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Rheological behavior of 3D printable cement paste: criterial evaluation

Критериальная оценка реологических характеристик цементных систем для строительной 3D-печати

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Ключевые слова: строительная 3D-печать; цементные смеси; реология; сдавливающий тест; экструдируемость; формоустойчивость

Abstract. The extrudability and firm stability are the criterial rheological characteristics of building 3D printable mixtures. From the point of view of classical rheology of disperse systems, the theoretical analysis of the rheological behavior of a cement paste has been analyzed for all stages of 3D printing process. Apparently both the theoretical analysis criteria and technological tools to control rheological behavior of a 3D printable mixture have been justified. The squeezing test is used in the experimental research as a rheological behavior identification tool of cement-based materials, in order to evaluate the extrudability and buildability. The squeezing test, with constant plate speed, is determining plastic yield value and elasticity criterion of a cement paste as criteria of the extrudability. The squeezing test, with constant strain rate, is determining structural and plastic strength, plastic deformations as a criteria for the ability of a cement paste to hold shape during multi-layer casting. It is shown that these properties are significantly controlled by the W/C-ratio, concentration of plasticizer additives as factors of changes in the concentration of the dispersed phase and properties of the dispersion liquid in a system «cement + water» as matrix for printing concrete.

Аннотация. С позиций классической структурной реологии дисперсных систем произведен теоретический анализ реологического поведения смесей в процессе 3D-печати. Обоснованы технологические факторы регулирования экструдируемости и формоустойчивости как критериальных реологических характеристик смесей. Представлены результаты экспериментальных исследований экструдируемости и формоустойчивости модельных цементных систем как матриц смесей для 3D-печати. Для оценки экструдируемости использован сдавливающий тест с постоянной скоростью деформирования, по результатам которого найдены критериальные значения пределов ползучести, текучести и эластичности цементных систем. Для оценки формоустойчивости использован сдавливающий тест с постоянной скоростью нагружения, по результатам которого найдены значения структурной и пластической прочности, пластических деформаций цементных систем, характеризующие их способность сохранять форму при действии возрастающих сжимающих напряжений в процессе печати. Получены количественные данные о влиянии В/Ц-отношения и концентрации суперпластификатора на комплекс реологических характеристик цементных систем. Установлено, что В/Ц-отношение, определяющее концентрацию частиц дисперсной фазы в системе «цемент + вода», является главным фактором структурирования и упрочнения цементных систем. Введение пластификатора как фактора изменения свойств дисперсионной среды является средством не только регулирования пластичности, но повышения формоустойчивости.

1. Introduction

3D-building printing is an innovative process of robotized creation of minor architecture forms, single structural elements of buildings and low storey houses by multilayer casting of viscoplastic materials [1]. Potential advantages of this process include ability to receive materials of different functionality directly at the construction site, to print freeform constructions without mould, to reduce materials consumption and labor input of construction [2, 3]. One of the top priority problems defining the ability to introduce this innovative method of constructing building sites into building practice is the problem of creating nomenclature of mixtures ensuring the implementation of this process. Efficiency and manufacturability of 3D-building printing depend on the adjustability of parameters of the mixtures at all stages of the process. To ensure the required quality and construction time, management of rheological behaviour of mixtures must be done according to the conditions securing fluidity for their transfer, plasticity for extrusion, integrity of surface shape after laying, structural durability for load accommodation of the upper layers. The processes of preparation and transportation of the mixture to the extruder are maximally adapted to the existing building machinery, therefore the issue of adjusting technical parameters of mixtures at these stages of the technological process has been studied quite well. However, at other stages of the process rheological behaviour has to be significantly different from traditional properties of building mixtures and composites. Fundamental possibility and efficiency of their implementation are defined by extrudability, buildability, structural build up of mixtures and composites.

Currently, the studies being conducted can be divided in two categories. In the first one, researchers focus their attention on the issues of optimization of mixture compositions [4–13]. As a result of collecting an array of experimental information, quite a big nomenclature of mixture has been received and tested. The obtained mixtures are multi-component, their compositions include superplasticizers, viscosity modifying additives, structural build-up regulators, fillers and filling materials of various chemical-mineral composition and dispersibility. Still, there is no systemized information and common approaches to explanation of the role of each of formula factors for guided regulation of extrudability, buildability and structural build up of mixtures. Only the influence of dosage of superplasticizer on the parameters of fluidity of mixtures has been definitely established (for instance, in studies [9–10]).

