Influence of composition of functional additives and deformation modes on flow behavior of polymer composite materials

N N Onoprienko, Sh M Rahimbaev

Belgorod State Technological University named after V.G. Shukhov, 46 Kostukov St., Belgorod, 308012, Russia

E-mail: dstt_80@mail.ru

Abstract. The paper presents the results of the influence of composition of functional water-soluble polymers and viscosity of domestic and foreign one-percent water solution polymer on flow parameters of cement and polymer test. It also gives the results of rheogoniometry of Eunice Granit tile adhesive used for large-size plates from natural stone and ceramic granite.

1. Introduction
Cement and polymer composite materials are widely used in modern construction industry in Russia and foreign countries during the production of dry building mixes to ensure plasterworks, masonry works, floor construction, sealing between construction elements and for soil stabilization under foundations, etc. [1-4].

The majority of dry building mixes produced in Russia use foreign polymer additives [5-7]. In this regard, to foster import substitution in this important branch of construction industry, there is a need for thorough study focused on compatibility and synergism of components of such building mixes, which will ensure their minimum cost and high technological and construction characteristics.

Despite the critical nature of this problem, there is no sufficient study of cement and polymer compositions with modern water-soluble additives in domestic scientific and technical literature. This issue is also not fully covered in foreign publications since it tackles a particular commercial interest.

2. Materials and methods
This work is devoted to the study of disperse systems on the basis of Eunice Granit tile adhesive produced on industrial scale to ensure surfacing and facing with the use of large-size plates from natural stone and ceramic granite. REOTEST-2.1 rotating viscometer was used to study flow properties of cement and polymer systems. The studied material was placed in an annular gap between two coaxial flow meter cylinders (external and internal). Comparative tests of tile glue were carried out under the water-solid ratio equal to W/S=0.4 … 0.6 when using two internal cylinders of various diameters: S3 and S2. Rotation from these cylinders is transmitted through a spiral spring with coefficient (K) equal to: S3 - K=0.52; S2 - K=0.57. The gap between coaxial cylinders of a flow meter was different: when S3 cylinder was used, the gap was 4 mm; in case of S2 cylinder, it was 1.5 mm. Two acceleration modes of a shear rate gradient, “a” (fast) and “b” (slow), were also studied.
3. Results and discussion
It is commonly known that more than a decade ago, the majority of dry building mixes were produced with the use of polyvinyl acetate (PVAC) as the modifying additive, which flow rate reached 10-15% in terms of the equivalent amount of polymer and various latex [1]. In recent years, the following water-soluble polymers are applied for the same purpose: carboxymethyl cellulose (CM), methyl cellulose (MC), oxyethyl cellulose (OEC), as well as polyoxyethylene (polyox) (POE) and polyacryl amide (PAA) [5-7]. In the earlier study [1], it was shown that the indisputable advantage of the latter ones in comparison with PVAC is explained by high viscosity of 1% water solution and a favorable structure of functional additives. It was also shown that water-soluble polymer additives shall not contain carboxylate groups -\(\text{COO}^-\), which actively react with calcium ions relieved during hydrolysis of cement minerals thus forming a high-viscosity hydrophobic deposition with properties unacceptable for construction.

Work [1] presents formulas and composition of functional groups of some water-soluble polymers used in production of cement and polymer compositions. The earlier study [1] shows that methyl cellulose (MC), oxyethyl cellulose (OEC), polyoxyethylene (polyox) (POE) and polyacryl amide (PAA) present the greatest interest as stabilizers of cement and polymer systems due to lack of carboxylate groups. PVAC contains a small amount of residual carboxylate groups, which makes it unstable to coagulating power of calcium ions Ca\(^{2+}\) in cement systems, and therefore this additive stabilizes the latter ones at increased dosages. PAA in strongly alkaline environment of a liquid phase of cement systems is exposed to hydrolysis with further formation of carboxylate groups, which is unstable in Ca\(^{2+}\) ions environment.

