ELASTIFIED SILICATE RESINS AND POLYURETHANE FOAM RESINS FOR THE STABILISATION OF STRATA – A COMPARISON.

Abstract

Polyurethane foam resin grouts (PUR) have been established for decades as a very effective means for stabilising coal and strata in hard coal mining industry. Their acceptance in the construction industry, especially in tunnelling, is still growing. Their main advantages are their simple application, fast action and ability to stabilise rock formations under high stress and movement. On the other hand, they were criticised for their flammability and the material cost. But up to now, no other grout was able to replace polyurethanes. Several years ago, a new type of elastified silicate isocyanate resins was introduced (ESR). This paper tries to give a report on the properties and application experiences which have been collected in the meantime in comparison to polyurethane resins.

1. Introduction

In underground coal mining, modern highly mechanised long walls only can work effectively, when the shearer or plough can cut the coal along the complete face line, which nowadays often has a length of 300 m and more. Any unstable spot along this distance may cause a halt to production. So it is necessary to stabilise such critical zones, especially tectonic fault zones and the face entry i.e. the intersection between long wall and road.

Since long grouting has been a proven method for this goal. But cementitious grouts build up their strength too slowly in order to maintain a continuous production.

In the sixties, fast curing synthetic resins were tested in the German coal mining industry. In the first attempt, epoxy resins were used. Soon they were outperformed by polyurethane foam resins, characterised by much shorter setting times.

One of their outstanding features was the fact that they expanded their volume while being injected into the coal or strata thus giving an extra propagation into the crack system and (not to forget) saving material.

While polyurethane grouts were gaining acceptance in the seventies, at the beginning of the eighties so called organomineral or silicate isocyanate resins (SIR) were introduced.
In the most common variety, they set just as fast as PUR resins, but without foaming up which makes them more or less incompressible. Thus, they can not yield under load and due to their brittleness, they tend to break under load more readily, despite of their mechanical strength. In thin cracks, adhesive strength is acquired only slowly. Especially in the Soviet Union, they tried to use urea formaldehyde (or so called carbamide) resins as a cheap and better available substitute for PUR.\textsuperscript{6.5} They failed to be accepted mainly because UF resins normally are brittle and shrink with hardening. The release of irritant formaldehyde was another reason. A similar type of resin, i.e. non-foaming phenol formaldehyde (PF) resins, has been introduced recently into the French and German coal mining industry, as an injection grout. The problems with the phenol and formaldehyde release can be managed as well as the extreme acidity of the hardener component. Resins with improved elasticity are being tested. Since 1998, also silicate resins with increased elasticity ESR, are available. They differ in a lot of decisive properties from the established silicate resins, and are discussed as an alternative for PUR. In the meantime, sufficient application experience has been collected, to give recommendations for the use underground and to compare them with PU resins, mainly for the application in securing the coal and or strata.

2. Basic chemistry of the resins

The formation of polyurethane resins is well known: Polyols, i.e. compounds with at least two hydroxyl groups per molecule react with polymeric isocyanates, i.e. compounds with two and more isocyanate groups, to yield polyurethanes. The reaction with water, no matter if contained in the polyol as an ingredient or encountered in the injection site-yields a similar chemical variety, i.e. polyurea with carbon dioxide, which as a by product which causes the formation of a foam.

<table>
<thead>
<tr>
<th>PUR:</th>
<th>polyol + isocyanate $\rightarrow$ polyurethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUR, SIR:</td>
<td>water + 2 isocyanate $\rightarrow$ polyurea + carbondioxide</td>
</tr>
<tr>
<td>SIR:</td>
<td>3 isocyanate $\rightarrow$ isocyanurate (trimmer)</td>
</tr>
<tr>
<td>SIR:</td>
<td>aqueous sodiumsilicate + carbondioxide $\rightarrow$ siliciumdioxide + soda + water</td>
</tr>
</tbody>
</table>

Fig. 1 Basic chemical reactions

The chemistry of silicate isocyanate resins (SIR and ESR) is more complex. A part of the isocyanate undergoes the reaction with the water contained in the A component, an aqueous sodium silicate solution. With the non foaming SIR and ESR, the carbon dioxide is scavenged by sodium hydroxide forming soda and simultaneously causing the precipitation of silicon dioxide. The other part of the isocyanate reacts with each other yielding a polysisocyanurate. So both the silicate and the isocyanate form separate polymer networks, which penetrate each other, though. (Some Ukrainian authors, however, discuss the formation of a chemical bond between isocyanate and silicate).\textsuperscript{6.6}
The formation of a homogeneous product requires a very good mixing of the components in order to obtain an emulsion of the sodium silicate in the isocyanate component. ESR are more flexible than SIR by employing a modified isocyanate component.

3. Application criteria

In grouting applications, the resins are processed as follows:
A hole (Ø 10 – 43mm, l = 0.3 – 8m) is drilled into the structure to be treated and a packer is inserted. The two components of the grout are pumped separately to the site, merged in an effective static mixer and fed through the packer at 10 – 40 bar pressure into the strata thus penetrating the zone to be treated.