The second category of research is aimed at the study and modelling of rheological behavior of disperse systems in the processes of 3D printing [14–22]. Approaches to implementation of the studies are based on squeeze flow theory, key points of which are summarized in the study [14]. As a result, methods of squeeze flow rheometry as a tool of identifying 3D printable building materials rheological behaviour under compression stress typical for extrusion and multi-layer casting have been formed and have become widely spread. One of the most effective methods of squeeze flow rheometry is grounded in the works of N. Roussel [15–16] who developed the squeezing test with constant plate speed. The constant plate speed may vary within the range of 0.1÷5 mm/s depending on the properties of the studied materials. Plastic yield value of viscoplastic materials is determined as quantitative criterion of extrudability based on the results of squeezing test. The second option of evaluation of 3D-printability of building mixtures under compression is grounded and implemented in the works of A. Perrot [17]. This option presupposes modelling the parameters of loading on the first poured layer from consistently growing pressure of the upper poured layers. During the test a sample is gradually loaded until cracks appear in is side faces. Based on the results of the experiment, structural strength and time of the beginning of destruction are determined as quantitative criteria of buildability. The developed approaches of squeeze flow rheometry and methods of squeezing tests should be accepted as maximally adapted to the conditions of 3D-building printing.

Problem statement of the studies is conditioned by the need to form common approaches to the parameters of mixtures optimization by the criteria of extrudability, buildability and structural build up. Formation of such approaches, acquisition of quantitative data on the influence of different formula factors on rheological behavior will allow unambiguously substantiating the requirements for their compositional analysis in accordance with the specified functionality. Therefore, it is necessary to conduct system research allowing to identify and quantitatively evaluate the influence on the set of rheological parameters of mixtures of each single formula factor used today in order to obtain them.

Two groups of mixtures are used to implement 3D-printing in building: coarsely disperse (size of particles d > 100 µm) and microdisperse (size of particles d ~ 1 ÷ 100 µm) systems. According to the classic structural rheology of disperse systems main factors of stability of these systems were identified in our work [23]. There are kinetic, electrostatic, molecular-adsorptive, hydrodynamic factors. Behavior of the disperse systems in dynamic (during transfer and extrusion) and static (during multi-layer casting) conditions of 3D-printing is limited by interaction of these factors. Effectiveness of their influence on stability of the systems is evaluated by criteria of aggregation and strength. Priority of theoretical justification of the criteria belongs to the classic fundamental works of the Soviet physico-chemical mechanic [24–28].

Concerning the mixtures for 3D-printing such as high-concentration pastes belong to heterogeneous disperse systems with close coagulation of particles, spontaneous formation of coagulation structures is possible in dispersions with the size of particles of about 50 ÷ 500 µm. Strength criterion defines the functional strength dependence of disperse system structure on the size of particles, strength of individual contacts and concentration of solid phase in liquid phase determining the amount of contacts in a unit of structure volume. It has been proved [24] that critical concentration of particles of solid phase under the formation of coagulation structure and its strengthening for each pair “solid phase – liquid phase” depend on the parameters of particles of solid phase and properties of liquid phase.

On that basis, in the work [23] we have justified basic means of management of rheological behavior of disperse system under the conditions of 3D-printing. In connection with solid phase, they include its concentration, size of particles and their morphology, chemical-mineralogical composition, physicochemical characteristics of the surface of particles defining the contribution of kinetic, electrostatic and molecular-adsorptive factors in the stability. In connection with liquid phase, they include its ionic composition, viscosity, density, defining the contribution of electrostatic, molecular-adsorptive and hydrodynamic factors in the stability. According to these means of management, a set of formula technological factors has been suggested for management of rheological characteristics of 3D printable concrete. They include the type of binding agent, type and granulometry of fillers and filling agents, types and dosages of additives of electrolytes, plastisizers, viscosity modifying additives, etc.

It should be stressed that in accordance with strength criterion of heterogeneous disperse systems, concentration of solid phase is the defining factor of its stability. Its optimal values for each specific disperse system are also defined by properties of its particles and characteristics of liquid phase. For this reason, it can be stated that the factors studied in this research are the main technological means of regulating rheological behavior of mixtures for solution of practical tasks. They include:

– water/cement ratio as a factor defining the concentration of solid phase in the disperse system,

– concentration of plasticizers as a factor defining the properties of liquid phase.

This article is dedicated to the results of the initial stage of comprehensive studies conducted by the authors on this issue. Presented are the data of system experimental evaluation of the influence of water/cement ratio and concentration of plasticizer for model cement pastes as matrixes of 3D printable concrete on the set of rheological parameters criterial for extrusion and multi-layer casting of the 3D-printing.

2. Methods

Three types of cement pastes were studied (Table 1). Portland cement CEM I 42.5 (EN 197 – 1 : 2011), plasticizer of Sika trademark based on polycarboxylic ethers, manufacturing water were used as initial components of the system.

