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How the strength and deformability of thixotropic resins depend on their structure and what is the true thixotropic behaviour of the mixture

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Abstract

Pumpable resins have already been used in various mining applications for a few decades. They were widely used in coal mining for stabilisation and consolidation of coal seams and surrounding strata, and from coal mining they found their way to civil construction and then into hard rock mining, mainly in connection with the latest development of bolting equipment. With a 'rapid development' program and increased productivity of mining equipment, industry was looking for fast-setting bolt grouts to be used with primary and secondary ground support systems. In the last five years, use of Newtonian-type resin grouts found their new application in the form of non-sagging, dense, yet easily pumpable resin pastes in combination with hollow core and self-drilling rockbolts or pre- and post-groutable cable bolts.

These dense, fast-setting, urea silicate resin paste grouts are generally known within industry as 'thixotropic resins'. Although being commonly called thixotropic, not all really behave as thixotropic materials. A misunderstanding with regards to the performance of these resins also exists, as it is just compared predominantly with uniaxial compressive strength (UCS) only.

Normet International Ltd, with the help of their research partner, spent a significant amount of time in past half decade to understand, research and develop truly thixotropic urea silicate resin grout by investigating the mechanical and chemical properties of the mix.

Although UCS values are still important, there are other properties of this resin mix which are actually more important than just UCS strength alone. Adhesiveness and plasticity/deformability without loss of strength is a more important parameter than just a high UCS number.

Understanding microscopic structure and being able to interpret that structure helped to develop high strength–high deformability yet high adhesive, truly thixotropic urea silicate resin grout.

Keywords: *thixotropy, organomineral, urea silicate, thixotropic resin bolt grout, deformability without loss of strength, adhesiveness*

1 Introduction

History of pumpable resin use in mining goes back to beginning of the 1960s. It was introduced and tested in RAG (German coal mining company) to improve efficiency of longwall mining. Firstly, to replace slow curing cementitious grouts, epoxy resins were tested for grouting of fault zones, face entries and intersections, but soon after, these epoxy grouts were outperformed by polyurethanes and polyurethane foams with much faster setting times and better penetration. Use of polyurethane resins was gaining popularity during the 1970s until the beginning of 1980s when organomineral – in other words, urea silicate resins – were introduced. Since then, use of polyurethane and urea silicate resins were fairly balanced and specific to application (i.e. ground consolidation, water sealing, water stopping, rockbolting etc.) (Cornely 2001).

Resins used for ground consolidation and water issues are of low viscosity, allowing easy flow-through fissures and cracks and therefore higher penetration at lower injection pressures. These resin hydraulic properties were utilised at RAG where they used long distance pumping of both polyurethanes, as well as silicate-type resins from central pumping stations to distances of up to 5,000 m (Sablotny 2012).

In civil construction and tunnelling, pumpable resins were mainly used for concrete crack repairs, water stopping and water sealing, and in hard rock mining for water stopping and water sealing and occasionally for ground consolidation.

Greater use in hard rock mining came with grouting of cable bolts. The set speed and the possibility of almost immediate pre-tensioning brought immediate safety benefits, which, thanks to increased productivity, had a positive effect on the economy of operation, even though the procurement costs of resins are several times higher compared to commonly used cement grouts.

With the development of new technologies and the introduction of a new type of bolting rigs, Boltec M and Boltec E by Epiroc using fast-setting pasty resins, pumpable resins are gaining new and wider applications in hard rock mining.

These pasty organomineral resins based on water glass and isocyanate are commonly referred to today as thixotropic, but not all of them actually behave that way.

2 Organomineral (thixotropic resin): urea silicate resins for bolting

The first study and description of the thixotropic behaviour of substances and mixtures comes from the end of the 1920s (Peterifi 1927).

We can find Freundlich's original 1935 definition of thixotropy in his book *Thixotropy*, which reads: 'Thixotropy refers to the property of concentrated gels that solidify in gels that they can be liquefied again into sol. Re-solidification reestablish behind stimuli temperatures and speeds.' (Freundlich 1935, p.3)

Another definition is also described in the Cheng & Evans (1965) paper on the phenomenological characterisation of inelastic thixotropic fluids. They systematised experimental observations and derived basic flow equations for thixotropic liquids (Cheng & Evans 1965).

> *'Today we define thixotropy as a rheological property of some pseudoplastic and plastic systems, which are showing a high viscosity at rest. However, if these systems are subjected shear stress (mixing, shaking, etc.), the viscosity gradually decreases with time. When leaving the system at rest there is a regrowth of viscosity that approaches asymptotically original value. This is because at rest the globular particles tend to clump and join into larger units, and thus the viscosity increases. When shearing under stress, these conglomerates will break up and thus the viscosity of the system will decrease'* (European Standard 2016)

Several types of organomineral resins from different manufacturers and of different qualities are now available on the market. These resins have a pasty form after mixing which is mistakenly referred to as thixotropic.

