally the idea of UV-curable acrylics was to make adhesive formulation (i.e., blending with resins and other additives) obsolete. The desired adhesion characteristics were to be controlled mainly with the applied UV dose. From the adhesives formulators view, this approach is only feasible in limited cases. Only the suitable formulation of acrylic base polymers can cope with demanding application requirements such as:

- Specific adhesion profiles on difficult surfaces (e.g., human skin).
- Complete removability from various substrates.
- Plasticizer resistance.
- Water vapor transmission.
- Water storage capability.
- Optical detectability (e.g., addition of optical brightener).

Adhesive formulation also leads to a wider curing window (range of applied UV energy without larger effect in adhesion/cohesion properties) than with the straight acrylic polymer. This gives the adhesive coater more freedom in selecting curing parameters.

Conventional formulation also has some drawbacks. After curing, almost all techniques lead to a crosslinked acrylic polymer with additives adsorbed like in a sponge (Figure 1).

Further side effects of conventionally formulated UV acrylics are reduced heat resistance and moderate fogging/outgassing performance.

The term fogging originates from the automotive industry and measures the amount of volatile, condensable substances emitting from car interior parts. A standard method is described in DIN 75201. Similar requirements for a low outgassing adhesive apply to the electronics and sensor industry (e.g., labels on computer disk drives).

The use of non-reactive formulation components dilutes the reactive polymer, which leads to a reduced reactivity of the UV-curable adhesive. The current level for formulation is around 30%. For technical and commercial reasons, a higher formulation level is desirable.

Novel Formulation Techniques

The search for raw materials suitable for blending with UV-curable

Figure 1

Additives not bonded to the polymer

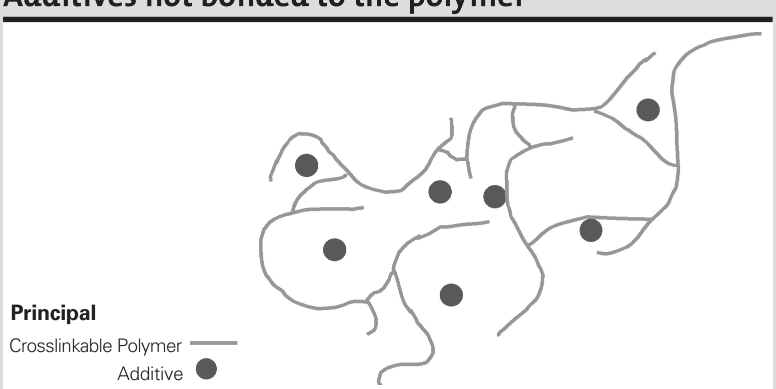
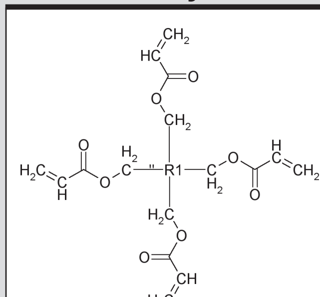


Figure 2

Tetrafunctional urethane acrylate



R1= Urethane oligomer

acrylics led us to a group of urethane, epoxy and polyester modified acrylates. These substances have a molecular weight of 100-1000 g/mol, are low-viscosity liquids at ambient temperature, show low-UV absorption (255 nm) and compared to acrylic monomers have a low odor.

A typical product is a commercially available tetrafunctional urethane acrylate (Figure 2) with a molecular weight of 1000 g/mol.

The mixture was able to polymerize under UV light without the addition of a photoinitiator. This is remarkable in so far as the neat urethane acrylate does not crosslink without a suitable photoinitiator.

Measurement of fogging values according to DIN 75201b, show the advantages of the new technique (Mixture 2) compared to traditional blends (Mixture 4). The fogging method displays two values: TML (Total Mass Loss) and VCM (Volatile Condensable Mass) (see Table 2).

The photoreactive groups in acResin act as photoinitiator and start the polymerization of the acrylate groups in the urethane acrylate. It is assumed that the urethane acrylate forms a covalent bond to the acrylic base polymer (Figure 3).

Comparing fogging values of the raw materials and the mixtures show that the use of these raw materials open a new direction for the formulation of UV-curable acrylics. Properties such as polarity and chemical resistance can be modified in a wide range.

The described new formulation techniques give promising opportunities to formulate UV-curable HMPSAs with optimized adhesion and cohesion characteristics. Table 3 shows the properties of two formulations, which support the above statement. Both products have a high peel adhesion at 176˚F, which is required for high-performance applications.

