Non-emissive blocking agents

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The overall performance properties and ease of application make one-component polyurethane systems popular in the surface coatings industry. In conventional systems, the blocking agents tend to be released and can migrate out of the coating system. When this happens they do not contribute to crosslinking or film formation and could cause changes to the coating properties. A new, non-emissive blocking agent, cyclopentanone-2-carboxyethylster, combats these problems and has been shown to be effective in helping polyurethane systems to flexibilize epoxy resins.

One-component polyurethane systems (also sometimes called 1K-PUR systems) are particularly popular in the surface coatings industry because of their excellent overall performance properties and their ease of application. Such systems are based on blocked (poly)isocyanates. The mechanism of the reaction with polyols and amines is shown (Diagram 4).

As can be seen (Diagram 4), no components are released. The ring of the CPEE blocked isocyanate is opened and integrated into the network, forming an ester amide or amide. To the authors' knowledge, a comparable system has not been described before now.

This new development is presented with the aid of an application commonly encountered in practice.

Flexibilizing epoxy resins with reactive polyurethanes

Because of their outstanding mechanical resistance, thermal stability, mechanical strength and excellent adhesion to many substrates, epoxy resins have been used for many years as casting resins, anti-corrosion coatings and adhesives. Many epoxy resins can be cured at ambient temperatures with aliphatic or cycloaliphatic primary diamines are used as the curing agent.

Because of their relatively high viscosity, higher-molecular weight epoxy resins must normally be reduced with suitable solvents before they can be used for casting applications. On the other hand, solvent-free casting resins can be formulated using epoxy resins of low molecular weight. In most cases, however, they cannot be used in practice because of their extreme brittleness. With all applications in which solvent-free casting formulations are required and therefore epoxy resins of low molecular weight are used, the brittle epoxy-amine network must be flexibilized. In the field of floor coatings, low-solvent or solvent-free formulations are now the state of the art.

For around 30 years, reactive polyurethanes have been successfully used for the flexibilization of epoxy resins [2-7]. Compared to many other plasticizers available on the market, reactive polyurethanes are more effective and have a particularly long service life, as they are joined to the epoxy-amine network through covalent bonds.

Flexibilizing epoxy resins with reactive polyurethanes

Because of their good, long-lasting flexibilization, products of this type are still in widespread use. However, many substrates, epoxy resins have been used for many years as the blocking agent was introduced only recently. Their mechanical properties match those of the first generation products, but importantly, they also have a much lower viscosity, which can be a major advantage for application. These second generation products are also based on the mechanism described above (Equation 1).

Three generations of reactive polyurethane resins

In the first generation of reactive polyurethane, alkyl phenols such as nonylnaphthol act as the blocking agent.

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A new class of reactive polyurethanes in which polymerized phenols are used as the blocking agent was introduced only recently. Their mechanical properties match those of the first generation products, but importantly, they also have a much lower viscosity, which can be a major advantage for application. These second generation products are also based on the mechanism described above (Equation 1).

The third generation of reactive polyurethanes for the flexibilization of epoxy resins makes use of a completely new reaction mechanism [9]. As outlined (Diagram 4), the amine ring opening of the reactive polyurethane blocked with cyclopentanone-2-carboxyethylster leads to the formation of a diamide, which now provides the covalent link to the epoxy network. An overview of the products used is given (Table 1). As can be seen, rPUR 3 has by far the...
lowest viscosity.

Initially, however, it was unclear whether the hard segment formation necessary to achieve the desired hardness/toughness profile was possible with these polyamide structures. The reactive polyurethanes of the first and second generation form, under appropriate conditions, urea groups that have a marked tendency to hard segment formation. Selected mechanical data of the rPUR grades 1-3 in an amine-cured epoxy resin is shown (Figure 1) [10]. It can be seen from this that the attained elongation at break, tensile stress at break and tear propagation resistance are definitely comparable. It can therefore be assumed that the blocked reactive polyurethanes that do not release any secondary components also have an adequate degree of hard/soft segmentation.