Urea silicate (organomineral) resin is a two-component system consisting of isocyanate and modified water glass, usually mixed in 1:1 volumetric ratio. The characteristics of both components significantly influence the behaviour and parameters of the resulting resin.

2.1 Isocyanates

One of the two basic components for the preparation of urea silicate (organomineral) resins are isocyanates prepared from different basic 'building blocks', as shown in Figure 1. For a suitable reaction with modified water glass, it is necessary to find specific properties of the isocyanate, which are evaluated according to the number of NCO (NCO is an isocyanate chemical group whose designation refers to the nitrogen, carbon, and oxygen atom of the isocyanate group. %NCO is a measure of the isocyanate content of a prepolymer or other isocyanate-containing compound measured as the weight percent of unreacted isocyanate groups in the material) functional groups reactivity, functionality and viscosity of raw material. Not every methylene diphenyl diisocyanate (MDI) is suitable for production of thixotropic type resin as it must react precisely with the additives contained in the modified water glass to produce the desired reaction Figure 1 (https://borsodchem.com/en).

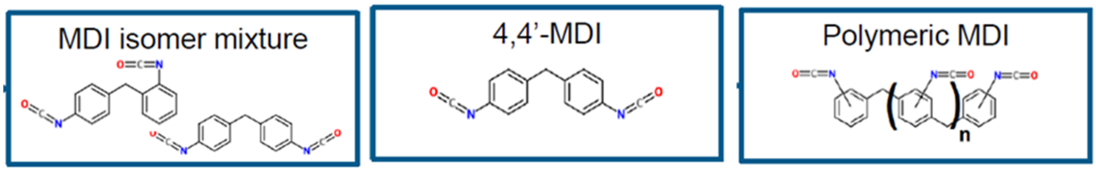


Figure 1 Basic isocyanate structures for organomineral resin products

2.2 Water glass

The second component for the preparation of the urea silicate (organomineral) resin consists of modified, usually sodium, water glass. After a long-term investigation, we found that the major influences on the final properties and behaviour of the product are composition, purity, and method of modification of the water glass used.

Water glass (alkalic silicate) is a colloidal solution, defined by two basic parameters: (1) solid phase content, i.e. dry matter; and (2) molar ratio of SiO_2 and Me_2O – alkali content (Figure 2).

Other important characteristics of water glass are density, viscosity, and turbidity measurable in nephelometric turbidity units (NTU) units. Ideal base water glass is colourless and clear; contaminants cause discoloration. Viscosity is influenced by the method of preparation and significantly affects the use of water glass in various applications. The molar ratio, dry matter of water glass and therefore the content of free water in the colloidal solution significantly influence the reaction of water glass solution with isocyanate.

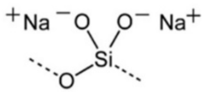


Figure 2 Water glass structure for organomineral resin products

Water glass is formed by two basic components suitable for creation of urea silicate resin: (1) alkaline hydroxide, which serves as a reaction initiator; and (2) SiO_2, which has the function of both a filler and a matrix-forming component of the final product.

The basic scheme of the reaction for the formation of organomineral resin is shown in Figures 3 and 4 (Brydson 1999; Antoš & Burian 2002).

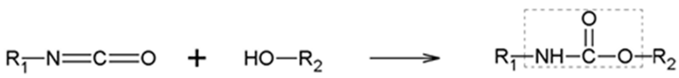


Figure 3 Reaction scheme between functional groups of isocyanate and water glass hydroxyl – creating organomineral resin products

$$O{=}C{=}N{-}R{-}N{=}C{=}O \;+\; HO{-}Si{-}OH \;\rightarrow\; {-}O{-}Si{-}O{-}CO{-}NH{-}R{-}NH{-}CO{-}$$

Figure 4 Reaction scheme of diisocyanates and polysilicates – creating organominaral resin products

Relative to the application use of the organomineral resin, the water glass is modified with suitably selected additives. Additives, in addition to influencing the reaction rate of resin formation, also contribute to the resulting structure of the product and thus influence other mechanical properties of the resin.

The reaction of resin formation is of an exothermic nature. The course of the reaction of the organomineral resin designed for bolting application is shown in the graph (Figure 5). After mixing A and B components, the product thickens immediately to a form of high viscosity yet pumpable, non-dripping, non-sagging material, which must exhibit thixotropic behaviour during open time. The maximum temperature of the reaction is very important for safety reasons and should be below 100°C to prevent eventual risk of fire in applications at combustible environment. At a temperature higher than desired, the soda solution also boils or sweats over the surface of the resin, thereby worsening the mechanical properties of the product.