3.1 Viscosity

The prerequisite for a grout to be effective is a viscosity which is low enough to pump it over long distances and to allow the penetration of crack structure in the strata, i.e. both resin components as well as the grout mix shall have a low viscosity, which should be maintained until shortly before setting of the grout. In Germany, DMT – Mintec has introduced a test method to evaluate the penetration capacity.6,7

Two concrete slabs with 0,02 mm grooves on the surface are put on top of each other; the distance between them is adjusted by spacers. Through a hole in the lower plate, grout is pressed between them with a well defined force. The spread of the resin and the work needed to enter the space are recorded.

By this method, the minimal crack width can be determined which just can be penetrated by the grouting.
Furthermore, in our lab we have recorded the development of the grout viscosity with time in a plate/plate viscometer.
Fig. 3 & 4 Development of viscosity for Bevedol WF – Bevedan and Geoflex

a) Polyurethane.
The observation of a grout mix in a beaker shows that with polyurethane, the viscosity is low at the beginning: it even decreases a little bit by the heat of reaction. Only a few seconds before solidification, it rises dramatically and gels. During the measurement in the viscometer the temperature was kept constant, as it is the case when resin runs through small cracks. That is why the curing process and the development of viscosity is slowed down and less distinct than in the beaker. (see fig. 3)
The minimal crack width is quite low. Slow reacting polyurethane grouts can penetrate smaller cracks than fast reacting grouts at the same starting viscosity.

b) ESR
Mixing silicate resins in a beaker shows that the resulting emulsion has a higher viscosity than the individual components and that the viscosity consistently rises with time until the grout sets.
With shear, the viscosity decreases. With time, it increases (unfortunately due to inconsistent flow, it could not be recorded until setting of the grout). (see fig. 4)
The viscometer measurements show that the emulsion has a certain thixotropy. The determination of the minimal crack width reflects the high level of viscosity of the emulsion.

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>Unit</th>
<th>PUR Bevedol S19 - Bevedan</th>
<th>SIR Geodur OM</th>
<th>ESR Geoflex</th>
<th>PF Wilflex VP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity Comp. A</td>
<td>mPa s</td>
<td>310</td>
<td>250</td>
<td>280</td>
<td>220</td>
</tr>
<tr>
<td>Viscosity Comp. B</td>
<td>mPa s</td>
<td>200</td>
<td>200</td>
<td>150</td>
<td>20</td>
</tr>
<tr>
<td>Mix viscosity</td>
<td>mPa s</td>
<td>630</td>
<td>&gt;2000 (thix)</td>
<td>5000 (thix)</td>
<td>~100</td>
</tr>
<tr>
<td>Minimal crack width</td>
<td>mm</td>
<td>0.09</td>
<td>0.14</td>
<td>0.24</td>
<td>0.04</td>
</tr>
<tr>
<td>Adhesive bending strength, 0.5 h</td>
<td>MPa</td>
<td>1.3</td>
<td>0.8</td>
<td>5.0</td>
<td>0.9</td>
</tr>
<tr>
<td>7 d</td>
<td>MPa</td>
<td>3.3</td>
<td>6.6</td>
<td>4.5</td>
<td>&gt;2.3</td>
</tr>
<tr>
<td>Border Time</td>
<td>25 min</td>
<td>18 h</td>
<td>&lt;15 min</td>
<td>35 min</td>
<td></td>
</tr>
<tr>
<td>Deformation Work, 7 d</td>
<td>N mm</td>
<td>1600</td>
<td>&lt;10</td>
<td>300</td>
<td>50</td>
</tr>
<tr>
<td>$T_{\text{max}}$</td>
<td>°C</td>
<td>135</td>
<td>131</td>
<td>98</td>
<td>68</td>
</tr>
<tr>
<td>$T_{\text{max}}$ with 2% water</td>
<td>°C</td>
<td>167</td>
<td>&lt;131</td>
<td>&lt;98</td>
<td>&lt;68</td>
</tr>
</tbody>
</table>

Fig. 5 Basic properties of resins at 30°C except for viscosity (25°C)
c. Evaluation.
As to the penetration capacity, PUR resins have advantages over ESR, this is caused not only by the lower viscosity, but also by the foaming of PU resins which creates an additional pressure in the cracks and effects the so called self injection.
In some applications however, the thixotropy of ESR offers some advantages.

3.2. Mechanical Strength.

Normally, the compressive strength is regarded as the most decisive mechanical property. This may apply for consolidation grouting, i.e. for enforcing the statitical strength and rigidity of a structure. The objective of the grouting we are dealing with is to prevent the further deterioration of a defective geological structure which tends to relieve stress and there by loosen its integrity. This process can be halted by rendering or enhancing the shear and or tensile strength of the structure. Experience in coal mining has shown that another decisive characteristic for stabilising grouts is the yield capacity, i.e. even though movements in the strata occur which may exceed the shear strength, the structure must not break and thus fall apart, but retain its coherence in order to prevent further disintegration.
That means that grouts should have;
° a high adhesive shear and tensile strength
° the capability of retaining this strength even under movement
° a certain work capacity to absorb the energy of deformation.

