The use of plant materials for the synthesis of superplasticizer

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Abstract. The paper presents data on the synthesis of phloroglucinol-furfural modifier (1,3,5-trihydroxybenzene-2-furaldehyde oligomer) based on 2-furaldehyde (furfural) and 1,3,5-trihydroxybenzene (phloroglucinol). The synthesis of a modifier with different molar ratios of phloroglucinol / furfural was carried out. It was found that an increase in the molar ratio leads to an increase in the plasticizing ability of the modifier. The optimal concentration of the catalyst was determined to be equal to 50% by weight of phloroglucinol. Two chemical forms of the modifier were obtained: H-form and Na-form. The structure of various forms of the modifier has been studied by scanning electron microscopy. It was found that the oligomers used in the work for the synthesis of the modifier, in addition to 2-furyl methyl alcohol, do not have plasticizing properties. Purified 2-furyl methyl alcohol has weak plasticizing properties. It is shown that to achieve the best plasticizing effect, it is necessary to gradually introduce a condensing agent into the reaction mixture. With gradual introduction, a complete condensation reaction occurs between the monomers, which affects the improvement of the plasticizing properties of the resulting product. The spread of the cement mixture when using 0.3% of the additive based on the mass of cement in terms of dry matter is 19 cm.

1. Introduction
Currently, due to major environmental problems, as well as a serious shortage of mineral resources in construction, there are active developments in the use of plant biorenewable raw materials. A special role is given to the use of agricultural waste. In this regard, furfural is promising, obtained by acid-catalyzed dehydration of polysaccharide-containing agricultural waste [1, 2], including corn cobs, beet pulp, bran, sawdust and other waste.

Furfural and its derivatives are widely used in many industries such as plastics, pharmaceuticals and agricultural chemicals, etc. Furfural is widely used in industry due to its good solubility and its easy recuperation by steam distillation. Today all major oil companies use furfural as selective solvent in the refining of lubricating oils.

Orlova [3] found that furfural can be used for the production of binders, including highly filled composites with high mechanical characteristics. Orlova has developed low viscosity furfural binders with a gel time of 40-60 min.

Analysis of literature sources shows that furfural can be used as a modifier (plasticizing additive) in cement compositions. Dr. Al-Hubboubi et al. [4] established an increase in the corrosion resistance of concrete by introducing furfural into the concrete mixture in an amount of 3%. The studies presented in the work showed that furfural dramatically reduces the corrosion rate; the inhibition efficiencies were 62.7 and 63.8% due to 3% furfural addition to 35 and 45 MPa-concretes respectively [4].
Hussain et al. found that the addition of furfural to Iraqi cement significantly improved mechanical properties. It has been established that with the introduction of even 1% furfural, a plasticizing effect is already observed, and the greatest effect is achieved with the introduction of 3% furfural [5].

In works [6,7] it is shown that furfural and its derivatives have a good plasticizing effect and can be used for the production of superplasticizers. It is known that superplasticizers are used to regulate the mobility and structure formation of cement mixtures [8]. Superplasticizers are surfactants, so their main property is the ability of their molecules to adsorb on the surface of cement particles, with the formation of a very thin mono- or bimolecular layer, which increases the zeta potential on the surface of cement particles. As a result, the interfacial cohesion energy of the particles decreases and the degree of disaggregation of the particles increases [8-10]. The released immobilized water acts as a plasticizing agent. The adsorbed layer reduces the microroughness of the particles, thereby reducing the coefficient of friction between them. And, finally, the appearance of an electric charge of the same name during the adsorption of superplasticizer molecules on the surface of cement particles excludes the possibility of their adhesion under the action of electrostatic forces, thereby reducing the viscosity of the suspension. Along with the growth of crystals of neoplasms in the process of hydration, the repulsive effect of molecules with the same electric charge ceases, and the mobility of the concrete solution decreases [11-14]. As a result, with the addition of a super-plasticizer, the proportion of fine fractions of cement particles increases almost 2 times [15-16].

This paper presents the results of using furfural for the synthesis of phloroglucinol-furfural modifier for cement mixtures.

2. Materials and methods
The following reagents were used to synthesize the modifier:
– 2-furaldehyde (furfural) – an organic substance of the class of aldehydes with a heterocyclic core, which is a dark brown liquid with a density of 1.16 g/cm³ in accordance with GOST 10437-80. The mass fraction of 2-furaldehyde was 99.8%. The chemical formula of furfural is C₅H₄O₂.
– 1,3,5-trihydroxybenzene (phloroglucinol) is an organic substance of a class of phenols with a benzene nucleus, to which three hydroxyl groups are attached at positions 1,3,5. This compound is a transparent needle-like crystals with a melting point of 215 °C. Chemical formula C₆H₆O₃.