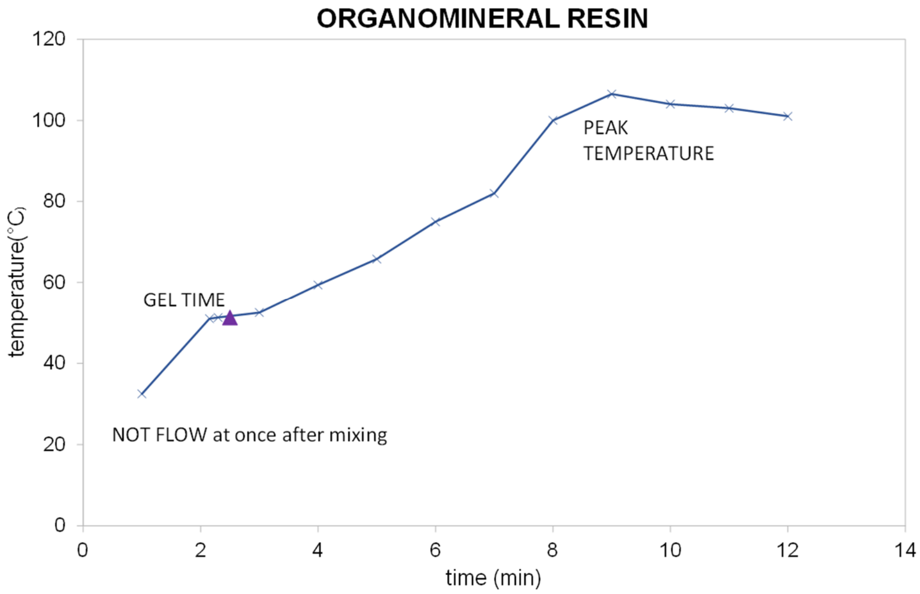


Figure 5 Behaviour organomineral resin: dependence of temperature on time

Using scanning electron microscope (SEM), we could discover and monitor individual types of resin. Figures 6 to 8 show how important composition and modification of water glass system is. The structure of water glass base type, right or wrong selection of additives, or their amount severely influence the final structure and properties of resin. The structure of ideal urea silicate resin is a homogenous matrix with silicate cells of even pattern based in polyurethane bedding made of MDI reaction.

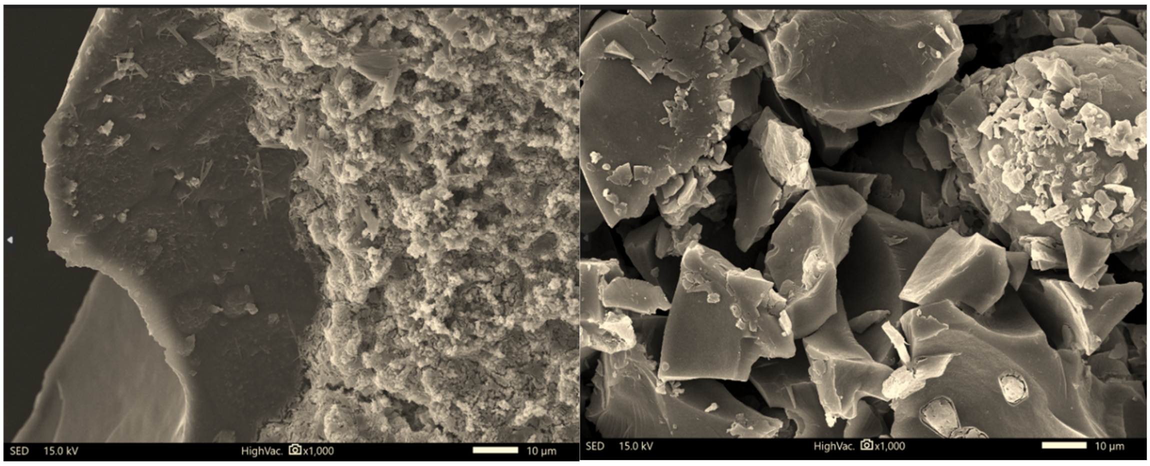


Figure 6 Example of scanning electron microscope resin structure without modification of water glass

