

Investigation of Cement Compositions Modification with Organosilicon Compounds

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Abstract. The authors conducted the research to identify a mechanism for polyphenylsiloxane inclusion into a cement composition and proposed an easier way to introduce an organosilicon modifier into cement clinker. In particular, the authors found out that polyphenylsiloxane reacts with portland clinker minerals during mechanochemical activation. The interreaction products were identified and studied. The authors synthesized the polymetallorganosiloxane compounds similar to the products obtained due to the reaction between polyphenylsiloxane and cement clinker at mechanochemical activation. It was demonstrated that polyphenylsiloxane reacting with calcium oxide and calcium carbonate results in polycalciumphenylsiloxane obtaining. Further, the article presents the comparative study of the physical and chemical and resistance characteristics of the cement compositions modified with polyphenylsiloxane and polycalciumphenylsiloxane. It was demonstrated that polycalciumphenylsiloxane improves cement composition freeze resistance as well as bending and compression resistance better than polyphenylsiloxane.

1. Introduction

The literature dwells upon the opportunity to apply organosilicon compounds as cement composition modifiers to improve their chemical and physical properties [1-4]. Previously, it was demonstrated that polyphenylsiloxane inclusion into a cement composition improves the material strength and freeze resistance. However, under industrial scale composition production one can point to the unequal distribution of the chosen additive throughout the whole composition leading to cement unpredictable properties. The purpose of our paper was to research the mechanism for polyphenylsiloxane inclusion into a cement composition and propose an easier method to add an organosilicon modifier to the composition.

2. Discussion

2.1. Study of the reaction between portland cement and polyphenylsiloxane

To identify the mechanism of polyphenylsiloxane inclusion into a cement composition, we carried out the reaction between polyphenylsiloxane and portland cement during mechanochemical activation. The reaction was conducted in the planetary ball mill "Pulverisette 6". Mechanical activation was



carried out at 650 r.p.m. for 4 minutes. The obtained composition was extracted with chloroform in the Soxhlets extraction apparatus and further divided into soluble and insoluble fractions.

The soluble fraction (PCaPS-0) represents a solid and non-melting (up to the decomposition temperature) white substance rapidly soluble in chloroform, toluene, dimethyl sulfoxide and benzene with a molar weight over 5,000. The soluble fraction elemental analysis demonstrated presence of calcium and silicon atoms in the compound composition. The test for aluminium and ferrum atoms contents in the soluble fraction was not successful. The soluble fraction research with the infrared spectroscopy (A.1) and X-ray phase analysis (A.2) showed that this fraction is polycalciumphenylsiloxane.

Calcium atoms can be contained in portland cement in the form of calcium oxide and calcium carbonate. When preparing cement compositions for setting, the practicable and simple mixing of cement components and modifiers is very important. To simplify and reduce the number of stages in the process of a ready cement composition obtaining, the authors suggested it is easier to introduce PPS into a composition providing calcium atoms were initially added to PPS and further add the obtained polycalciumphenylsiloxane modifier into clinker during grinding. Besides, we studied the opportunity to conduct preliminary synthesis of the polycalciumphenylsiloxane compounds at mechanochemical activation using calcium oxide and carbonate as the initial compounds.

2.2. Polycalciumphenylsiloxane synthesis

To study the process of calcium atoms and PPS reaction, the authors decided to conduct the polycalciumphenylsiloxane formation reaction in the similar conditions in compliance with the following schemes:

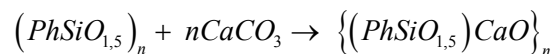
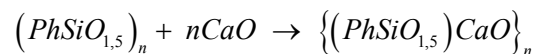


Table 1. Polycalciumphenylsiloxane elemental analysis.

N o.	Polymer index	No. of the fraction	Given Si/Ca	Found out, %					Calculated for (PhSiO _{1.5})CaO, (%)	
				ω, %	C	Si	Ca	Si/Ca	Si	Ca
1	PCaPS - 1	1	1:1	65.2	40.1	17.5	19.7	0.85	16.4	20.1
		2		34.8	-	1.4	51.2	0.04	1.7	65.6
2	PCaPS - 2	1	1:1	50.8	37.2	19.2	18.4	0.75	15.6	20.6
		2		33.8	-	1.54	48.8	0.03	1.54	61.32

The compounds obtained by means of mechanochemical activation were extracted with chloroform in the Soxhlets extraction apparatus and divided into two fractions. Soluble and insoluble fractions were studied by means of elemental analysis (Table 1) [6], infrared spectroscopy (A.1), NMR-spectroscopy, X-ray phase analysis (A.2) and electron force microscopy (EFM). The obtained data confirm the soluble fractions represent the polycalciumphenylsiloxane compounds with the silicon/calcium ratio close to one while insoluble fractions are unreacted calcium containing reagents.

