Novel binders for sealants and adhesives, based on silane-modified polymers with lateral silane groups

This article presents a new class of silane-modified polymers with lateral silane groups, designated below as NEW-SPs. Novel technical aspects of the polymers and their advantages in various applications are described. NEW-SPs differ significantly in their production process from all the silane-terminated polymers so far available on the market.

1. Introduction

Most polymers on the market are produced from high-molecular weight polyethers, which are reacted with silane groups after an allylation reaction (to give MS polymers or SPEs = silane-modified polyethers) or by using a urethane group, which is reacted with a silane (to give SPURs = silane-modified polyurethanes).

NEW-SPs do not require polyethers as a raw material base for synthesis of the polymer chain because the polymer backbone can have various and different polymeric or monomeric components of any kind, which in a further step can be reacted with one or more building blocks in a modified alkoxylation reaction. In the latter reaction, alkoxylation agents with lateral silyl groups can be used either on their own or mixed with alkoxylation agents not containing silyl groups. Thanks to the possibility of synthesising parts of the polymer backbone, or the entire polymer, during the reaction, a wide range of options is available for designing the polymer backbone, in contrast to pure PPG (polypropylene glycol) structures (fig. 1).

The resulting variability of the polymer backbone can be used to increase strength, adhesion power, and initial tack. Modification with lateral silane groups accounts for the improved elastic recovery, higher degree of through-cure, and greater stability of the polymers.

To allow a better description of the properties of the new silane-modified polymers, systematic studies have been carried out on appropriate structures. The aim of these investigations was to establish structure-effect relationships and thus to be able to describe better the advantages of the NEW-SPs. In the initial basic investigations, three characteristics were found that distinguish the NEW-SPs from commercially available products:

1. Improved elastic recovery for high resilience requirements,
2. a higher degree of through-cure for deeper joints or area bonding, and
3. improved resistance to cold and boiling water for longer life-cycles of sealants and adhesives.

Tab. 1: Basic formulation for NEW-SPs

<table>
<thead>
<tr>
<th>Component</th>
<th>Fraction / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silane-modified polymer</td>
<td>20 – 25</td>
</tr>
<tr>
<td>Filler</td>
<td>45 – 55</td>
</tr>
<tr>
<td>Plasticiser</td>
<td>12 – 18</td>
</tr>
<tr>
<td>VTMO</td>
<td>1 – 3</td>
</tr>
<tr>
<td>Adhesion promoter</td>
<td>1 – 3</td>
</tr>
<tr>
<td>TiO₂/pigments</td>
<td>ca. 0.5</td>
</tr>
<tr>
<td>Thixotropic agent</td>
<td>1 – 3</td>
</tr>
<tr>
<td>Stabiliser</td>
<td>ca. 1.5</td>
</tr>
<tr>
<td>Curing catalyst</td>
<td>0.1 – 0.4</td>
</tr>
</tbody>
</table>

2. Elastic recovery and the resulting resilience

Various molecular weights and numbers of crosslinking points were investigated to find the optimal product design for sealants and flexible adhesives. For good mechanical properties, it is essential to set an adequate length between individual crosslinking points so as to achieve the maximum possible elongation of the polymer. In addition to allowing...
interaction between the individual polymer chains, however, the crosslinking points are needed also for development of tensile strength. It is therefore absolutely necessary to set the correct crosslinking density to attain the optimum balance between elongation and tensile strength. The basic formulations in Table 1 were used for the evaluation.

Figure 2 shows a low-modulus polymer with a decreasing number of crosslinking points from P1 to P4. With a reduction in the number of crosslinking points, and thus an increasing distance between them, the elongation is seen to increase. In contrast, the tensile strength increases from P4 to P2. However, a further increase in the number of crosslinking points to P1 produces a reduction in tensile strength. This behaviour is observed in the base polymer over a molecular weight range of 12,000 – 20,000 g/mol. The optimal concentration of crosslinking units lies in the range of 3.7 – 6.5 % of crosslinking units per base molecule. All of the crosslinking units in the molecule may be bi- or tri-functional.

If the proportion of crosslinking points is reduced, good elongation is obtained, as is seen in product P4; however, the product is not completely cured, as is indicated by its decreasing tensile strength. A formulation with a polymer of this type is expected to show plastic behaviour with poor resilience properties. For good elastic recovery, and the good resilience that results from this, optimal formation of a polymer network is required, with a not excessively high proportion of free ends (i.e., those not integrated into the polymer). Polymer types such as the P2 and P3 polymers are particularly suitable for formulation of elastic sealants of high resilience. High resilience and good elastic recovery are required, for example, for sealants in the construction sector and for glazing applications that must satisfy the requirements of ISO 11600-F-25LM or ISO 11600-F-25HM. With current sealants based on silane-terminated polymers, problems often arise in attaining the necessary resilience. Figure 3 is a compilation of commercially available formulations based on silicone-terminated products.