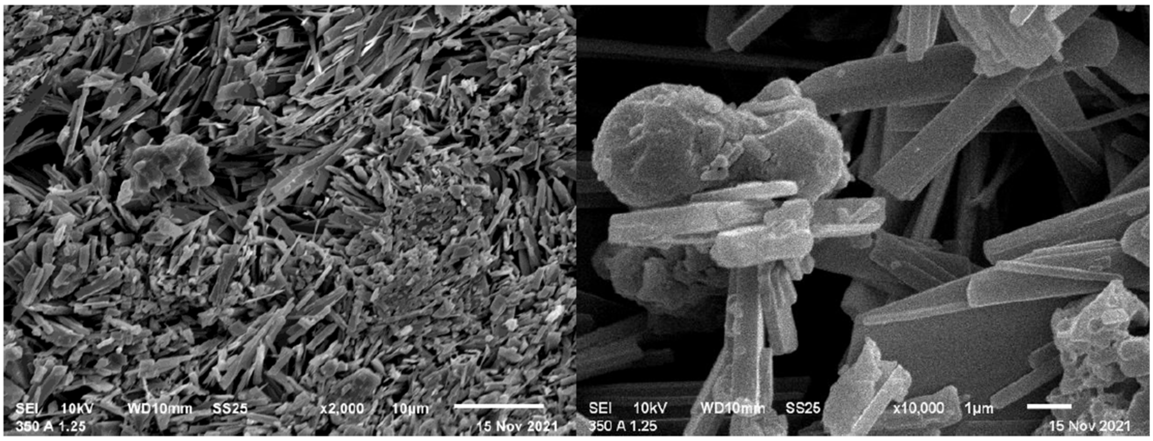


Figure 7 Example of scanning electron microscope resin structure with wrong parameters of raw material

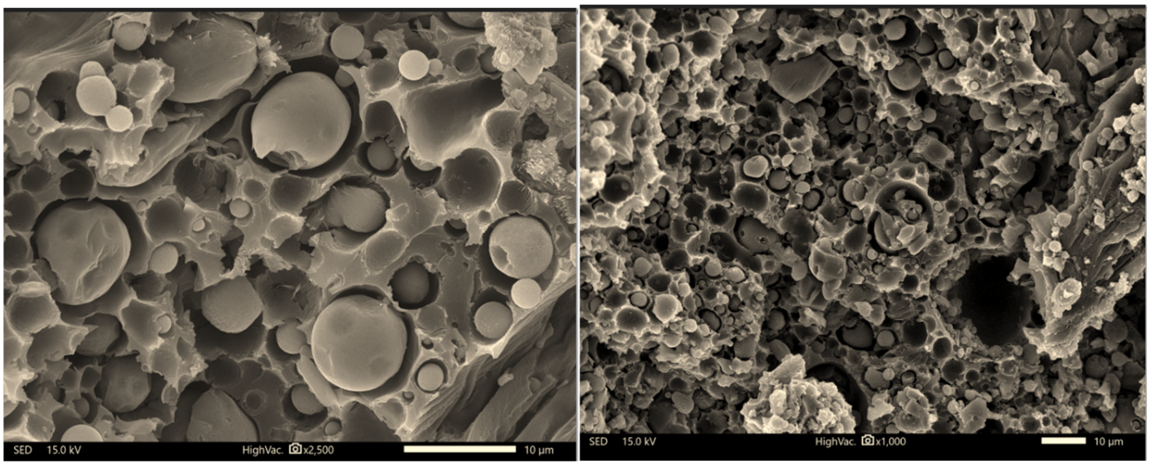


Figure 8 Example of scanning electron microscope structure of ideal thixotropic homogenous organomineral resin

3 Major mechanical properties of urea silicate resin for bolting

During numerous field and laboratory tests (Oyu Tolgoi in Mongolia and Canadian mines in the Great Sudbury Basin and Northern Quebec grouting of cable bolts, self-drilling hollow bolts and self-drilling dynamic hollow bolts, and impact testing at Canmet), we discovered that uniaxial compressive strength alone is not the major parameter for identification of final quality of the resin. Industry, however, mistakenly tends to look at this parameter only, as they try to compare that with known properties of cementitious grouts.

Resin, at large, is of very different mechanical properties compared to cement. Cement is polycrystalline material with has ten times higher compressive strength compared to its tensile strength, however, composite materials have tensile strength higher than compressive. Urea silicate resin, when prepared truly thixotropic, behaves like composite material, where the homogenous matrix is reinforced by silicate cells (Figure 8). Therefore, we should look at thixotropic urea silicate resin as composite material and not compare it with common cementitious grouts (Kottner & Zemcik 2022).

The major mechanical parameter and easy to understand property of truly thixotropic urea silicate resin is deformability without loss of strength Figures 9 to 12 (Canmet and UNICre multiple lab testing 2019–2023). However, this property is just one side of the coin. A second major parameter of equal importance is adhesion to reinforcing element (rockbolt), as well as to strata, creating strong and deformable interface between the two (Figure 13).