Table 1. Mix composition.

Systems	System’s specimen	Plasticizer, mass/mass cement (%)	Water/cement ratio
“cement + water”	$C-W$	-	0.24
			0.25
			0.26
			0.27
			0.28
“cement + water + plasticizer 1”	$C-W-P1$	0.1	0.23
			0.24
			0.25
			0.26
			0.27
“cement + water + plasticizer 2”	$C-W-P2$	0.2	0.22
			0.23
			0.24
			0.25
			0.26

Cylindrical samples of fresh cement paste with radius R equal to their height h_0 = 25 mm were used for the implementation of the experiment. For squeezing test, the sample was put between two smooth plates diameter of which corresponded to the size of the sample and was loaded into a universal floor hydraulic testing system “INSTRON Sates 1500 HDS”.

To evaluate the plasticity of cement pastes, defining their extrudability, the squeezing test with constant plate speed was used in accordance with the methodology developed in the works of N. Roussel [15–16]. The test was conducted on a fresh sample for all compositions of cement paste directly after their manufacture. High compression speed test using constant plate speed v = 5 mm/sec was implemented as the behavior of the system in the process of extrusion is most adequately modelled with this speed. The curves "compression force N – displacement Δ" obtained during the experiments were interpreted as influence curves of reduced compression load F^* from relative change of height of the sample h_i/R.

$$F_i^* = \frac{Ph_i}{pR^2}, \quad (1)$$

where $h_i = (h_0 - \Delta)$, h_0 is initial height of the sample, Δ is transfer in the i point of time, value R was taken as constant and equal to the radius of the sample at the beginning of the experiment.

According to the results of the analysis of the received experimental curves for the studied systems values K_i, called plastic yield value by N. Roussel [15], were calculated:

$$K_{\text{i}}\left(h/R \right) = \frac{\sqrt{3}F^*}{2}. \quad (2)$$

For compositions of cement paste the samples of which visually kept their form, the squeezing test with constant strain rate was conducted. Methodology of its implementation corresponds to the approaches of A. Perrot [13] to evaluation of buildability of the 3D printable mixtures. The squeezing test was conducted with constant strain rate v = 0.5 N/c which conforms to the average speed of load increase during multi-layer casting of building sites by industrial printers. Thus, the load on the first poured layer from gradually increasing pressure of upper layers during 3D-printing was simulated.

The squeezing test with constant strain rate was conducted for the samples: 1) directly after molding, 2) after curing during 30 min, 3) after curing during 60 min. Squeezing was conducted until the rupture of the samples, during the experiments the curves "displacement Δ – time t", "compression force N – displacement Δ" were recorded. Based on the obtained experimental curves, values of structural strength of cement pastes were calculated for the moments corresponding to the start of deformation and the start of cracking in the samples by the formula:

$$\sigma = \frac{P}{\pi R^2}. \quad (3)$$

Thus, rheological behavior of cement pastes and their stability under the conditions simulating the influence of compression stress during extrusion and multi-layer casting was evaluated by the following criteria:

– plastic yield value K_i,

– structural strength σ_0 at the beginning of the deformation,

– plastic strength σ_{pl} and value of plastic deformations Δ_{pl} which were evaluated at the beginning of cracking.

3. Results

3.1. F* vs. h_i/R experimental curves and plastic behavior

As a result of interpretation of the squeezing test with constant plate speed we received experimental curves $F^* = f(h_i/R)$ (Figure 1) which correspond to the similar curves of N. Roussel [15]. Analysis of experimental curves $F^* = f(h_i/R)$ for description of rheological behavior of cement paste during squeezing was conducted on the basis of approaches of fundamental structural rheology of disperse systems priority of theoretical justification of which belongs to P.A. Rehbinder [27].