2.3. Influence of the silicon containing modifier inclusion on the cement composition strength and freeze resistance

The influence of non-functional silicon containing compounds influence on the cement composition strength and freeze resistance was studied with the help of the cement systems modified with PPS containing the superplasticizing agent s 3 (0.2 % of PPS + 0.6 % of S-3) and PCaPS containing the superplasticizing agent s 3 (0.2% of PCaPS + 0.6% S-3) of the clinker weight.

The study was conducted for three cement and sand grouts produced in accordance with GOST 310.4 on the basis of standard uniform sand with the normalized grain one.

Modified cement compositions with a similar grind fineness were used as cementing components: the specific area under the air permeability method was 410-430 m²/kg. The amount of water for mixing was calculated as necessary for obtaining of the grouts with the consistence characterized by the water pollution class of 114-116 mm. The research were conducted for grouts of the cement compositions without any modifiers. Before sample freezing the authors conducted control measurements of bending and compression resistance under normal conditions. Further the samples were exposed to twelve cycles of freezing after which the bending and compression resistance values were tested again. The results are provided in the Table 2.

Table 2. Results of freeze resistance tests conducted for modified samples.

Index and modifier percent composition	Specific area of cement compositions, cm ² /g	Water need	WPC, mm	Bending/compression resistance, MPa		Bending/compression resistance reduction, %
				control (-bending-) (-compression-)	After 12* cycles (-bending-) (-compression-)	
without a modifier	4321	0.4	116	7.21 55.90	2.03 19.85	-71.84 -66.29
0.2% PPS 0.6% S-3	4263	0.34	117	5.84 58.13	2.28 20.50	-60.95 -62.81
0.2% PCaPS 0.6% C-3	4570	0.34	115	8.12 64.40	6.14 43.90	-24.38 -31.83

The research results (Table 2) demonstrated the grouts without any additives after 12 cycles of freezing-defrosting in the water had the bending resistance lowered by 71.84% while the compression resistance lowered by 66.29% comparing to the control samples.

The sample containing PPS demonstrated the 60.95% decrease of its bending resistance and the 62.81% decrease of the compression resistance. The sample modified by PCaPS demonstrated the bending and compression resistance decrease equal to 24.38% and 31.83%, correspondingly. Therefore, the cement composition with PCaPS has virtually the same strength after freezing and reaches maximum bending/compression resistance values comparing to the sample modified with PPS.

3. Conclusions

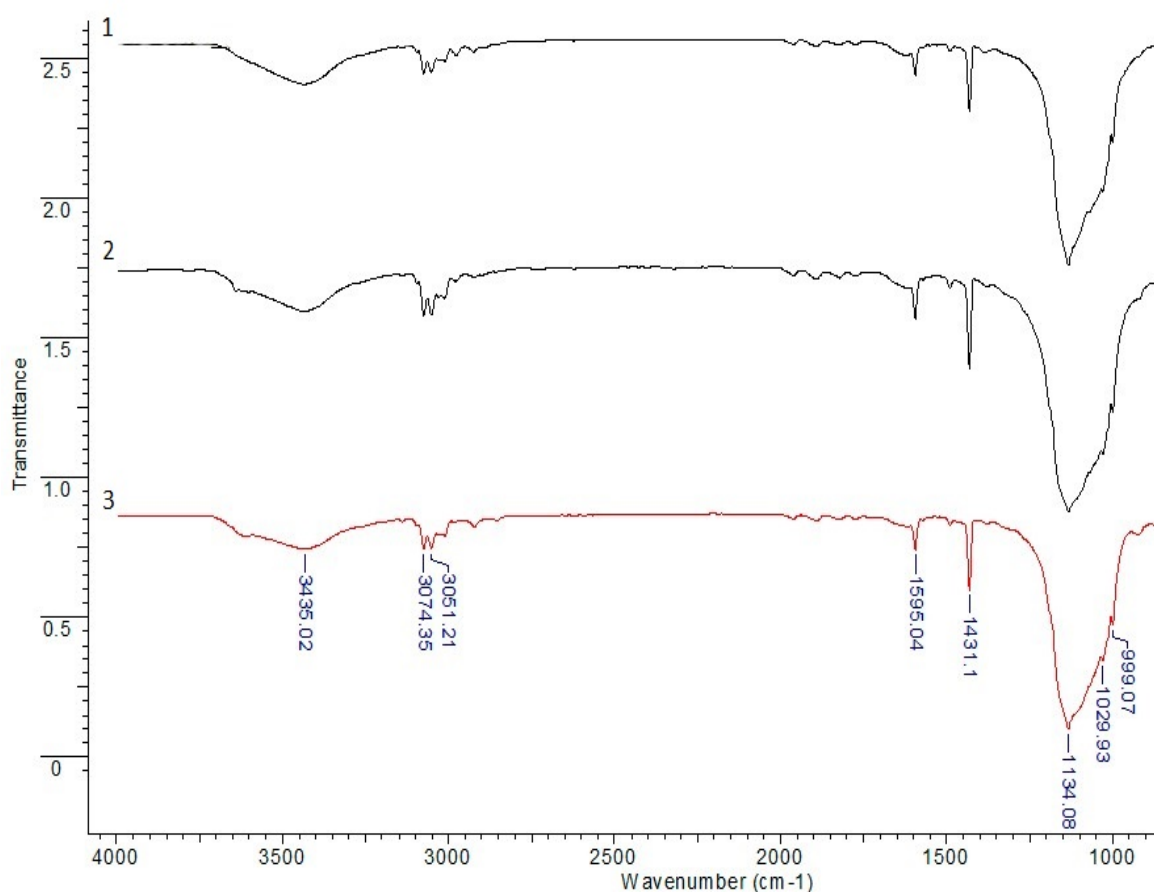
The research of the mechanism for PPS inclusion into the cement composition demonstrated that the latter reacts with the calcium containing clinker components. The authors synthesized polymetallorganosiloxane compounds similar to the products obtained due to the reaction between polyphenylsiloxane and cement clinker at mechanochemical activation. It is shown that PPS

