New silane-modified polymers

Flexible design for adhesives and sealants

New silane-modified polymers with a polymer backbone of flexible design allow formulation of adhesives and sealants with many improved properties. What distinguishes the new class of silane-modified polymers from conventional SPUR/SPE polymers, and what application possibilities do they offer?

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The application spectrum of silane-modified polymers has broadened considerably over the years. Classic applications include sealing compounds for building façade joints and all-purpose adhesives for assembly applications. Due to their excellent performance, however, such polymers are increasingly being used also for more sophisticated adhesive and sealing tasks, such as plastic-metal adhesion in transportation, and for efficient implementation of eco-friendly construction methods.

If the resulting, highly diverse, requirements are to be met, the raw material base offered must be as flexible as possible. And it is not only the technical requirements that are important: End users and formulators are also insisting on ecologically safe products that protect people and the environment. All of these requirements are addressed by the new class of silane-modified polymers described in this article.

Issue 03/2011 of adhäsion reported on a new class of silane-modified polymers (NEW-SPs) that, thanks to a very large degree of design freedom in the polymer, allows expansion of the property profile of the resulting binders. These differ in three important points from the technology of the commercially available silane-terminated polyethers (SPEs) or silane-terminated urethanes (SPURs) (Figures 1 and 2).

Distinctive features

In contrast to SPUR/SPE polymers, the polymer backbone of the NEW-SPs is not mainly restricted to pure PPG structures. In a departure from the simple PPG backbone, NEW-SP technology also allows the use of other base structures: For example, polyesters, polycarbonates, polycaprolactones, and a very wide

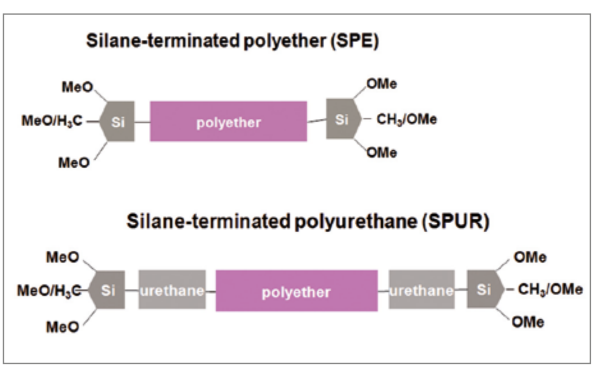

Figure 1: Schematic of commercially available silane-terminated polymers

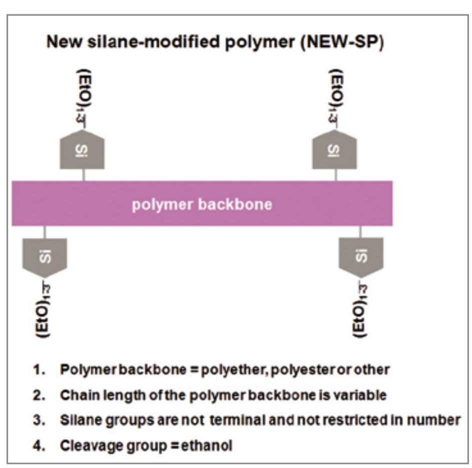

Figure 2: Schematic of the novel silane-modified polymer (NEW-SP)

range of monomers can be used in the products. These products are referred to below as NEW-SP hybrids. In the production processes of commercially available products, the use of structures of a type different from PPG is often very difficult because the products cannot be manufactured reproducibly and cost effectively, due to high viscosities. In the new production process for NEW-SPs, virtually any desired polymer backbone can be produced by DMC catalysis, that is, the corresponding additional monomers are also incorporated and distributed during the reaction; the overall viscosity of the NEW-SPs is therefore lower in direct comparison with comparable SPEs/SPURs.

Another feature distinguishing the NEW-SPs from SPE/SPUR polymers is the crosslinking density. SPE/SPUR products, for example, have exclusively terminal silane groups, which can result in a lower crosslinking density and thus lead to plastic flow. In the new class of NEW-SP products the crosslinking density of the polymers can be controlled because the corresponding silane groups are not, or not exclusively, incorporated terminally but, in particular, laterally, so that a larger number of the crosslinking functional groups can be distributed over the polymer backbone.

In the SPEs, the molecular weight of the polymer is defined by the polyether used. In certain SPUR technologies, the molecular weight can be adjusted within certain limits; however, this technology quickly comes up against viscosity limitations, due to an already relatively high density of urethane linkages. NEW-SPs can encompass a wide range of low-molecular to high-molecular structures without any problem.