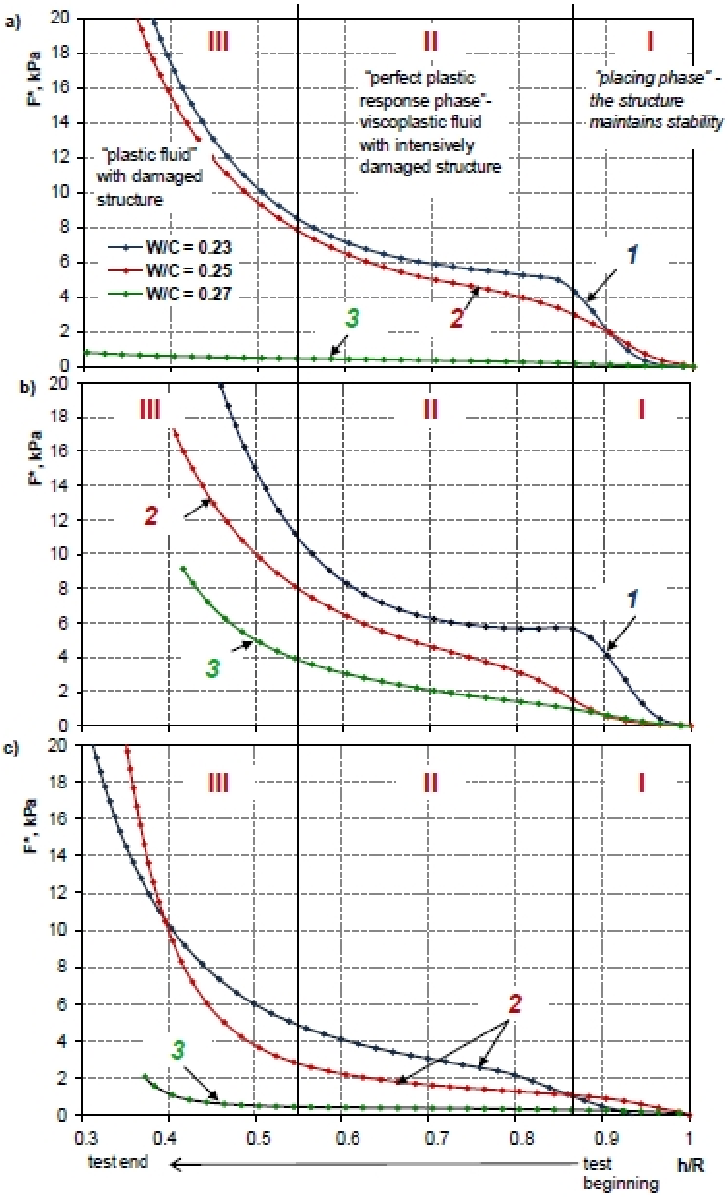

Figure 1. Typical tested cement pastes F*(h$_i$/R) curves.
a) system C – W; b) system C – W – P1; c) system C – W – P2.

Under the action of low compression stress on the first section of the curve within deformation range ~ 0.8 < h_i/R < 1 the structure maintains stability («placing phase» according to terminology of N. Roussel). Comparison $F^* = f(h_i/R)$ with classic rheological curve first obtained in the works of P.A. Rehbinder [27] allows correlating this section of «placing phase» with the section of viscoplastic fluid of disperse system with undisturbed structure on the curve of P.A. Rehbinder (Shvedov's model). When the stress on the second section increases with 0.5 < h_i/R < 0.8, the system is plastically deformed while its structure loses its stability («perfect plastic response phase» according to N. Roussel). This section can be correlated with the section of viscoplastic fluid with intensively damaged structure on the curve of P.A. Rehbinder (Bingham's model). Sudden increase of load and intensification of fluid on the third section h_i/R < 0.5 are related to full destruction of cement paste structure.

On this basis, it is suggested to evaluate the following criterial rheological characteristics by experimental $F^*(h/R)$ curves.

Value K_i suggested by N. Roussel for the identification of the material plastic properties is suggested to be calculated in two inflection points of $F^*(h/R)$ curves. In this case, value K_i corresponds to Shvedov's plastic yield stress (hereafter plastic yield value $K_i(I)$) in the first inflection point and to Bingham's yield stress (hereafter yield value $K_i(II)$) in the second inflection point.

It appears effective to use elasticity criterion λ first suggested by N.N. Kruglitsky [28] as a comprehensive parameter of evaluation of plasto-elastic properties to evaluate stability and durability of viscoplastic heterogeneous disperse systems

$$\lambda = \frac{E_1}{E_1 + E_2}, \tag{4}$$

characterizing the ratio of moduli of elasticity E_1 and E_2 corresponding to the developments of deformations at different stages of viscoplastic flow of disperse system.

Concerning the conditions of the implementation of squeezing test, the calculation of their values was conducted according to ratios

$$E_1 = \frac{K_i(I) \cdot h_0}{\varepsilon_0}, \tag{5}$$

$$E_2 = \frac{K_i(II) \cdot h_0}{\varepsilon_2}, \tag{6}$$

where h_0 is thickness of the deformed layer corresponding to the initial height of the sample, ε_0 is fast elastic deformation in the first inflection point of the curve $F^* = f(h_i/R)$, ε_2 is slow plastic deformation at the arrival to the second inflection point of the curve $F^* = f(h_i/R)$.