interacting with calcium oxide and carbonate leads to PCaPS obtaining. The authors offered a method for a simple organosilicon modifier inclusion in cement clinker. Further, the article presents comparative study of the physical and chemical and strength (resistance) characteristics of cement compositions modified with polyphenylsiloxane and polycalciumphenylsiloxane. It was demonstrated that polycalciumphenylsiloxane improves cement composition freeze resistance as well as bending and compression resistance to a greater extent than polyphenylsiloxane.

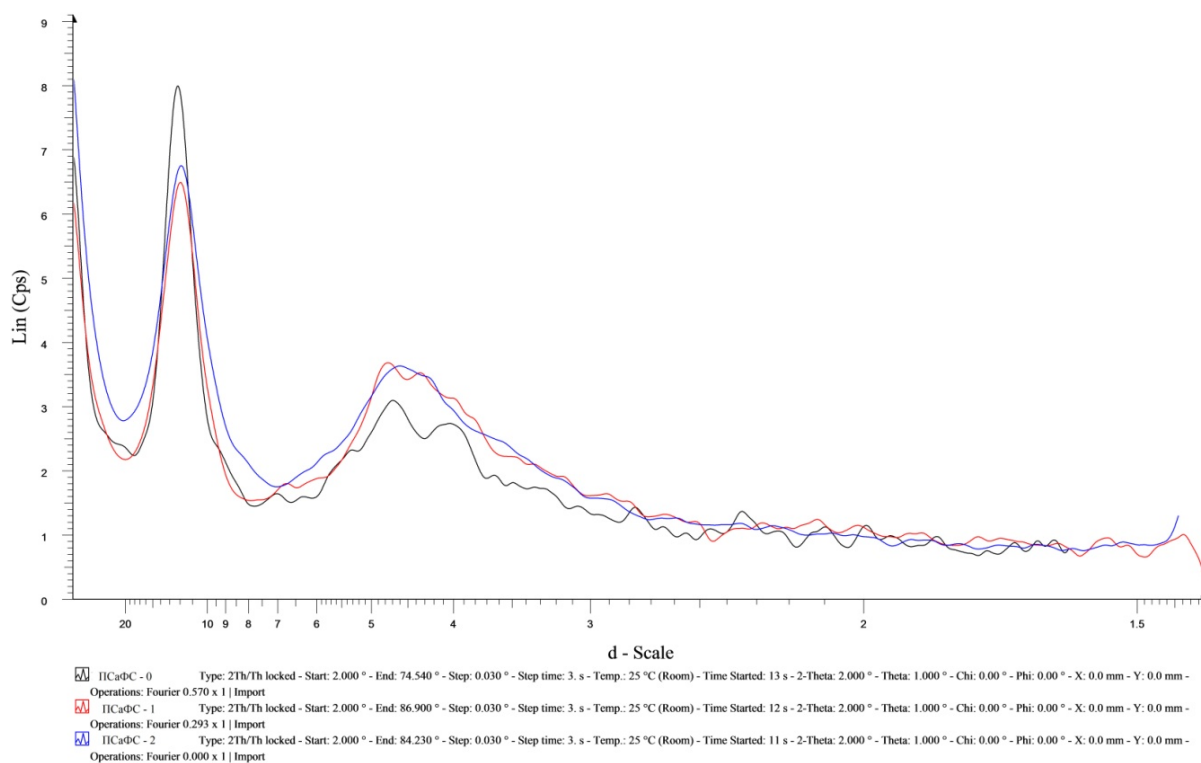
Acknowledgments

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Appendix A



A.1. Infrared spectra of the PCaPS compounds: 1 – PCaPS-0; 2 – PCaPS-1; 3 – PCaPS-2.



A.2. XRF spectra of the PCaPS compounds: 1 – PCaPS -0; 2 – PCaPS-1; 3 – PCaPS-2.

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