In some cases the listed products clearly show plastic flow even for small elongations, as can be seen from the non-linearity of the plot. If plastic flow already occurs for small elongations, the resilience of a sealant is not adequate for challenging applications in construction or for glazing applications. For a sealant to satisfy the requirements of, for example, ISO 11600-F-25LM, the tensile modulus (modulus at 100 % elongation) must be <0.4 N/mm² with a resilience of >70 % being achieved simultaneously. Products like construction sealant I shown in Figure 3 only barely attain these values.

Figure 4 shows formulations based on NEW-SPs. Here the plot is clearly closer to linear in the range of elongation up to 100 %, and a higher elastic behaviour is therefore present. This ensures that adequately high resilience can be achieved. Due to their higher elastic recovery, however, products based on the NEW-SP technology show lower elongation overall in direct comparison with commercially available products such as construction sealant I.

3. Through-cure behaviour of NEW-SPs

The NEW-SPs have crosslinking units that release ethanol during cure. In direct comparisons with commercially available polymers, however, their skin formation times are no higher. This is particularly true in relation to in-depth curing.

Unlike commercially available products, which release only methanol during crosslinking, NEW-SPs show complete in-depth curing. In current systems based on silane-terminated polymers, the rate of through-cure is reduced, beyond a depth of about 6 – 7 mm,
to almost zero, whereas a through-cure of 10 mm could be achieved with a NEW-SP in the same period. These measurements were performed on formulated polymers using Teflon wedges with an indentation of depth ranging from 1 – 10 mm. The formulation is filled into the wedge and the progress of the cure is recorded after 24 h in each case.

**Figure 5** shows the impact of incomplete curing on the adhesion performance of formulations. Comparable formulations based on SPUR/SPEs and NEW-SPs were measured. It is clearly seen here that the incomplete curing of the SPUR/SPE-based formulation results in an almost complete loss of tensile strength. The superior through-curing of the NEW-SPs is explained by the apparently better availability of crosslinking units due to their lateral disposition and statistical distribution in the NEW-SPs. An incomplete cure, as shown in **Figure 5**, means that area bonding may not be reliably used for assembly of large components. The through-cure behaviour of NEW-SP-based formulations could offer significant advantages here for assembly adhesives.

**4. Improved resistance in cold and boiling water immersion tests**

For the NEW-SP technology based on pure polyether structures, a fairly extensive series of tests was performed on behaviour during cold and boiling water immersion. The aim was basically to show whether the lateral arrangement of groups and the comparatively high proportion of crosslinking sites offer an advantage in resistance over the known SPUR/SPE systems. In various tests carried out in direct comparison with commercially available materials, a positive result was obtained (**fig. 6**).

In a direct comparison, NEW-SPs show significantly lower degradation of tensile strength than comparable commercially available SPE/SPUR materials. Cohesion failures occurred in all the products tested. It can therefore be deduced that a configuration with crosslinking points located mainly on side groups also leads to higher stability in tests with cold and boiling water. This strength degradation test is particularly relevant for applications in the area of wood bonding. At present polyurethane adhesives are often used for this purpose, but will most likely need to be replaced due to ecological requirements. Silane-modified products based on NEW-SP technology could provide an interesting alternative here.

**5. Outlook**

In addition to the above-mentioned product advantages of the NEW-SPs, applications are expected to be addressed in the future where strengths >6 MPa are required. This is expected to be achieved particularly through the use of polymer structures that differ from standard polyether structures of NEW-SPs. It has been possible to show in various basic investigations that the strengths of polymers and bonded joints could be doubled or even tripled. As new silane-modified polymers, NEW-SPs offer interesting advantages over currently available polymers. These products are very well suited for technically sophisticated sealing or bonded joints. Moreover, in the face of increasingly stringent regulatory requirements, NEW-SPs offer the possibility of tin- and plasticiser-free formulations; they are also free from isocyanate and methanol.

The technology will continue in the future to offer a wide range of application possibilities by exploiting the variability of molecule design. The addressing of markets in the adhesives sector to a greater extent than at present opens up additional possibilities in market development.