According to the approach the experimental results show three kinds of $F^*(h/R)$ curves. The first kind has expressed horizontal section of plastic deformation between the two points of inflection (No 1, Figure 1, a, b). For the systems rheological behavior of which corresponds to this kind the value of reduced load F^* required for the transfer from stable condition to plastic flow accounts for ~ 6 kPa, transfer into the condition of the flow with damaged structure happens with F^* = ~ 9 kPa. For such systems the values of plastic yield value $Ki(I)$ are within the range of 3.5 ÷ 5 kPa, yield value $K_i(II)$ – 5.5 ÷ 8.5 kPa (Table 2). These systems do not possess sufficient extrudability due to insufficient plasticity.

Table 2. Change of structural-mechanical characteristics of cement pastes depending on W/C-ratio and dosage of plasticizer.

<table>
<tr><th>System's specimen</th><th>Plasticizer, mass/mass cement (%)</th><th>W/C-ratio</th><th>plastic yield value $K_i(I)$, kPa</th><th>yield value $K_i(II)$, kPa</th><th>Elasticity λ</th></tr>
<tr><td rowspan="6">C – W</td><td rowspan="6">-</td><td>0.23</td><td>4.02</td><td>7.98</td><td></td></tr>
<tr><td>0.24</td><td>3.98</td><td>7.49</td><td>0.59</td></tr>
<tr><td>0.25</td><td>2.38</td><td>5.96</td><td>0.55</td></tr>
<tr><td>0.26</td><td>2.06</td><td>4.39</td><td>0.51</td></tr>
<tr><td>0.27</td><td>0.26</td><td colspan="2" rowspan="2">The system loses elastic-viscoplastic properties and stability while acquiring fluidity at the initial moment of loading at F^* < 0.3 kPa</td></tr>
<tr><td>0.28</td><td>0.24</td></tr>
<tr><td rowspan="5">C – W – P1</td><td rowspan="5">0.1</td><td>0.23</td><td>4.93</td><td>8.31</td><td>0.74</td></tr>
<tr><td>0.24</td><td>2.66</td><td>5.54</td><td>0.69</td></tr>
<tr><td>0.25</td><td>1.12</td><td>2.64</td><td>0.66</td></tr>
<tr><td>0.26</td><td>0.61</td><td colspan="2" rowspan="2">The system loses elastic-viscoplastic properties and stability while acquiring fluidity at the initial moment of loading at F^* < 0.3 kPa</td></tr>
<tr><td>0.27</td><td>0.44</td></tr>
<tr><td rowspan="6">C – W – P2</td><td rowspan="6">0.2</td><td>0.22</td><td>4.07</td><td>4.23</td><td>0.78</td></tr>
<tr><td>0.23</td><td>2.08</td><td>3.22</td><td>0.59</td></tr>
<tr><td>0.24</td><td>1.06</td><td>2.79</td><td>0.49</td></tr>
<tr><td>0.25</td><td>0.43</td><td colspan="2" rowspan="3">The system loses elastic-viscoplastic properties and stability while acquiring fluidity at the initial moment of loading at F^* < 0.3 kPa</td></tr>
<tr><td>0.26</td><td>0.24</td></tr>
<tr><td>0.27</td><td>0.18</td></tr>
</table>

For the second type of curves there are no expressed transitions between the section of the curve recorded (No 2, Figure 1 a, b; c). Value F^* corresponding to the start of plastic flow accounts for ~ 3 kPa, values of plastic yield value $Ki(I)$ are within the range of 1.0 ÷ 1.5 kPa, yield value $K_i(II)$ – 2.5 ÷ 3.0 kPa. Such systems possess best extrusion ability exactly due to their sufficient plasticity and capacity for viscoplastic flow without the damage of the structure.

The third type of the curve is typical for systems the structure of which is inevitably destroyed at the starting moment of loading with $F^* < 0.3$ kPa (No 3, Figure 1 a, b, c). As a result, they lose stability and acquire fluidity. Such systems do not possess the required elastic-viscoplastic properties and stability for extrusion ability.

3.2. The squeezing test with constant strain rate and firm stability

Potential of resistance of cement paste to deformations and destruction under the increasing load was evaluated by the example of three mixtures, one for each of the systems C – W, C – W – P2, C – W – P2. The mixtures were chosen by the criterion of required plasticity (comparable to values of plastic yield value $Ki(I) \cong 2.0 \div 2.5$ kPa) and capacity for visually holding the shape (Figure 2). Analysis of the received experimental data of the curves "displacement Δ – time τ" (Figure 3) shows that 3 typical sections can be distinguished on them.

Figure 2. Photo of the cement paste samples having firm stability.