The plasticizing properties of the obtained modifier were determined on Portland cement grade PC500 D0. The values of the results of physical and mechanical tests of the original Portland cement without mineral additives are presented in Table 1. The study of the mobility of the modified cement suspensions was carried out using a mini-cone by determining the diameter of the spreading of the cement suspension under the action of gravity.

| No | Characteristic                                      | Value |
|----|----------------------------------------------------|-------|
| 1  | Residue on a sieve with a mesh size of 45 µm, %    | 2.1   |
| 2  | Blaine specific surface, cm²/g                     | 3420  |
| 3  | Normal density of cement paste, %                  | 26    |
| 4  | Water separation, %                                | 27    |
| 5  | Start setting, min                                 | 140   |
| 6  | End of setting, min                                | 250   |
| 7  | Compressive strength 3 days, MPa                   | 41    |
| 8  | Flexural strength 3 days, MPa                      | 5     |
| 9  | Compressive strength 28 days, MPa                  | 58    |
| 10 | Flexural strength 28 days, MPa                     | 6.5   |
3. Results and discussions
The synthesis of phloroglucinol-furfural modifier (1,3,5-trihydroxybenzene-2-furaldehyde oligomer) is a multistage process consisting of several stages: preparation of a solution with a given concentration of phloroglucinol and catalyst, heating the solution to the optimal temperature, adding furfural, heating the reaction mixture at a certain amount of time and its further slow cooling.

In the course of the study, for the synthesis of the modifier, several samples were prepared with different molar ratios of phloroglucinol / furfural. Having carried out the synthesis and studied the obtained oligomers, we can say that with an increase in the molar ratio, the plasticizing ability of the modifier increases. Also, the optimal concentration of the catalyst was found equal to 50% by weight of phloroglucinol. The medium of the modifier must be alkaline (pH = 11), since at pH less than 5 the modifier passes into its insoluble form (Fig. 1).

![Figure 1. Structural chemical formulas of various forms of the resulting modifier: a) Na-form, b) H-form.](image)

Temperature is also important during synthesis. After numerous studies, the optimal synthesis temperature was found equal to 70 ° C. Heating of the reaction mixture should be uniform, using a water jacket.

Two chemical forms of the modifier were obtained: H-form and Na-form. The H-form was obtained from a 20% modifier solution acidified with mineral acid to pH less than 5. Figure 2 shows SEM-images of various forms of the obtained modifier.

![Figure 2. SEM images of various forms of the resulting modifier: a) Na-form, b) H-form.](image)

Analysis of Figure 2 showed that the shape and size of the Na-form and H-form of the obtained modifier are significantly different. The Na-form particles have a smooth surface and rather large sizes, reaching several microns. In addition, the particles are lamellar with dense packing, pores are practically absent. H-shaped particles, on the contrary, have an uneven, highly rough surface. However,
their size is much smaller and is in the nanoscale; large porosity of particles and insignificant agglomeration are noticeable.

Determination of the plasticizing ability of the obtained modifier and the starting monomers was carried out using a miniconus according to the methodology developed at the Research, Design and Technological Institute of Concrete and Reinforced Concrete named after A. A. Gvozdev in Russia. The process of determining the plasticizing ability is shown schematically in Figure 3. The cement paste is loaded into a mini-cone, then it is lifted and the diameter of the spreading of the mixture is measured.

**Figure 3.** Schematic process for determining the plasticizing ability of additives for cement systems.

Were prepared a series of cement pastes with different consistencies of the investigated plasticizing additive. In this case, the water-cement ratio in all experiments was the same 0.4. Analysis of the data obtained showed that without the addition of a plasticizing additive, the spreading diameter of the cement paste is minimal (4.5 cm). With an increase in the amount of added additive, a significant increase in the diameter of the mini-cone spread is observed. The minimum dosage of phloroglucinol / furfural additive at which the maximum plasticizing effect is achieved is 0.3% by weight of the cement. Thus, the optimal dosage of the developed plasticizing additive is 0.3% of the cement weight (calculated on dry matter).

Cement mixtures were prepared with the same concentration of monomers and synthesized oligomers. The miniconus was filled with these mixtures, after which the cone was raised and the amount of spreading of the mixtures was measured with an accuracy of 0.5 cm using a ruler. The control mixture without added additives has a spread of 4.5 cm. The obtained data on the spread of the cone are presented in Table 2.

Analysis of the data presented in Table 1 showed that the monomers used in the work for the synthesis of the modifier, except for 2-furyl methyl alcohol, do not have plasticizing properties. Purified 2-furyl methyl alcohol has weak plasticizing properties. When used, the spread of the minicone increases by 1.6 times. However, this is not sufficient for using the oligomer as a superplasticizer.