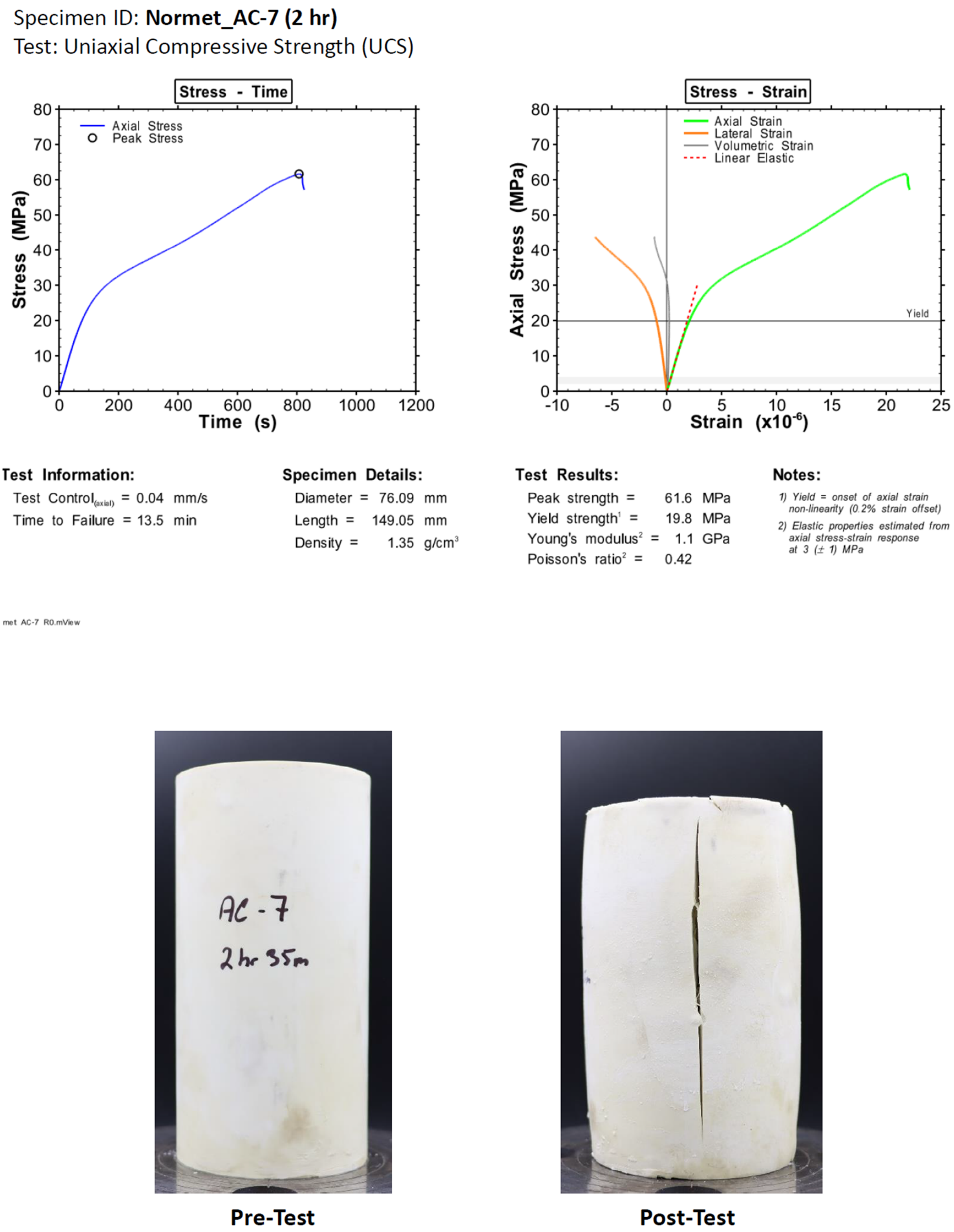


Figure 9 Example of high deformability without loss of strength: resin with thixotropic behaviour