NEW-SP polymers can be so designed that during crosslinking they evaporate ethanol only instead of the hazardous methanol usually released by SPEs/SPURs. The curing rates of the NEW-SPs are nonetheless comparable with those of commercially available SPE/SPUR technologies.

The advantages of the new molecular design

The advantages arising from this molecular design for the NEW-SPs are improved elastic recovery and better through-cure, even in deep layers or for bonding of large surface areas. Moreover, improved adhesion to a very wide variety of substrates is achieved by adaptation of the polymer backbone, for example by adjusting its polarity and crystallinity.

These properties allow the use of polymers in applications that were previously addressed only with difficulty. Examples of application of NEW-SPs in the construction and transport industries are given below.

More than just a joint sealant

For building applications, the first thing that usually comes to mind in connection with sealing compounds is a product for expansion or sanitary joints. But building applications also extend to many other fields of use with highly demanding adhesive requirements. Particularly in eco-friendly construction, a range of highly diverse application possibilities opens up for NEW-SPs.

Wood bonding, for example, is becoming increasingly important. But the requirements on a good wood adhesive are extremely high. An adhesive bond must resist immersion in both cold and boiling water in order to receive approval for certain applications. In particular, the technologies based on silane-terminated products that are available today do not easily pass the highly demanding D3 and D4 tests of DIN EN 204 and WATT 91. There is often significant reduction in polymer strength after water immersion, and in some cases very severe embrittlement of the materials as a result of post-crosslinking. Such products are not suitable for withstanding the constant loads imposed in application. But products based on silane-modified polymers are nevertheless in demand, particularly in the area of wood adhesives, because they allow to work with an eco-friendly technology that avoids formaldehyde, isocyanate etc. Products formulated on the basis of NEW-SPs have shown improved stability in direct comparison with SPURs and SPEs. Loss of strength in boiling water tests and after cold-water immersion is

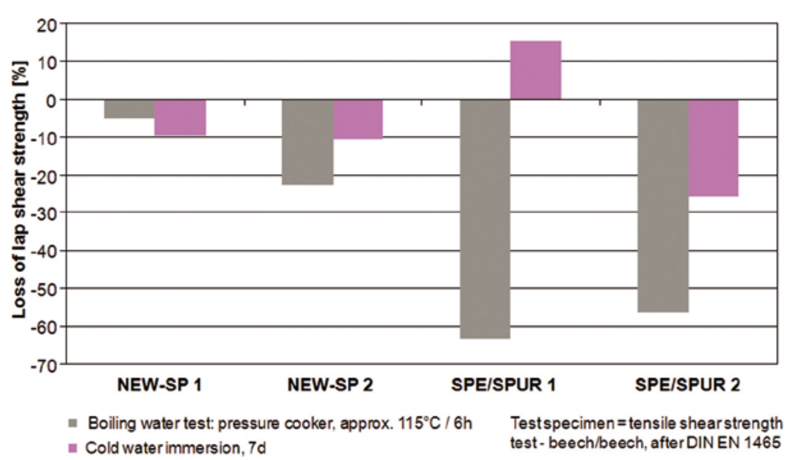

Figure 3: Loss of lap shear strength in flexible sealing adhesives after immersion in boiling and cold water

significantly lower in NEW-SP polymers than in commercially available SPUR/SPE formulations (Figure 3).

A further example of a building application is the production and assembly of sandwich elements. These are increasingly being used for energy-saving construction in new buildings, but also for building restoration. As in the case of the wood adhesives described above, great importance is given here to eco-friendly and resistant products. For production of sandwich elements, and also for their assembly, a high initial tack is also required, combined with high requirements on the storage stabilities of the adhesives used. The NEW-SP hybrids described before can offer particularly suitable product solutions here, with initial tack exceeding 200 kg/m² on mineral substrates.