Theoretical justification of methods that regulate properties of existing dry mixes and ensure development of new ones requires deep knowledge of selection principles of water-soluble additives, especially according to the composition of functional groups, a degree of polymerization (characterized by viscosity of 1% water solution).

It is obvious that various requirements are imposed on cement and polymer compositions depending on their purpose in construction industry [8-11]. Plaster mixes shall have high yield point and adhesion to various surfaces. If cement and polymer compositions are used in floor construction in civil and industrial engineering, then the yield point has to be close to zero, which causes the need for good thixotropic properties and low viscosity.

The analysis of rheograms performed in [1] shows that dispersions with addition of high-viscosity oxyethyl cellulose (OEC-4) and methyl cellulose (MC) satisfy the first requirement. POE in low dosage may be recommended for floor construction. Mixtures with PVAC additive meet this requirement; however, the dosage of this additive is too high, which makes it economically inadvisable.

Rheograms described in [1] are considered model of simplified systems not containing fillers, stabilizers, dispersants, thickeners, etc., which are mainly used for modern dry mixes on the basis of cement and polymer compositions. In this regard, there is an urgent need to study flow properties of industrial dry building mixes used in construction industry in Russia.

Fig. 1-3 show rheograms of disperse systems on the basis of Eunice Granit tile glue produced on the industrial scale for surfacing and facing works with the use of large-size plates from natural stone and ceramic granite. The manufacturer recommends preparing tile glue from this type of dry mix at a water-solid ratio equal to W/S=0.22-0.23. Since the Reotest does not operate in such low W/S ratio, different tile glues with W/S=0.4-0.6 were used. W/S variation in this wide range was done to define the influence of a specified parameter on the rheogram nature.

Fig. 1 shows the rheogram of tile glue with various W/S ratios with a 4 mm gap between cylinders (S3 cylinder), spring coefficient K=0.52 in a fast acceleration mode of a shear rate gradient (“a” mode).
Figure 1. Rheogram of Eunice Granit tile glue at various W/S ratios (0.4 ... 0.6): 4 mm gap (S3 cylinder); “a” mode

The analysis of rheograms demonstrates the following. At minimum W/S=0.4 in area $\dot{\gamma} = 1-3 \, \text{c}^{-1}$, the Shvedov’s mode flow with $P_0 = 58 \, \text{Pa}$ is observed. The acceleration mode of a shear rate gradient up to $\dot{\gamma} = 3-4 \, \text{c}^{-1}$ and shear stress $P = 72 \, \text{Pa}$ gives deformation of dispersion within the Saint-Venant’s mode, i.e. elasto-plastic strain, and the rheogram represents the straight line parallel to X-axis. Authors believe that such flow is caused by the separation of the measuring cylinder from tile glue dispersion and further adhesive friction between them in dynamics.

With the growth of W/S up to 0.45 the yield point decreases from 58 to 32 Pa, and plastic viscosity within the Shvedov’s mode decreases twice. The shear rate gradient of 5-6 c$^{-1}$ causes short-term wall-adjacent of a cylinder towards suspension, and then at $P = 5-30 \, \text{Pa}$, there is a small viscosity flow almost in the rectilinear Bingham mode. In the area of gradients $\dot{\gamma} = 25-150 \, \text{Pa}$, Saint-Venant plastic deformation is observed at the shear stress of 73 Pa. The hysteresis loop significantly increases with a W/S increase.

Further growth of W/S to 0.5 led to the fact that the Saint-Venant flow area was reduced since it only began when $\dot{\gamma}$ was more than 60 c$^{-1}$. It is interesting that the shear stress characterized by purely plastic deformation with W/S growth from 0.4 to 0.5 and up to 0.55 was at the same level.

The W/S increase to 0.55 caused the reduction of elastoviscoplastic Shvedov’s flow, the area of which stands within the shear stress ranging from 10 to 25 Pa, i.e. it is narrowed in comparison with thick paste. It was further followed by tixotropic plastic viscous flow up to $\dot{\gamma} = 75-80 \, \text{c}^{-1}$. In area $\dot{\gamma} = 75-150 \, \text{c}^{-1}$, purely plastic deformation according to Saint-Venant is observed. The hysteresis loop is observed within all intervals of measured values, but it is rather narrow.