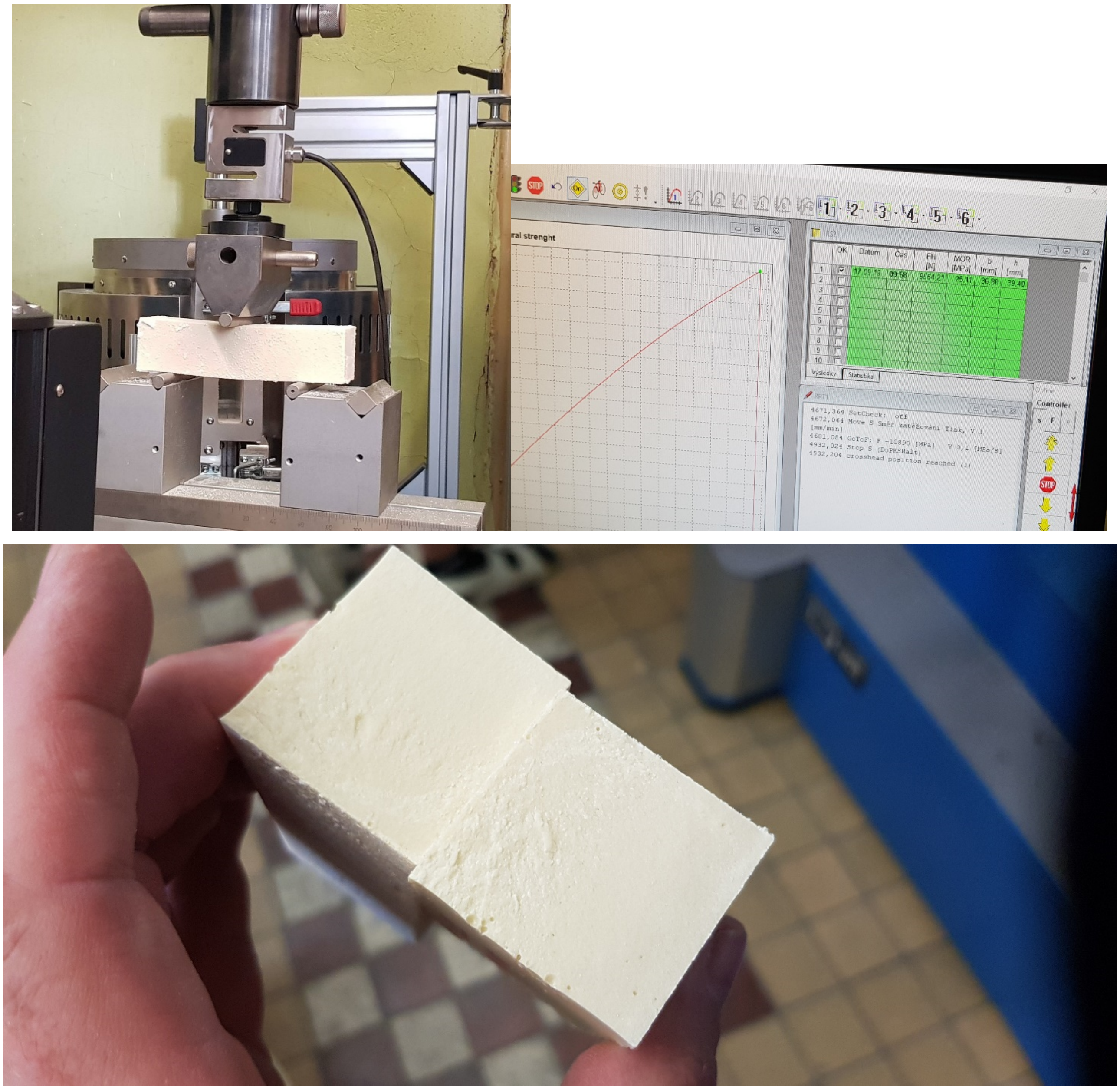
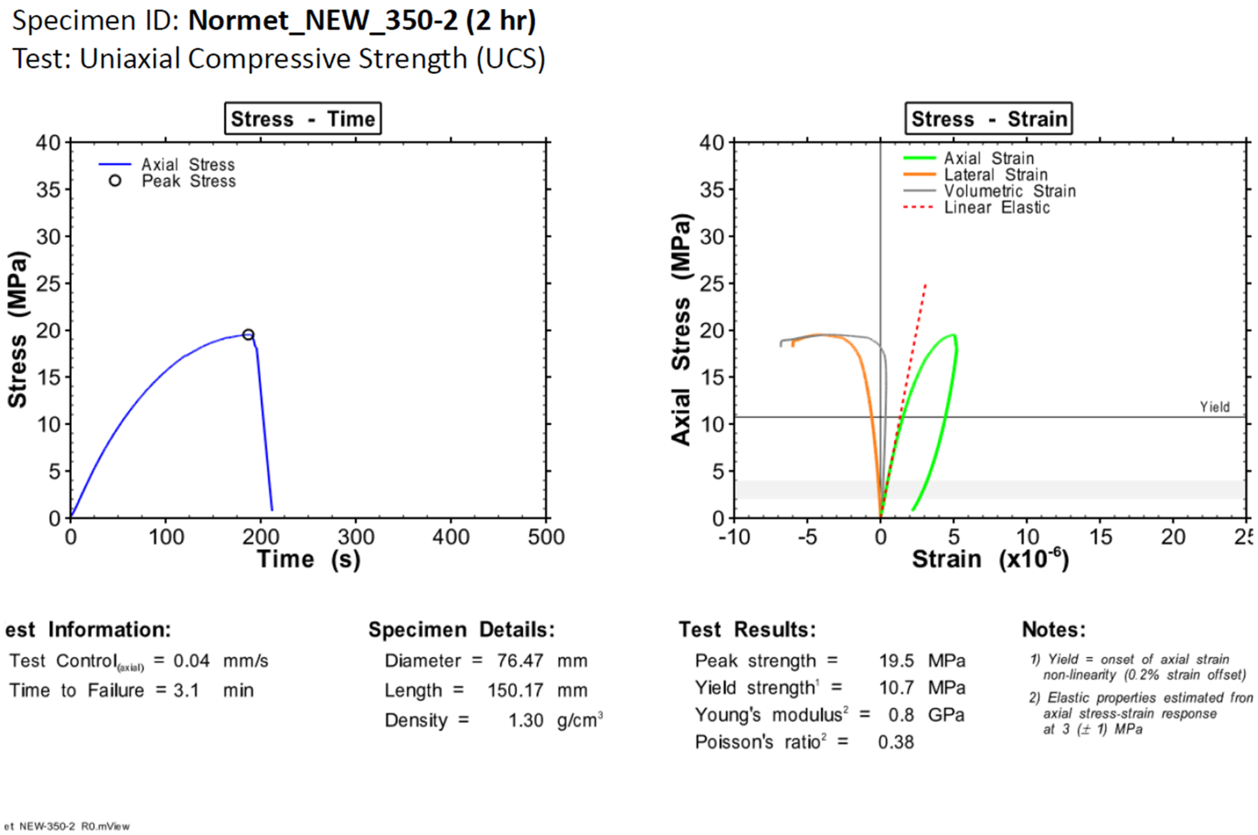