Fig.6 Measurement of adhesive bending strength.

a. PU resins.
PU resins are regarded as the most established tool to fight these phenomena. They achieve a high adhesive strength, optionally within less than an hour, and even after releasing the maximum stress they still cohere with further displacement of the substrata. Evidence for this can be found by the adhesive strength measurements in a three point bending test, as it is established in the German coal mining industry.
A 160 x 40 x 40mm concrete block is split into two moieties, stored 24h at 30°C / 80% rel. humidity, then glued with the grout in 3mm thickness and again kept at 30°C/80 rel. humidity. Finally undergoing a three point bending test, according to EN 196, part 1.6, (see fig.6) Fig. 7 and 8 Development of adhesive bending strengths for Bevedol WF – Bevedan.

As can be seen from the figure for a well defined time spell PU grouts perform this test still retaining work capacity after passing the maximum strength as represented by the integral of the curve.

In German mining, an adhesive strength of 1 MPa is regarded as sufficient to keep the strata from disintegration. This so called border strength is reached after 20 min to 3 hrs, depending on the PU brand.

![Development of adhesive bending strength for Bevedol WF-Bevedan and Geoflex.](image)

3.3 Other Features.

For PU resins, on the other hand, foaming is the main reason for their yield capacity. This does not apply for silicate resins according to present experience.

Foaming is also a big advantage in the economy of grouting because, after all, it is a volume which has to be filled, a gap which has to be bridged, with the least use of material possible for economic reasons.

b. Silicate grouts.

For the established silicate isocyanate grouts, it used to be a problem to achieve this strength of 1 MPa in thin layers i.e. 3 mm. It took them 15 h and more. The final strength of 6 MPa is reached after 7 d. But even then, the adhesive bond breaks abruptly (brittle failure) and, consequently, the deformation work is low and actually below detectability.

With ESR, this situation could be improved considerably, the modulus is much lower, but still higher than with PUR foam. The bond still breaks in a brittle failure. The most amazing characteristic however is the fast acquisition of strength: with the first measurement, i.e. after 15 min., the final strength of approx., 4 MPa is reached!

This performance is also achieved in the field, provided the grout does not foam, which may happen under certain circumstances with inadequate product formulations, but not so with Geoflex.
But there are other features to be taken into consideration:
Recently, there has been a great concern on mine fires, with PU resins allegedly being responsible. ESR have a low curing temperature of less than 100°C. Their flammability is definitely less than PUR foams due to their high content of non combustible ingredients (more than 55%). (see fig.7 )
As to the occupational hygiene, both PUR and ESR have isocyanates as B component which may cause sensitisation with people having allergenic disposition. Whereas the PUR – A component is classified as harmless, sodium silicate is classified as corrosive for the use in mines, skin contact should be avoided. For other areas of application, it is only classified as irritant.

3.4. Phenolic resins.
Based on the concern for the high curing temperature of polyurethane resins and a possible risk of mine fires, the French coal mining industry has replaced polyurethane with non-foaming phenolic resins. Phenolic resin foams, as they are used for cavity filling and similar applications, are too brittle to provide an effective strata stabilisation. As to their mechanical properties evaluated in the lab, they show a performance similar to ESR. Their viscosity is lower. They can cure fast M mix at 70 – 80°C as a maximum but not as fast as ESR. Their final adhesive strength is good, with a brittle failure similar to ESR. The application experience is still limited, improved formula with higher flexibility are being tested.

4. Fields of Application
As can be derived from the reported findings as well as from underground experience, PUR is still the optimum solution for applications which require a medium or long term performance and yield capacity. Injection of mine roadways some 40m prior to the passing of the long wall and monitoring of the strata in the roof has shown, that with ESR the bond was over stressed and broken, whereas PU injected strata still was coherent.
ESR, on the other hand, is a good solution for grouting work in the long wall face or in its vicinity. The cracks are relatively wide and advantage can be taken of the extremely fast
strength increase and the low flammability. In some cases, the high elasticity of PUR can be a disadvantage, i.e. when zones have to be worked through after intermediate stabilisation. For these applications, ESR is the preferred solution.
Also other types of ESR have proven to be a useful tool, especially in sewer repair. CarboLith AS, e.g., is used for the repair of lateral junctions by injection with special repair robots. Slow reacting ESR, as e.g. CarboLith PL, can be used for impregnating fibre glass mats forming short inliners for sewers, or used as a mastic which can be trowelled in repair zones.
ESR with high thixotropy can be used for the fixing of bolts. The bolts are load bearing only a few minutes after installation.
The full range of ESR applications still has to be explored.

5. Conclusions

Elastified silicate-isocyanate resins (ESR)
- have a limited elasticity and work capacity.
- have an extremely fast build-up of strength (optionally)
- can be used as a trowellable mastic (optionally)
- have a low curing temperature and flammability.

They offer new options and several interesting applications. They are not a replacement for PUR in grouting operations, but represent an extension of the applications for resins grouts.

6. Literature

5. V.V. Vasilev, “Polymernye Kompozicii v gornom dele”, Moscow, 1986, p.57ff.