Crosslinking the photoinitiator

Novel UV-crosslinkable PUR dispersions for pressure-sensitive adhesives.
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Photoreactive, water-based polyurethane dispersions are an effective way of making pressure-sensitive adhesives which have good physical properties. They are finding wide use in industry, particularly in medicine due to their compatibility with human skin. Polyurethanes have been known since approximately 70 years and are widely used in a broad range of applications. However, radiation curing polyurethane pressure-sensitive adhesive (PSA) water-based dispersions are a relatively new group of materials. Their industrial application has grown tremendously over the past decade. The growing success of UV crosslinking technologies in a wide variety of industrial products and processes can be attributed to their productivity and environmental benefits [1-2]. They are used in self-adhesive tapes, labels and protective films. They can also be found in applications such as footwear manufacture, packaging, plastics bonding as well as dermal and transdermal dosage systems for pharmaceutical applications and medical bioelectrodes.

The photoreactivity of polyurethanes
The UV-crosslinking of various photoreactive PUR coatings is based on the photoinitiation of free radical crosslinking reactions. The ultraviolet crosslinking technique calls for the use of a photoinitiator. This element is therefore one of the key components in UV-crosslinking. The outcome of such a polymerisation is highly dependent on the choice of the photoinitiator, its chemical nature and the concentration used. For PUR systems, two types of radical photoinitiators are currently available. The first class (type I) undergoes direct photofragmentation in the excited state into free radicals. Depending on the structure of the molecule, scission may occur in an α or β position relative to a carbonyl functionality. The second class (type II) undergoes a primary process of hydrogen atom abstraction from the environment (R-H), which may be the resin itself or a solvent, to produce a ketyl radical. The photoreductive ability of the environment is also an important factor and is related to the carbon-hydrogen bond strength of the species donating the hydrogen atom.

However, there is a very interesting new group of photoinitiators that is suitable for addition reactions. One side of the photoinitiator molecule is a conventional chemical group, which tends to addition reaction or reaction with carbonyl or hydroxyl groups of the polymer chain and of the other photoreactive side group (Figure 1). These photoinitiators are generally used in concentrations ranging from about 0.01 to 5.0% by weight of the total polymerisable composition.

Incorporating the photoinitiator
There are photosensitive PSAs where the photoinitiator suitable for addition reactions is incorporated into a UV-crosslinkable composition. This causes crosslinking of the adhesive with attendant improvement in cohesive strength. Examples of these photoinitiators are hydrogen abstraction with a benzophenone group (Figure 2). The transformation of the isocyanate group of a PUR PSA takes place after synthesis by an addition reaction without side products and leads to highly efficient pressure-sensitive adhesives with UV-crosslinking properties (Figure 3).

This group of additionable H-abstractors consists of saturated photoinitiators, which contain at least two photoreactive structures in the molecule and crosslink with the polymer chain of the PSA. In this way, it is possible to obtain migration-free photoinitiators by specific constructions, for example multifunctional benzophenones, xanthones, thioxanthones, antraquinones, fluorenones or benziles. Polyurethane polymer structures that crosslink directly under the influence of ultraviolet energy require special photosensitive groups that have additionable hydrogen abstractors incorporated into polymer backbone to make the chemistry and the synthesis process of these water-borne UV-crosslinkable polyurethane PSA; which represent a very novel type of self-adhesive sytems.

Balancing tack and peel strength vs shear strength
Three properties are useful in characterising the nature of PUR pressure-sensitive adhesives. They are tack, which measures the adhesive’s ability to adhere quickly, peel adhesion, which is its ability to resist removal by peeling, and shear- or cohesive strength, which is the ability to hold its position when shear forces are exerted. These properties depend on the type of monomers, the synthesis method, the addition of photoreactive components and particularly the type and quantity of the crosslinking agents used [3].

The balance between adhesive and cohesive characteristics is very important. With UV-curable polyurethane PSA, the ratio of tack and peel adhesion to shear strength can be varied within wide limits, by controlling the PUR-photoreactivity, UV-exposure time and amounts of radiant energy applied to the adhesive film after it has been coated [4-6]. The effect of the UV radiation dose (mJ/cm²) and UV-crosslinking time on the adhesive and cohesive properties is shown schematically in Figure 6 where all curves pass through a “curing window” within the same range of UV doses. This “curing window” represents the optimum conditions for crosslinking [5].

Test methods and results
The photoreactive polyurethane PSA dispersions with benzophenone photoinitiators suitable for addition reactions, in concentrations ranging from about 0.5 to 3.0 wt.%, were applied with a knife coater at 60 g/m² on a polyester film. After drying for 10 min at ca. 105°C, the adhesive was crosslinked for three minutes by UV light using about 500 mJ/cm². Figures 7-8 show the effect of UV-crosslinking of the adhesive on tack, peel adhesion and shear strength for the same crosslinking time of three minutes.

Figure 7 indicates that the best tack and peel adhesion performance are achieved with the benzophenone photoinitiators suitable for addition reactions at a concentration of about 1.0 wt.%. Increasing the level of photoinitiator incorporated into polymer backbone clearly leads to a deterioration of tack and peel adhesion.

As shown in Figure 8, the abstractor photoinitiator suitable for addition reactions also shows an adequate improvement in shear strength of crosslinked PSA acrylics at 20°C and 70°C. The relatively high cohesion was measured with about 3.0 4-chloro-4-propyleneiminecarbonyl benzophenone.

A future in medicine
It is clear that it is possible to make photoreactive UV-crosslinkable polyurethane solvent-free adhesive or...
polyurethane dispersions with attractive performance. These PUR solvent-free products are intended for high-end innovative ecological markets in the form of UV-powders or UV-hotmelts. Their inherent compatibility with human skin, as well as their non-aggressive adhesive properties makes photoreactive polyurethane solvent-free pressure-sensitive adhesives predestined for application in the medical field.

References

Results at a glance
- Photoreactive polyurethane pressure-sensitive adhesive water-based dispersions are a relatively new development in PUR adhesive technology
- The choice of the photoreactive components and particularly the type and quantity of the crosslinking agents is critical for good performance.
- A very interesting new group is photoinitiators suitable for addition reactions can be used at low concentrations to give good tack, peel adhesion and shear strength performance.
- An inherent compatibility with human skin and non-aggressive adhesive properties make photoreactive polyurethanes predestined for use in medical applications.

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Figure 1: Structure of saturated photoinitiators suitable for addition

Figure 2: Example for a photoinitiator tending to addition

Figure 3: Transformation of polymer backbone isocyanate groups with additionable photoinitiator

Figure 4: Polyurethane UV-crosslinking by using of additible H-abstractor photoinitiators

Figure 5: Synthesis of photoreactive polyurethane dispersions
Figure 6: Tack, peel adhesion and shear strength as a function of UV dose and UV-crosslinking time.

Figure 7: Tack versus amount of additionable benzophenone photoinitiator.

Figure 8: Shear strength versus amount of additionable benzophenone photoinitiator.