When W/S=0.6, there is rheogram normalization of elastoviscoplastic tixotropic body with the yield point of 10 Pa with low viscosity and very narrow hysteresis loop which is observed within $\dot{\gamma} = 25-100 \, \text{c}^{-1}$.

Fig. 2 shows rheograms of the same suspensions and at the same parameters, but with a small gap between flow meter cylinders, which equals 1.5 mm (S2 cylinder, K=0.57 spring coefficient).
Comparison of cement glue rheograms with W/S=0.4 and W/S=0.5 showed that the growth of W/S leads to the decrease in the yield point. Another interesting fact is that the yield point of cement glue with W/S ranging from 0.4 to 0.6 does not change and approximately equals 52 Pa. At the same time, the growth of W/S from 0.4 to 0.6 led to narrowing of the area of purely plastic deformations according to Saint-Venant more than 1.5 times. There is also an increase of hysteresis loop alongside with the growth of W/S from 0.4 to 0.55. With the increase of W/S to 0.6, the hysteresis loop is reduced.

The comparison of cement glue rheograms with the gap between cylinders (4 and 1.5 mm) shows that narrowing of a gap led to expansion of the area of purely plastic deformation and narrowing of the area of plastic viscous flow. When the gap equals 1.5 mm; purely plastic viscous flow is not observed even at W/S=0.6.

Fig. 3 shows rheograms of cement glue dispersion with W/S=0.5 at various intensity of acceleration modes of a shear rate gradient (“a” and “b” modes), for S3 (4 mm gap) and S2 (1.5 mm gap).
Figure 3. Rheogram of Eunice Granit tile glue at various W/S ratios (0.5): 4 mm gap (S3 cylinder) and 1.5 mm gap (S2 cylinder); “a” and “b” modes.

When the gap between cylinders equals 4 mm, the intensity of $\dot{\gamma}$ increase strongly influences the nature of character rheograms. At intense acceleration of rotation speed of a cylinder (“a” mode), the mixed flow mode is observed: at $\dot{\gamma} = 60$ c$^{-1}$ – plastic viscous flow, and at increased shear rate – purely plastic flow according to Saint-Venant. At low intensity of rotation speed (“b” mode) and the same W/S ratio, the rheogram has a standard form typical for plastic viscous flow with a yield point of 5 Pa.

When the gap between cylinders is small and equals 1.5 mm, the intensity of rotation speed does not play an essential role and rheograms have almost identical nature, except for the yield point, which differs by 6-7 Pa upon shift from 4 mm to 1.5 mm gap.

4. Conclusions
The comparison of flow curves for cement suspensions of model systems [1] and Eunice Granit tile glue (Fig. 1-3) makes it possible to assume that industrial multicomponent dry mixes, except for stabilizers (water-soluble polymers), contain strong viscosifiers and thickeners, which change characteristics of rheograms.

The analysis of plaster and masonry works with the use of cement and polymer mixes, as well as the study of rheological features of industrial dry mixes for Eunice Granit plates made it possible to conclude that at the increased water-solid ratio they have small elasticity since it fosters crack formation, and small hysteresis loop, which characterizes the relaxation rate of internal stresses. The increased yield point and plastic viscosity improve adhesion of plaster and glue mixes to working surfaces.

The decrease in thickness of cement and the polymer layer (reduction of a gap between flow meter cylinders during pilot studies) does not only improve technological parameters of cement and polymer composition, but also reduces sensitivity of the latter ones to water-content variation.

The main disadvantage of polyvinyl acetate emulsion in comparison with water-soluble polymers is low viscosity of one-percent water solution, which accounts for its high cost.

Considering complex composition of modern dry building mixes, the authors consider that the
conducted study can be useful for targeted regulation of rheological and rheotechnological parameters of cement and polymer compositions taking into account specifics of their practical application.

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