System "dispersed polyvinyl acetate-calcium silicate" in furnishing materials

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Received 01.10.2023, accepted 20.12.2023
https://doi.org/10.32347/tit.2023.61.0106

Abstract. This article focuses on the processes of interaction between calcium silicate hydrates and dispersed polyvinyl acetate in tight films with the aim of developing compounds meant for restoration and finishing works. The basis of this development relies on the concept concerning the determining role of the crystal-chemical factor of the silicate phase in the formation of organic-mineral compounds of increased durability. The characteristics of dispersed calcium silicate hydrates are portrayed. The preparation conditions, accounting for the synthesis of the product of submicrocrystalline structure, conforming with the stoichiometry $CaO:SiO_2=0.8-2.0$ have been determined. The interaction has been studied for compounds achieved by mixing ingredients in a rapid whirling mixer, and subjected to hardening at T=20+2 °C. With the aid of XRD, DTA and Infra-Red Spectrometry methods the formation process of the sophisticated polymer silicate phase in the material was observed for a period of 90 days. The properties of the film were investigated and its high resistance against the influence of external factors was established. On this basis a conclusion concerning the quite high effectiveness of substituting portland cement with dispersed calcium silicate hydrate in polymer cement compounds has been made White colour and other various special properties determine the suitability for repair and finishing works on facades of buildings.

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Key words: calcium silicate hydrates, submicrocrystalline structure, dispersed polyvinyl acetate, polymer silicate phase, dispersed calcium silicate hydrate.

INTRODUCTION

The phenomena occurring during the hardening of polymer cement materials are sufficiently and widely studied, especially the sophistication of their mechanism. It is presumed that [1] during the initial period of structure formation, the needle like crystals constituting the cement germinate to accumulate the macro-molecules of the polymer. During this period the hydration of cement is limited. A notion exists [2] that, when polyvinyl acetate dispersion is added into concrete the cement particles are covered by a thin film of polymer and during hardenig the crystals join together in a membrane. The water contained in the dispersion unites and an elastic membrane composed of polyvinyl acetate remains.

Agreeing with certain understandigns [3], anhydrous mineral and high polymer bonds do not chemically react together. It is assumed that, during the hardening process of polymer-cements, there occurs the formation of an independent framework that reinforces the polymer-cement. The differences in the correlation of the ingredients lead to the alterations of the character of structure formation, hence affecting the properties of the composite.

Subsequently, the complexity of the processes facilitating the hardening of polymer cement compounds, determines a certain contradiction concerning the ideas about the mechanism. However s is of necessity to focus research on the study of specifically such conditions of interaction. Note that the structure formation of such systems is basically considered to be that of a dense body of a moulded concrete mixture. In accordance with our assessmer special attention was not paid to the peculiarities of structure formation in thin films at increased water content of the system. The current research focuses am study of specifically such conditions of interaction.

RAW MATERIALS AND METHODS

Dispersed calcium silicate hydrates obtained through hydro-thermal synthesis, based on the famous methods [4,5] were used, Slaked lime and quartz sand were employed as raw materials also. The quantity of reactive calcium and magnesium oxides in the lime constituted 80-90% by mass, while that of carbon dioxide was not more than 5% Quartz sand constituted not less than 80% mass of silica. The correlation between the oxides of calcium and silicon in the raw material mixture for synthesis was attained on the basis of the acquired basicity of the produced calcium silicate hydrate [2,3,13].

The grinding of raw materials was carried under wet method in a ball mill with ceramic lining. The achieved suspension was subjected to hydrothermal treatment in a chemical reactor with an intermixing device, later filtered and dried. These well studied and exhausted parameters facilitated the attainment of a non¬crystalline product, that isofan unstable state. The identification of the products was performed with the aid of physical-chemical methods. The properties of dispersed calcium silicate hydrates are as follows: specific surface 10.000-30.000 m^2/kg; density 1.500-1.800 kg/m^3; bulk density 200-250 kg/m^3 [5].

In order to observe the fluctuations of the interaction character, depending on the structure of the silicate, the wollastonite, calcium carbonate and silica were employed.

Polyvinyl acetate dispersion (PVAD) mark DF 48/5 CL of particle size 1-3 microns was used as water dispersed polymer. The compounds were prepared by mixing ingredients in a high-speed mixer so as to achieve compounds having viscosity of 20-30 sec. The solidification of the coating occurred under normal conditions at 18+2 °C [6-11].