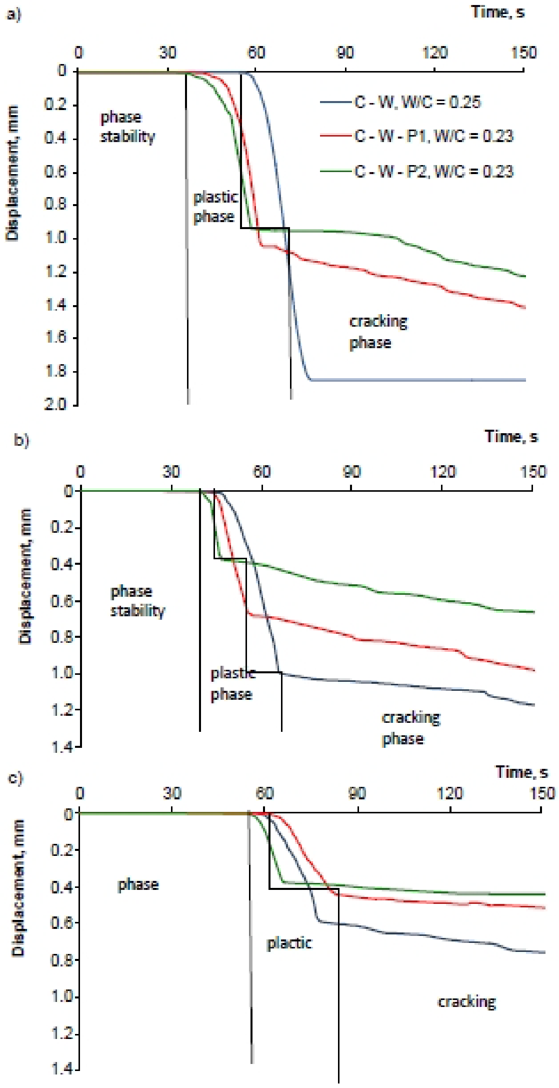

Figure 3. Tested cement pastes «displacement Δ – time τ" experimental results a) fresh cement paste; b) after 30 minutes from the beginning of cement paste hardening; c) after 60 minutes from the beginning of cement paste hardening.

The first section is characterized by the lack of deformations under the influence of load. The quantity of structural strength σ_0 calculated on the basis of the quantity load N at the start of deformation can be considered as the main criterion of buildability (Table 3). This is condition by the fact that structural strength σ_0 characterizes the ability of the system to maintain stability and resist to deformation when loaded.

Table 3. Change of strength and deformation of cement systems during setting time.

Setting time	Structural strength σ_0, kPa	Plastic strength σ_{pl}, kPa	Plastic deformation Δ_{pl}, mm
C – W (W/C = 0.25)			
~5 min	0.87	45.22	1.85
30 min	4.72	33.82	0.99
60 min	9.92	21.02	0.43
C – W – P1 (W/C = 0.24)			
~5 min	1.92	41.40	1.42
30 min	5.38	39.00	0.68
60 min	12.18	33.12	0.59
C – W – P2 (W/C = 0.23)			
~5 min	2.86	38.84	0.93
30 min	14.11	29.33	0.37
60 min	16.15	23.43	0.24

The second section is a section of plastic deformation. The system's ability to deform without destruction is evaluated by the quantity plastic strength σ_{pl} calculated on the basis of the quantity load N at the beginning of cracking. To characterize buildability, it seems reasonable to evaluate the quantity of plastic deformations on this section Δ_{pl}, which have to be minimized for 3D printable materials.

The third section is a section of crack formation and irreversibly destruction of the structure. On the experimental curves "compression force N – displacement Δ" the moment of the beginning of crack formation is definitely fixed by the peak of sudden drop of load (Figure 4).

4. Discussion

The transition between three test curves $F^* = f(h_i/R)$ types is linked to W/C-ratio and dosage of plasticizer.

W/C-ratio defining the concentration of particles in solid phase in the system is the main factor of structuring and strengthening of cement paste. This is why plastic yield value $Ki(I)$ as evaluation of structural stability for all systems naturally decreases with the increase of W/C (Table 2). When critical values are reached, W/C systems lose stability. These values of W/C in their turn depend on the properties of liquid phase in the system "cement + water".

Introduction of plasticizer into disperse system "cement + water" is a regulating factor of liquid phase properties changing surface developments on the border of the division of phases and molecular interactions between solid particles. When high-concentration disperse systems solid particle are formed under the influence of polar molecules of water, dispersion of solid phase particles takes place and its specific surface is increased. At the same time, adsorption of plasticizer molecules takes place on the surface of cement particles. Their monomolecular layer on the surface of particles suddenly lowers the level of free interfacial energy on the border of the division of phases, reduces the interaction force in the contacts between the particles by several digits. As a result, plasticity of the system increases and its flow under stresses becomes easier. Therefore, when plasticizer is introduced and its dosage is increased, the value of load required for the transfer of systems with the same concentration of disperse phase (W/C = const) from the state of stability to the state of viscoplastic flow reduces. For instance, for cement paste with W/C = 0.24 viscoplastic flow of systems C – W, C – W – P1 starts at $F^* \sim 6$ kPa and systems C – W – P2 at $F^* \sim 2.5$ kPa. Thus, the introduction of plasticizer is a regulating factor for plasticity of cement paste.