Figure 10 Example of high deformability without loss of strength (flexural strength): resin with thixotropic behaviour


Specimen ID: **Normet_NEW_350-2 (2 hr)**
Test: Uniaxial Compressive Strength (UCS)

est Information:
Test Control$_{(axial)}$ = 0.04 mm/s
Time to Failure = 3.1 min

Specimen Details:
Diameter = 76.47 mm
Length = 150.17 mm
Density = 1.30 g/cm^3

Test Results:
Peak strength = 19.5 MPa
Yield strength^1 = 10.7 MPa
Young's modulus^2 = 0.8 GPa
Poisson's ratio^2 = 0.38

Notes:
1) Yield = onset of axial strain non-linearity (0.2% strain offset)
2) Elastic properties estimated fron axial stress-strain response at 3 (± 1) MPa

et NEW-350-2 R0.mView

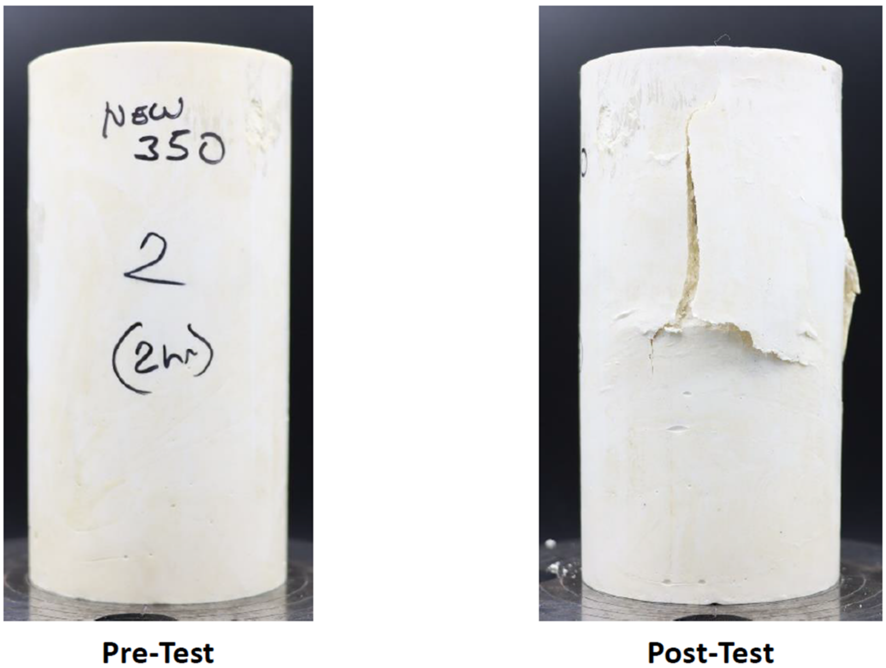


Figure 11 Example of low deformability without loss of strength: high viscosity resin without thixotropic behaviour (paste)