Use of modern polyethers

In recent years, special polyethers with an extremely low level of unsaturation and thus a significantly reduced content of monohols have become increasingly established on the market. Unlike traditional polyethers, for the production of which a base - generally KOH - serves as a catalyst, these polyethers are manufactured using special catalysts and IMPACT technology. Whereas the presence of a base (KOH) for the isomerization of propylene oxide can lead to the formation of allyl alcohol, which triggers the growth of a polyether chain with an unsaturated state at one end and ultimately, in the case of bifunctional starters, produces monohols, this secondary reaction can be effectively avoided by using IMPACT technology.

Especially with higher molecular weights, the deviation from the theoretical functionality can then be very considerable. Since it is important that the reactive polyurethane reacts as completely as possible with the epoxide-amine network, these low-monoiol polyethers were used for the second- and third-generation reactive polyurethanes.

In addition to introducing new blocking agents, viscosities were optimized through selection of the most suitable polyethers.

As can be seen from Figure 2, both the blocked polyurethanes with a low molecular weight (MW) and those with a high MW have a rather high viscosity, which is undesirable in most applications. Interestingly, the viscosity curve is U-shaped, with a minimum at moderate molecular weights. This 'U shape' evidently results from two counteracting factors: a high concentration of hydrogen bridges in the case of polyethers with a low MW (high content of blocked NCO), and increasing viscosity with rising MW.

The curve for the phenol-blocked polyurethanes followed a pattern similar to that for the CPEE-blocked polyurethane-thanes, but the viscosity of the latter was on the whole much lower [11].

References

[10] The mechanical data were obtained with a casting resin formulated from the relevant polyurethane resin rPUR 1-3 and a conventional epoxy resin ('DER 358') in the weight ratio 1:1, cured with bis(aminomethyl)cyclohexylamine. Curing accelerator, antifoam and oleic acid were also added.

Results at a glance

A completely new blocking agent for (poly)isocyanates, cyclopentanone-2-carboxyethylster (CPEE), has been developed that can react according to a completely new mechanism with hydroxyl groups in polyols at elevated temperatures or with amines at ambient temperature.

The blocking agent is not released, which means that the properties of a coating cannot change through the possible loss of the blocking agent during application or in use.

This new blocking agent has been demonstrated for use in reactive polyurethanes for the flexibilization of epoxy resins, where good mechanical properties and very low prepolymer viscosity were observed. However, a wide range of other new applications in the field of one-component polyurethane systems are possible.

Bayer MaterialScience is among the exhibitors at the ECS 2005 in Nuremberg: Visit hall 4, stand 147.

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Figure 1: Mechanical properties of various reactive polyurethanes in amine-cured epoxy resins
Figure 2: ‘U-curve’ for the viscosity of reactive polyurethanes, blocked with polymerized phenols (blue) and cyclopentanone-2-carboxyethylester (yellow)
Equation 1: Reaction of a blocked polyurethane with a diamine
Diagram 1: Blocking and crosslinking of polyisocyanates
Diagram 2: Blocking agents for isocyanates

caprolactam butanone oxime Dimethyl pyrazole (DMP) N-t-butyl-N-benzylamine malonic acid diethylster
Diagram 3: Blocking of an isocyanate with cyclopentanone-2-carboxylester (CPEE)
Diagram 4: Crosslinking of a CPEE-blocked isocyanate with an amine to form a polyamide
### Table 1: Characteristic data of reactive polyurethanes

<table>
<thead>
<tr>
<th>Name</th>
<th>rPUR 1</th>
<th>rPUR 2</th>
<th>rPUR 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blocking agent</td>
<td>Alkylphenol</td>
<td>Polymerized phenol, nonylphenol-free</td>
<td>Blocked without release of any components</td>
</tr>
<tr>
<td>Blocked NCO content</td>
<td>~ 2.5 %</td>
<td>~ 2.5 %</td>
<td>~ 3.0 %</td>
</tr>
<tr>
<td>Viscosity/23 °C</td>
<td>~ 100,000 mPas</td>
<td>~ 65,000 mPas</td>
<td>~ 24,000 mPas</td>
</tr>
</tbody>
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