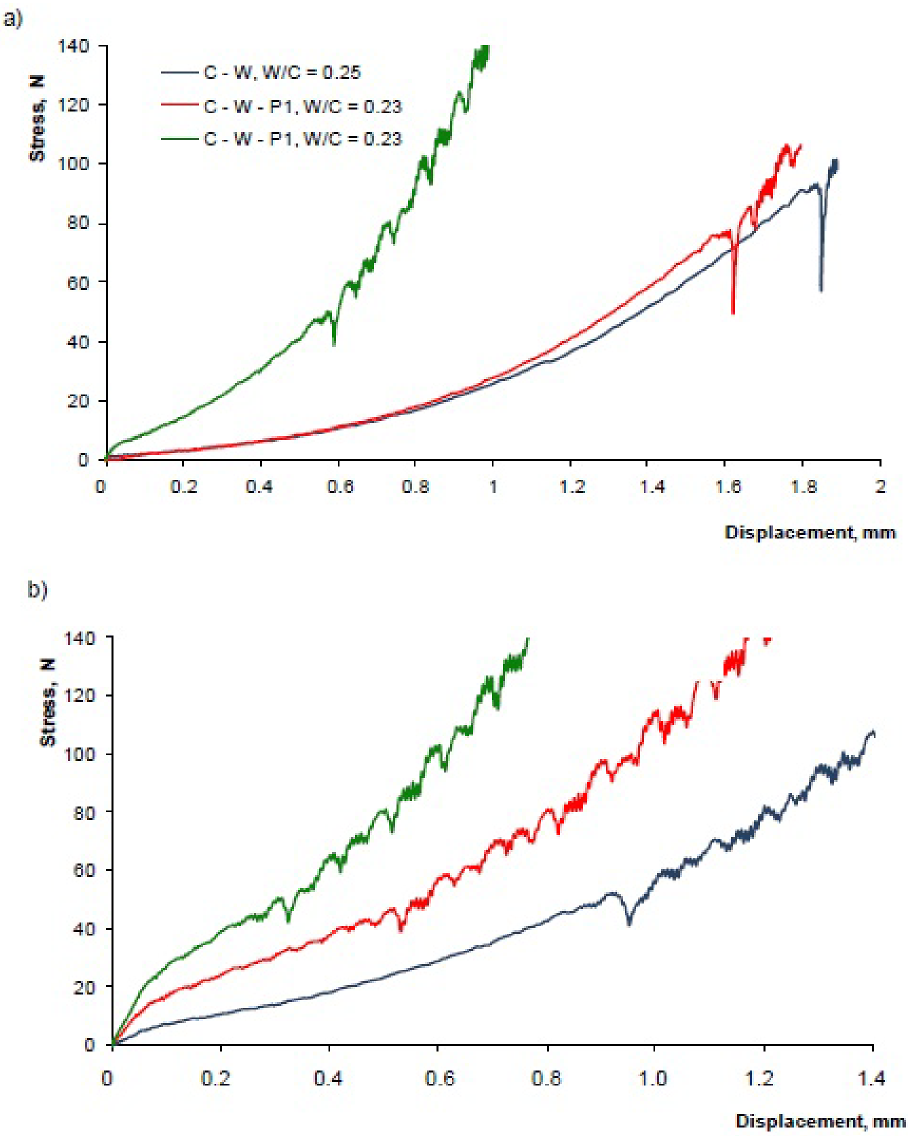

Figure 4. Tested cement pastes “compression force N – displacement Δ” experimental results a) fresh cement paste; b) after 30 minutes from the beginning of cement paste hardening.

Thus, the extrudability is defined by stability of cement pastes and their capacity for plastic flow with undisturbed structure under the influence of compression stress. To ensure this, the values of plastic yield value $Ki(I) \cong 1.0 \div 2.5$ kPa and elasticity criterion $\lambda \cong 0.5$ should be considered critical. With values $Ki(I) > 2.5$ kPa cement-based materials are not plastic enough for extrusion. With values $Ki(I) < 1$ kPa, $\lambda < 0.5$ the systems lose stability almost immediately after load application, their structure is irreversibly destroyed, the flow begins. The obtained values of quantities $\lambda = 0.51 \div 0.59$ for cement pastes possessing stability fully correspond to the data of N.N. Kruglitsky [28] according to which the value of elasticity criterion of at least $\lambda = 0.5$ corresponds to the stable state of disperse systems.