The source materials and the interaction products were identified with the aid of XRD, DTA and Infra-Red methods, as well as the measurements of potential difference by the method of electro-osmosis [1]. The effective viscosity was determined with the aid of a viscometer at a temperature of 20+1 °C. The coefficient of water resistance and impact strength of the film (membrane) were determined in accordance with the research methods [12].

RESULTS AND DISCUSSION

As shown on Fig. 1 polymer-silicate materials are characterised by a general law expressing the increase in strength and elasticity at the initial period of solidification with stabilisation with respect to time when preserved in air as well as in water.

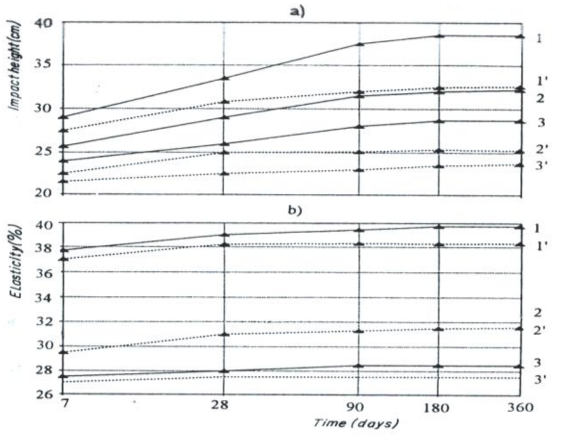

Fig. 1. Kinetic curves for impact height (a) and elasticity (b) of coatings based on CSH with basicity: 1,1'-2.0; 2,2'-1.5; 3,3'-0.8. Remarks: — conservation in air in water

The comparison of strength properties of the studied compounds based on lime powder, wollastonite and chalk paste that is a substance of stable and crystal structure, shows that the latter possesses impact resistance of 2-2.5 times less than the polymer silicate coating based on CSH like C-S-H (I) (Fig. 2). Besides the studied coatings based on C-S-H (I) with concentration PVAD 13-30% have coefficient of water resistance 0.85-0.99 differing from the compared analogues. Hence, the principle differences in properties may be linked with the role of mineral components of a compound, whereby active physical-chemical processes probably occur in the system containing CSH of submicrocrystalline structure, and facilitating the synthesis of strength [13-15]. According to thermographic readings for samples, the interaction in the system is accompanied with the appearance of a complex polymer silicate phase “X” which can be assessed owing to the presence of a double exothermal effect at maximum of 325 and 420 °C, with the absence on curves, of the initial components.

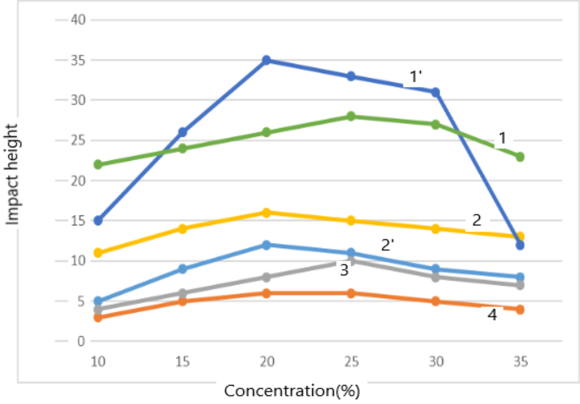

Fig. 2. Influence of PVAD content on the coefficient of water resistance (1', 2') and impact height of coatings (1, 2, 3, 4) based on: 1, 1'. CSH; 2,2'. Wollastonite; 3. Lime powder; 4.Chalk paste

It is of necessity to note that, an alternative process in the systems containing anhydrous mineral compounds of stable crystalline structure is viable for instance with silica, calcite and anhydrous wollastonite. Curve on the DTA charts shows that the compound based on wollastonite is characterised of an exoeffect at a temperature range of 320-650°C and maximum at 400 and 600 °C, thus corresponding to PVAD [16,17].

