Study of polymer compositions for formation of impermeable inclusions in rock mass

TV Shilova*, LA Rybalkin
Chinakal Institute of Mining, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia
E-mail: *shilovatanya@yandex.ru

Abstract. Laboratory studies of two-component compositions based on polymersilicates and polyurethanes, developed to strengthen destroyed rocks and create impermeable inclusions in the rock mass, were carried out. The rheological properties of liquid components of polymer compositions for the temperature conditions of underground mining of solid minerals, physical and mechanical characteristics of hardened polyurethane and organomineral compositions have been determined.

1. Introduction
The actual problem of underground mining of solid minerals is water and gas flows. In order to eliminate them, anti-filtration curtains and screens, as well as insulating coatings applied to the surface of mines, are used. It is advisable to form impermeable inclusions (screens, curtains) in the rock by the hydraulic fracturing, filling the resulting cracks with hardening insulating compounds based on polymer resins.

Polymer resins are extensively used in mining to reinforce fractured, disturbed rocks and for waterproofing, including conditions of groundwater pressure filtration [1–3]. The advantages and disadvantages of the main types of resins are considered in works [4, 5]. The most common are two-component compositions based on organomineral (polymersilicates) and polyurethane resins. The use of polyurethanes requires less resin consumption due to the fact, that its components react to each other and, they react with formation water, causing foaming and an increase in the volume of the composition by 5–6 times. It is not always acceptable, since it contributes to the destruction of rocks. Unlike polyurethanes, organomineral resins do not foam, and they are characterized by higher strength in the cured state [5, 6].

Currently, the development of polymer compositions with optimal operational, technical and economic indicators to carry out water and gas insulation in difficult mining conditions is relevant. The article presents the results of studies of the dependence of the viscosity of liquid components, as well as the strength properties and elasticity of cured compositions based on polyurethane and organomineral resins, on the temperature. The compositions were developed at the Chinakal Institute of Mining to create impermeable inclusions in the rock mass.

2. Methods and materials
In the experiments we used organomineral (OM) and polyurethane (PU) resins. Resin OM is formed by mixing two components, one of which A is 79% sodium water glass, 10% water, 10% glycerin, and it contains the additive of the DMDEE catalyst. The other component B contains 65% polyisocyanate
and 35% dibutyl phthalate. PU resin also consists of two components, one of which is A. A is a composition of laprol (39%), low molecular weight polyethylene glycol (10%), triethanolamine (10%), catalyst based on DMDEE and triethylenediamine (together 1%) and a premix (40%) of low molecular weight polyethylene glycols with ethylene glycol and polymethylene isocyanate. The second component B is pure polymethylene isocyanate. Components A and B of both resins are mixed immediately before injection into the rock mass in a volumetric ratio of 1: 1.

A distinctive feature of the developed PU resin is the fact, that in order to increase the efficiency of reinforcement of watered rocks and to form impermeable inclusions in rocks, the hydroxyl-containing component contains the product of the reaction of an isocyanate with an excess of polyol, which does not contain free isocyanate groups. It enables the increase of the strength of the foamed polyurethane formed by the interaction of the PU components with each other and the formation water.

In order to determine the viscosity of the compositions, the vibrating viscometer SV-10 with the «A&D WinCT-viscosity» software was used. A sample of the studied resin component with a volume of 40 ml was placed in a container, hermetically sealed, heated to a temperature of 40–45° C and placed in a viscometer installed in a climatic chamber at a temperature of -10° C. The study of viscosity was carried out during process of cooling of the composition to -6° C with the viscosity measurement being performed once for 10 s. According to study results, the dependences of the viscosity of the components of both resins on temperature were plotted.

The study of the deformation-strength properties of the cured resin samples was carried out by compression tests using an INSTRON 8802 servo-hydraulic press according to standard methods [7–9]. The press provides soft and hard loading conditions with the construction of complete deformation diagrams in the coordinates “load – longitudinal and transverse deformation”. In a hard loading mode the press provides the possibility to obtain strength and deformation characteristics at all stages of loading of the samples up to their destruction. The values of uniaxial compressive strength, tensile strength and Young's modulus were determined according to the methods of GOST 21153.2-84, GOST 21153.3-85, GOST 28985-91, respectively [7–9]. The loading of the cylindrical specimens was carried out at the speed of the traverse movement 0.5 mm / min. Due to its structural properties (specifically porosity) the mechanical tests of the PU resin were limited to the uniaxial compression test.

To carry out study to determine the deformation-strength properties, cylindrical samples of hardened resins with a diameter of 37 mm and a length of 75 mm were formed (Figure 1). The end surfaces of the samples corresponded to the tolerances specified in GOST 21153.2-84 [7]. During development of prototypes of PU resin the foaming factor was taken into account, the value of which \( f = 6 \) was determined empirically. Laboratory studies of deformation and strength properties were carried out using the equipment of the Center for Collective Usage of the Chinakal Institute of Mining.
3. Results and Discussion

The obtained dependences of the viscosity of components A and B of the OM resin on temperature are shown in Figure 2a. It was determined that with a gradual decrease in temperature, the viscosity $\tau$ of component A increases from 69.3 mPa·s at $T = 39.4 \, ^\circ C$ to 1385 mPa·s at $T = -6.6 \, ^\circ C$, or approximately by 20 times, and component B – from 82.5 mPa·s at $T = 31.9 \, ^\circ C$ to 2911 mPa·s at $T = -7.6 \, ^\circ C$, i.e. by 35 times.