Analysis of the received curves “$\Delta - \tau$” for the samples tested right after their manufacture shows that system C – W displays the least values of structural σ_0 and plastic σ_{pl} strength and the largest values of plastic deformations Δ_{pl} (Table 3, Figure 3). At the same time, the curves “$N - \Delta$” show that complete destruction of the structure for this system happens right after the first cracks appear (Figure 4).

When plasticizer is introduced into the system, values of structural and plastic strength increase by 2–3 times and value of plastic deformations Δ_{pl} decreases by 1.5–2 times in the systems C – W – P1, C – W – P2. The nature of destruction changes: after the beginning of crack formation, it is typical for the samples of systems C – W – P1, C – W – P2 that multiple peaks of load fluctuation appear on the curves

"$N - \Delta$" indicating the appearance of microcracks. As a result, the interval between the moment when first cracks appear and destruction becomes longer, which is a sign of increased system stability to the influence of the load.

This effect of increased stability of cement paste is logically related to the influence of plasticizer. During adsorption of molecules of plasticizer on the surface of cement particles, functional groups of their radical (for example, OH^-, ONa^-, etc.) are directed to the dipolar medium due to their polarity and likeness to the liquid phase (water). The liquid phase lyophilic in respect to the radical will be drawn into the gap between cement particles, the thickness of adsorption-combined water layer will exceed the double length of the radical. As a result, the presence of adsorbed polar molecules of plasticizer in the system allows structuring the water in the interlayers between cement particles. Such structuring of disperse medium in cement pastes ensures the increase of their firm stability and consequently buildability. According to the experimental data, system C – W – P2 with the largest content of plasticizer is characterized by the maximum value of structural strength σ_0 and minimal plastic deformations Δ_{pl}. The nature of deformation and destruction of the studied cement systems logically changes in the process of their setting and hardening (Figure 4 b). As coagulation-crystallization phase contacts are formed in the structure during setting, the value of structural strength σ_0 grows for all the studied systems with increased time of hardening. At the same time, the ability of the system to plastically deform without destruction is reduced. Correspondingly, plastic strength σ_{pl} is reduced, too. The nature of destruction changes: after the beginning of crack formation, prolongation of the period of formation and accumulation of microcracks preceding the destruction is typical for all samples of the studied systems hardening during 60 min. According to the experimental data, system C – W – P2 with the largest content of plasticizer is characterized by the maximum value of structural strength σ_0 and minimal plastic deformations Δ_{pl} not only right after the manufacture but also after hardening during 30 and 60 minutes.

Therefore, introduction of plasticizer into cement paste allows increasing the stability of cement systems also during flocculation and hardening.

5. Conclusions

An effective method of evaluation of rheological behavior of viscoplastic 3D printable building materials is squeeze flow rheometry determining quantitative values of rheological parameters criterial for extrudability and buildability. Analysis of the study results shows that the use of the squeezing test with constant plate speed is effective for evaluation of extrudability. Interpretation of the results of this test from the positions of structural rheology of disperse systems allows categorizing the parameters of plastic yield value $K_i(I)$ *and* yield value $K_i(II)$, elasticity criterion λ as criteria defining the ability of 3D printable materials to plastically deform without structure destruction and maintain stability during extrusion. To ensure this, values of plastic yield value $Ki(I) \cong 1.0 \div 2.5$ kPa and elasticity criterion $\lambda \cong 0.5 \div 0{,}6$ should be considered criterial.

The squeezing test with constant strain rate is effective for the evaluation of buildability. The values of structural and plastic strength, plastic deformations defined by the results of this test characterize the system's ability to hold its form, resist the influence of increasing compressions stresses during multi-layer casting.

It has been established that W/C-ratio defining the concentration of solid phase particles in the system is the main factor of structuring and strengthening of cement paste. Structural stability of cement paste can be changed by 3–4 times by regulating W/C. Introduction of plasticizer as a factor changing the properties of liquid phase in the system "cement + water" is an effective method not only for plasticity regulation but also for increasing the resistance of 3D printable cement-based materials to the influence of load during the printing of constructions.

Development of the studies is related to the identification of effectiveness of the influence of viscosity modifying additives, fillers and filling agents of different chemical-mineralogical composition and dispersion on parameters of extrudability and buildability of 3D-cement based materials. Optimization of compositions and effective regulation of the properties of mixtures at all stages of 3D printing process requires quantitative evaluation and determination of criterial values of the specified set of their rheological parameters.

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