Table 2

Fogging values of different mixture

	Mixture 1	Mixture 2	Mixture 3	Mixture 4
acResin A 203 UV	100	85	0	85
Tetrafunctional urethane acrylate	0	15	100	0
Foral 85	0	0	0	15
Melt viscosity				
at 100°C (mPas)	165’000	75’000	<100	120’000
SAFT (°C)	110	133	25	80
Fogging-Values	0	0	0	0
TML (%)	0.0	0.0	3.1	1.0
VCM (%)	0.0	0.0	1.1	0.7

Coating weight: 50 g/m^2
Curing dose: 40 mJ/cm2 UV-C (250-260 nm)

The new formulation technique (patent pending) allows the preparation of low-viscosity, UV-curable acrylic hotmelt adhesives with 68-86˚F lower coating temperatures and excellent fogging values, and adds another possibility to develop adhesives with specialty properties.

Application Examples

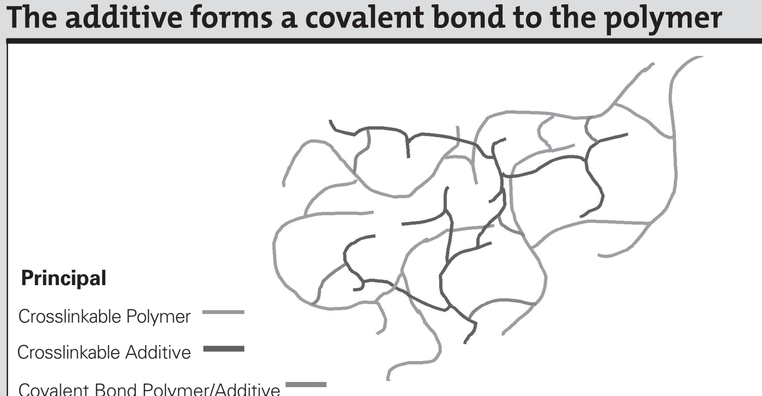
Low Fogging, Low Outgassing Adhesives

The following two application examples were possible to solve with the described new formulation technique.

For automotive interior applications the adhesives are tested for their fogging behavior. The emissions of an adhesive layer are observed for 16 hours at 212˚F. Condensable materials are collected on a 21˚C aluminium foil (Figure 4). Traditionally, formulated UV-curable hotmelts give poor results because the additives are not bonded to the polymer matrix. With the new formulation technique, it is possible to modify the adhesion profile without compromising the fogging performance negatively.

Figure 3

The additive forms a covalent bond to the polymer



High-Temperature Resistant PSAs

The new formulation technique is suitable for pressure sensitive adhesives, which are exposed to long-term high temperatures. A typical application area is for self-adhesive insulation materials (heat and sound) in the automotive industry.

The use of double-sided adhesive tapes or transfer coating of the actual insulation materials are typical methods (Figure 5).

Figure 4

Determination of fogging values (according to DIN 75201b)

Figure 5

Self-adhesive insulation material, UV-curable hotmelt adhesive

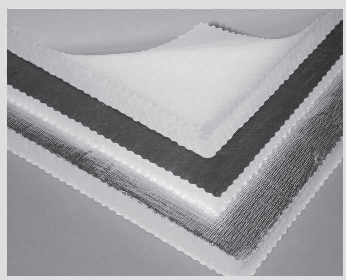


Table 3

Adhesive properties of UV-curable HMPSAs

Adhesive Formulations	A	B
UV-C dose (PowerMap) mJ/cm²	approx. 40	approx. 40
180°-Peel adhesion to stainless steel		
after 20 Min. N/25 mm	21	29
after 24 Hr. N/25 mm	27	28
180°-Peel adhesion to glass		
after 20 Min. N/25 mm	26	27
after 24 Hr. N/25 mm	26	26
180°-Peel adhesion to PE		
after 20 Min. N/25 mm	5	8
after 24 Hr. N/25 mm	7	11
180°-Peel adhesion to PP		
after 20 Min. N/25 mm	12	14
after 24 Hr. N/25 mm	13	18
180°-Peel adhesion to stainless steel		
at 80°C N/25 mm	7	7
180°-Shear Adhesion Failure Temperature (SAFT) 0, 5°C /min. 1000 g/25x25 mm Bonding time: 24 Hr.	>150	>150

Carrier material: Polyester 50 micron

Coating weight: 60 gsm

Outlook

The use of reactive additives in UV-curable acrylic hotmelt adhesives allows the reduction in processing viscosity without the need for a further photoinitiator system. Furthermore, an interesting set of adhesive properties have been found:

- Outstanding adhesion and cohesion properties.
- Excellent fogging behavior.

New combinations of materials together with innovative adhesive coating and curing technology help to further promote and establish UV-curable adhesive systems. ◗

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