The results of study of the viscosity of components A and B of PU resin are shown in Figure 2b. It was determined that with a gradual decrease in temperature, the viscosity of component A increases from 70 mPa·s at $T = 35 \, ^\circ C$ to 2080 mPa·s at $T = 8 \, ^\circ C$, or approximately by 30 times, and component B increases from 65 mPa·s at $T = 34.5 \, ^\circ C$ to 3200 mPa, or approximately by 50 times.

Figure 1. Samples of the cured OM (a, b) and PU (c, d) resins before and after compression tests: a, c – samples before compression tests; b, d – samples after compression tests

Figure 2. Dependence of the viscosity of the two-component polymer resins on temperature: a – resin OM: the solid line shows the dependence of the viscosity of the
component A on temperature, the discontinuous line shows the dependence of the viscosity of the component B on temperature; b – resin PU: the solid line shows the dependence of the viscosity of the component A on temperature, the discontinuous line shows the dependence of the viscosity of the component B on temperature.

Based on the results of mechanical tests, the uniaxial compressive strength and tensile strength of the cured two-component resins OM and PU were calculated (Table 1). For resin OM, the average values of the uniaxial compressive and tensile strength are 31.6 MPa and 4.3 MPa, respectively. The Young's modulus value varies from 211.5 to 294.4 MPa, and the average value is 256 MPa. With a decrease in the ratio of the length to the diameter of the tested specimen, the ultimate strength values and Young's modulus increase.

| Parameter                      | OM (Organomineral resin) | Geoflex (Organomineral resin) | PU (Polyurethane resin) |
|-------------------------------|--------------------------|-------------------------------|-------------------------|
| Component ratio (volume) A:B   | 1:1                      | 1:1                           | 1:1                     |
| Foam factor                   | 1                        | 1                             | 6                       |
| Tensile strength, MPa         | 4.3                      | 2.5                           | –                       |
| Uniaxial compressive strength, MPa | 31.6                    | –                             | 10–11                   |
| Elastic modulus, MPa          | 256                      | 250                           | 34.4                    |

According to the test data, the uniaxial compression strength of the cured PU resin is 10–11 MPa, and the elastic modulus is 34.4 MPa. Comparison of the obtained results with the characteristics of the known two-component organomineral composition Geoflex (Minova, Germany), which is used for insulation in underground mining, shows that the tensile strength of the developed OM resin is 1.8 times higher.

Additionally, the influence of the injection of OM and PU resins on the physical and mechanical properties of sand has been determined. It was found that the polymer silicate composition (OM resin) provides more stable reinforcement of the loose rock than PU resin does. Thus, the uniaxial compression strength and the elastic modulus of the consolidated fine-grained sand reinforcing with OM resin are, on average, 8 and 11 times higher than, when it is treated with PU resin.

4. Conclusions
The original organic-mineral and polyurethane two-component compositions of increased strength have been developed to form impermeable inclusions in the rock mass. These compositions can be used as working fluids in the formation of impermeable screens by hydraulic fracturing. High efficiency of reinforcement of watered rocks with a polyurethane polymer is achieved by the injection of the product of the reaction between an isocyanate and an excess of a polyol that does not have free isocyanate groups into the hydroxyl-containing component of the resin.

Experimental studies show, that the uniaxial compression strength of the developed organomineral resin is 4.3 MPa, which exceeds this indicator for the known compositions for a similar purpose. This resin provides better reinforcement of a loose rocks than polyurethanes. Thus, the
uniaxial compressive strength of the consolidated fine-grained sand impregnated with the developed organomineral resin is 8 times higher, than when it is treated with polyurethane resin.

The temperature dependences of the viscosity of the components of the compositions are close to each other, that guarantees the uniformity of the impregnation of loose rocks during the component injection of the compositions. In order to reduce the viscosity of the compositions at low temperatures, it is recommended to heat them to room temperature immediately before the injection into the rock mass.

Acknowledgements
The study was supported by the Russian Science Foundation, Project No. 20-17-00087.

References
[1] Klimchuk IV and Malanchenko VM 2007 Experience of the application of polymer technologies at the mining enterprises in Russia Mining Industry No 4 pp 22–25
[2] Serdyukov SV, Shilova TV and Drobchik AN 2016 Polymeric insulating compositions for impervious screening in rock masses Journal of Mining Science Vol 52 No 4 pp 826–833
[3] Shatirov SV and Vasilev VV 2014 Measures to prevent rock collapses in mine workings of coal mines Safety in the industry No 1 pp 26–28
[4] Hu XM, Cheng WM and Wang DM 2014 Properties and applications of novel composite foam for blocking air leakage in coal mine Russian Journal of Applied Chemistry Vol 87(8) pp 1099–1108
[5] Vasilev VV 1986 Polymer compositions in mining Science 294 p
[6] Šňupárek R and Souček K 2000 Laboratory testing of chemical grouts Tunnelling and Underground Space Technology Vol 15 No 2 pp 175–185
[7] GOST 21153.2-84 Rocks. Methods for determination of uniaxial compressive strength Moscow, Standards Publishing House 2001 7 pp
[8] GOST 21153.3-85 Rocks. Methods for determination of uniaxial compressive strength Moscow, Standards Publishing House 1986 14 pp
[9] GOST 28985-91 Rocks. Methods for determination of deformation characteristics under uniaxial compressive Moscow, IPK Standards Publishing House 2004 10 p