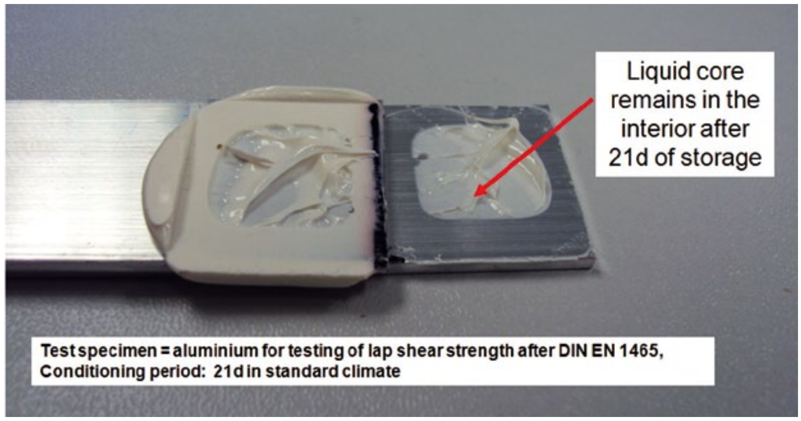

Figure 4: Example of a SPUR/SPE-based formulation for flexible bonding with incomplete cure.

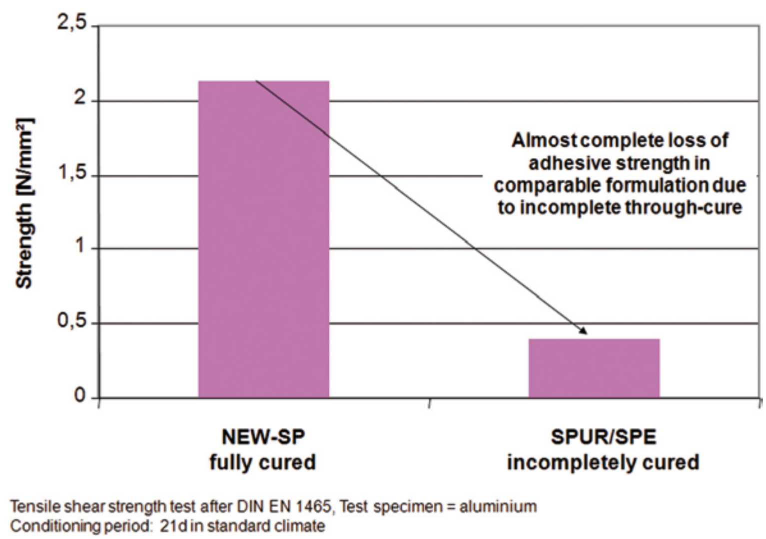

Figure 5: Loss of strength in lap shear specimens due to incompletely cured material

High strength combined with flexibility

In the area of transport, mechanical fastening methods are increasingly being replaced by adhesive bonds. It is advanced adhesive technology that makes it possible in the first place to bond various plastic components efficiently to metal components without causing significant damage to the material. One hybrid class of the NEW-SPs is, due to its modification, particularly suitable for bonding of polar, oxidic substrates. In direct comparison, the NEW-SPs achieved two to three times the adhesive strength of comparable SPE/ SPUR formulations.

In the area of assembly and industrial assembly, bonding of large areas may be required; in such cases it must be strictly ensured that the adhesive cures completely in order to achieve maximum performance (Figure 5). Single-component moisture-curable systems often show weaknesses here (Figure 4), which is why the curing of many bonds stops, or heavily slows down, beyond a certain depth. The NEW-SPs have the advantage here of complete through-curing even if, as in bonding of large surface areas, only small areas of the adhesive come into contact with atmospheric moisture. This avoids the need for the commonly required pre-treatment of the substrate with moisture, and thus eliminates one step in the process. Moreover, the silane-modified polymers allow efficient bonding of closed, plane substrates, for which pre-treatment with moisture is not possible.

Outlook

Particularly for assembly, bonds with high strength of between 6 and 10 MPa are required. Currently, such applications often use PUR systems or high filler loaded SPE/SPURs. The high strength desired could hardly be achieved with a polyether backbone alone. Even SPURs containing a high proportion of urethane groups can attain these values only with difficulty in comparison with PUR systems. Any attempt to satisfy such strength requirements by using higher

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quality functional fillers results in marked decrease of elasticities and relatively poor extrudability.

The missing polymer interactions, particularly in SPEs, that hinder strength development can easily be produced in the NEW-SP hybrid structures by incorporation of co-monomers or of polymer segments different from PPG. The NEW-SP hybrid structures thus open up new fields of application in the area of semi-structural adhesives where high strengths are required.

The unique product variety of the NEW-SPs makes it possible to produce eco-friendly products as well as to master technologically demanding problems. The class of novel silane-modified polymers allows innovative formulations of adhesives and sealants and thus opens up a wide range of system solutions. ■

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