With the introduction of synthesized phloroglucinol / furfural additive, the value of the spread of the miniconus increases significantly: with the instant introduction of the condensing agent (2-furaldehyde) by 3.5 times and 4.2 times with the gradual introduction of the condensing agent in comparison with the cement slurry without the additive. The improved plasticizing properties of phloroglucinol / furfural additive with the gradual introduction of the condensing agent is most likely due to the fact that with the gradual introduction of the condensing agent into the reaction mixture, a complete condensation reaction occurs between the monomers. It can be assumed that with the instant introduction of the condensing agent, the reaction of disproportionation of the condensing agent additionally occurs with the formation of 2-furyl methyl alcohol.
5. References

[1] Machado G, Leon S, Santos F, Lourega R, Dullius J, Mollmann M, Eichler P 2016 Literature Review on Furfural Production from Lignocellulosic Biomass Natural Resources 7 115-129

[2] Mariscal R, Maireles-Torres P, Ojeda M, Sádaba I, López Granados 2016 Furfural: a renewable and versatile platform molecule for the synthesis of chemicals and fuels Energy Environ. Sci 9 1144-1189

[3] Zaichenko M, Zaichenko S, Korsun A 2015 The Influence of Extra Mixing Water on the Properties of Structural Lightweight Aggregate Concrete Procedia Engineering 117(1) 1041-1047

[4] Al-Hubboubi S, Raouf Z, Abbood R H 2012 Corrosion-Resistance Characteristics of Concrete Containing Furfural Journal of Engineering 4 472-484

[5] Hussain H K, Wei L G, Hamdi H A, Abed D S 2011 Using of Furfural to Modify the Ordinary Portland Cement Applied Mechanics and Material 147 3-8

[6] Shapovalov N A, Poluektova V A 2015 Nanomodifier for cement mixtures and concrete Bulletin BSTU named after V G Shukhov 5 72-76

[7] Chen H, Ding J, Liang H, Yu H 2020 Synthesis and Application of Sustainable Furfuryl Alcohol-based Plasticizer ChemistrySelect 5 4085-4090

[8] Mollah M Y A, Adams W J, Schennach R, and Cocke D L 2000 A review of cement–superplasticizer interactions and their models Advances in Cement Research 12:4 153-161

[9] Han S, Plank J 2013 Mechanistic study on the effect of sulfate ions on polycarboxylate superplasticizers in cement Advances in Cement Research 25 (4) 200-207

[10] Ohtsuka Y, Atarashi D, Miyachi M, Sakai E 2015 Action Mechanism of Superplasticizer in Consideration of Early Hydration of Cement Journal of Advanced Concrete Technology 1(7)
373-378

[11] Salem M, Alsadey S, Johari M 2016 Effect of Superplasticizer Dosage on Workability and Strength Characteristics of Concrete Journal of Mechanical and Civil Engineering 13(4) 153-158

[12] Yamada K, Ogawa S, Hanehara S 2001 Controlling of the Adsorption and Dispersing Force of Polycarboxylate-Type Superplasticizer by Sulfate Ion Concentration in Aqueous Phase Cement and Concrete Research 31 375-383

[13] Vinogradova L A, Rusakova Yu P 2019 Investigation of the influence of the superplasticizer SP-2VU on the construction and technological parameters of concrete Bulletin BSTU named after V G Shukhov 3 93-99

[14] Shachneva E Yu, Khentov V Ya 2018 The main features and characteristics of chemical and physicochemical methods for the analysis of surfactants Chemical bulletin 1(3) 4-15

[15] Heikal M, Morsy M S, Aiad I 2006 Effect of polycarboxylate superplasticizer on hydration characteristics of cement pastes containing silica fume Ceramics – Silikáty 50(1) 5-14

[16] Smirnova O M 2016 Compatibility of portland cement and polycarboxylate-based superplasticizers in high-strength concrete for precast constructions Magazine of Civil Engineering 6 12-22

[17] Wang H, Yang X, Xiong W, Liu X, Zhang Z 2013 Synthesis and the Effects of New Melamine Superplasticizer on the Properties of Concrete International Scholarly Research Notices 2013 708063

[18] Xiang S, Gao Y, Shi C 2020 Progresses in Synthesis of Polycarboxylate Superplasticizer Advances in Civil Engineering 2020 8810443

[19] Sathyan D, Anand K B, Mini K M, Aparna S 2018 Optimization of superplasticizer in portland pozzolana cement mortar and concrete IOP Conf. Series: Materials Science and Engineering 310 012036

[20] Pourchet S, Comparet C, Nonat A, Maitrasse P 2006 Influence of three types of superplasticizers on tricalciumaluminate hydration in presence of gypsum 8th CANMET/ACI International Conference on Superplasticizers and other chemical admixtures in concrete (Sorrento, Italy) pp 151-158

Acknowledgments

The study was carried out within the framework of the State task of the Ministry of Education and Science of the Russian Federation regarding the allocation of funding for the creation of new laboratories in 2021, including under the guidance of young promising researchers of the national project "Science and Universities" (the name of the laboratory "Development of scientific and technical foundations for the creation of polymer systems from renewable plant raw materials", agreement №075-03-2021-061 / 3) using equipment of High Technology Center at BSTU named after V G Shukhov.