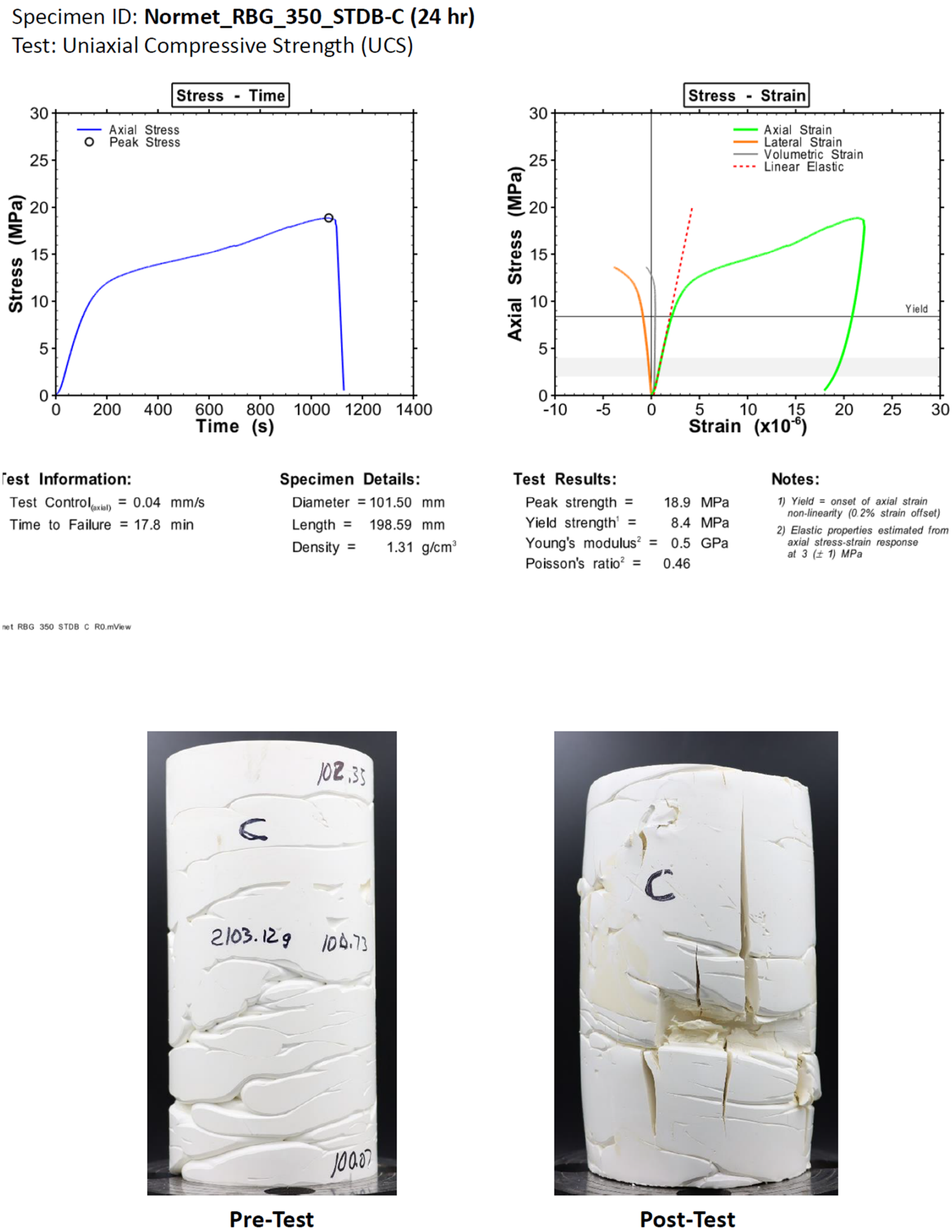


Figure 12 Example of high deformability without loss of strength: high viscosity resin without thixotropic behaviour (paste)

Figure 13 (Left) Example of bad adhesion after impact test; (Right) Example of good adhesion after impact test

4 Conclusion

Comparing cement anchor grouts with resin grouts is an elementary mistake because they are two completely different materials. The difference lies in the fact that cement grouts are a crystalline material with a large number of divisible surfaces of different sizes in any direction, which are created at different times and therefore the internal stress of the material can occur. In contrast, organomineral resin is formed in a shorter time, is not crystalline in nature and, due to the influence of SiO_2 cells, behaves like a composite material with minimal possibility of spatial defects. Therefore, resins have more favourable mechanical properties, especially their deformability without loss of strength.

Non-thixotropic, pasty resin forms have an irreversible viscosity development and although they are usable for rockbolt grouting, their application properties are more similar to cement grouts, i.e. they only fill the free space (void) around the anchor and their only added value is just faster setting speed.

Thixotropic resins, on the other hand, have a high added value because – due to mechanical stress and shearing – the highly viscous mixtures created during application reduce their viscosity and, thanks to this, can flow into cracks, cavities and irregularities in the rock within the immediate vicinity of the anchor, thereby increasing the contact area of the materials. With their high adhesion, they not only grout the rockbolt, but at the same time consolidate and strengthen the strata around the installation.

High deformability without loss of strength of thixotropic resins amplifies their advantages over other types of grouts. Therefore, it is important not to confuse the term thixotropic resin with a resin that only has a pasty form.

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