Earlier investigations on compounds possessing silica and calcium carbonate have established [8] the prolongation of unstable disintegrating phases in such systems. Distinguishing from the above process, the presence of CSH provides an intensive and a complete interaction by accelerating the system's structure formation. The DTA data, based on specimen aged 48 hours, 90 and 360 days of hardening provides the proof. All the compounds have practically the same thermal effect, notwithstanding the significant differences in time conservation.

The most reactive part of PVAD molecules is considered to be the carbonyl C=0. Its presence is confirmed by absorption band of 1700 cm^{-1} (Fig. 3, curve 1).

Besides, the C-O-C, group characterised by spectral band 1.200 cm^{-1} (Fig. 4), is necessary for the reaction capacity. Particularly, according to changes in absorption band, which is related to these groups, we can judge the changes in the whole system.

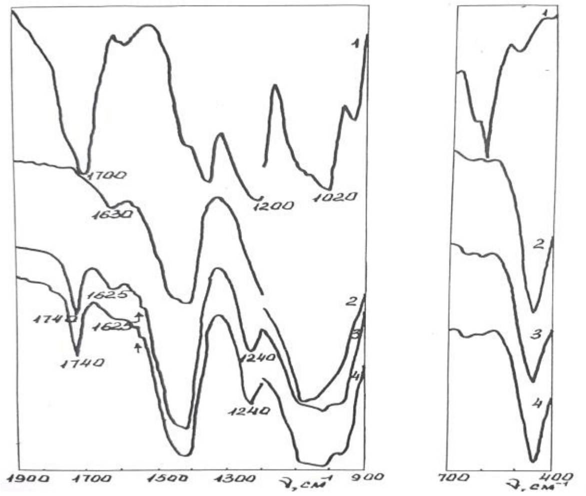

Fig. 3. IR spectrograms: 1-PVAD: 2-calcium hydrosilicate CSH 1); 3-a sample of polimersilicate coating with A concentration 20%; 4-the same with a concentration of 30%

The availability of un-divided electron pairs in the oxygen atom, which takes part in the mentioned bondings stipulates it to acquire the properties of an electron-donor as well as the possibility in conjunction with these of forming a donor- acceptor bond [8]. Calcium ion acts as the eletron acceptor in the CSH with the formation of a compound [17].

The Infra-Red spectroscope (IRS) (Fig. 3, curve 3,4) graphs of the investigated compounds record a visible displacement of 1.630 cm^{-1} of about 5 cm^{-1} less, which is caused by the nature of the binder [18,19].

Besides, the characteristic of the donor-acceptor interaction between Ca-ion and carbonyl group, evaluated by the absorption band 1.550-1.560 cm^{-1} of low intensity, is known [8]. In the studied polymer silicate system it is difficult to record such a band, due to its coincidence with the vibration of the silicate group C-S-H (I) at 1.420 cm^{-1}. In this zone on the IRS graphs spectroscope insignificant vibrations at 1.550-1.560 cm^{-1}, (Fig. 3, curve 3,4) corresponding to the formation of complicated compounds, characterisign of donor-acceptor interaction between the calcium ion and the carbonyl group of PVAD are observed.

As shown by curves of IRS, a shift of vibrations of carbonyl group 1700 cm^{-1} by 40 cm^{-1}, that is 1.740 cm^{-1}, is obvious also for the C-O-C group 1.200 cm^{-1}, that is 1240 cm^{-1}. The film formation process is accompanied by changes in bond shape of the silicate components. The IRS graphs, expressed the increase in absorption band in zones of 900 - 1.200, 450 - 650 cm^{-1}, relating to the valency vibrations of Si-O.

As indicated by the investigations, the electrokinetic potential (EKP) of the polymer containig dispersions of CSH can vary in wide limits, depending on the PVAD concentration (Fig 4, curve 1). The initial CSH possesses a negative EKP (-64 mv), which is characteristic for the majority of the natural and synthetic silicates [51] and explained by the peculiarities of the crystalline structure. Distinguishing from CSH, the PVAD in water possessses a positive EKP (+11 mv). The difference in charge sign on the surface of the CSH and PVAD particles in the blended dispersion facilitates the interaction of particles thus providing conditions for heterocoagulation. Thus, varying the correlation of the concentrations contrary to the charged phases ought to alter the structure state of the system. Experiments show that, the addition of PVAD into CSH dispersion decreases the EKP to zero and later attains positive values. However, isoelectrical point is attained at very high PVAD concentration 90%.

Curve η-C is characterised by two sections (Fig. 4, curve 1): a rapid reduction in EKP is observed for regions with minor concentrations of PVAD. whereas after inflection when PVAD content is 10-20% a relatively gradual change in EKP with respect to rise in concentration is observed.

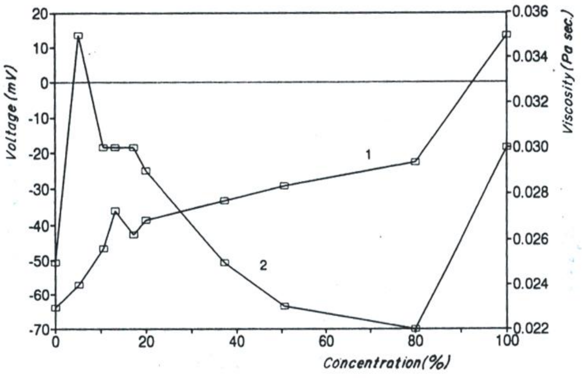

Fig. 4. Dependence of EKP (curve 1) and effective viscosity (curve 2) of polymer silicate suspension upon the PVAD concentration

The appearance of the point of inflection on the curve proves of the transition of the dispersion from one structure state to the other, which is caused by the achievement of a specific correlation of the surface charges of CSH and PVAD particles. Therefore, in the same regions of PVAD concentrations (10-20%), the maximum value of effective viscosity of dispersions is observed (Fig. 4, curve 2). The addition of PVAD and increase in viscosity, corresponding to the strengthening of structure continues till the achievement of anisotropy on the surface charge of the CSH particle.

Such a state is linked with the formation of a large quantity of bridge bondings of the CSH particles and PVAD globules.

The results of interaction of the system under consideration account for the formation of a film (thickness 1.5-2.5 mm) with the following properties: total drying (dehydration) 1.0-1.2 hrs,; impact strength 6.3-7.4 MPa; adhesion to foundation 1.6-1.8 MPa; coefficient of water resistance 0.94-1.0; frost resistance 35-60 cycles; atmospheric resistance 350-600 cycles.

The experience of utilising active interaction of calcium silicate hydrates and polymer in film is relevant for the preparation of painting materials.

CONCLUSION

1. Physical-chemical investigations on the process of structure formation of the compounds under consideration confirm that their interaction activity is higher than for similar systems, containing anhydrous minerals of stable crystalline structure.
2. The achieved coatings are found to be water- resistant, and this is regarded as one of the most significant properties accounting for the durability of paints as construction materials.

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Система "дисперсний полівінілацетат-силікат кальцію" в оздоблювальних матеріалах

Євгенія Петрікова, Наталія Амеліна, Алла Майстренко, Оксана Бердник

Анотація. У статті розглядаються процеси взаємодії гідратів силікату кальцію з дисперсним полівінілацетатом у тонких плівках з метою розробки сполук, призначених для реставраційних та оздоблювальних робіт. В основу даної розробки покладено концепцію щодо визначальної ролі кристалохімічного чинника силікатної фази в утворенні органо-мінеральних сполук підвищеної міцності. Наведено характеристики дисперсних гідратів силікату кальцію. Визначено умови отримання, що враховують синтез продукту субмікрокристалічної структури, що відповідає стехіометрії CaO:SiO2=0,8-2,0.

Взаємодія була вивчена для сполук, отриманих шляхом змішування інгредієнтів у швидкісному вихровому змішувачі та твердіючих при T=20+2°C. За допомогою методів XRD, DTA та інфрачервоної спектрометрії процес утворення складної полімерсилікатної фази в матеріалі спостерігався протягом 90 днів. Досліджено властивості плівки та встановлено її високу стійкість до впливу зовнішніх факторів. На підставі цього зроблено висновок про досить високу ефективність заміни портландцементу дисперсним гідратом силікату кальцію в полімерцементних сумішах. Білий колір і інші різноманітні особливі властивості визначають придатність для ремонтних і оздоблювальних робіт на фасадах будівель.

Ключові слова: гідрати силікатів кальцію, субмікрокристалічна структура, дисперсний полівінілацетат, полімерсилікатна фаза, дисперсний гідрат силікату кальцію.