Repair compositions based on methyl methacrylate modified with polyphenylsiloxane resin for concrete and reinforced concrete structures

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Abstract. In this paper, we consider the development of repair compositions for concrete and reinforced concrete structures based on methyl methacrylate modified with polymethyl phenyl siloxane resin. The condition has been studied and the problem analyzed in the country and abroad, as well as the selection of components for the repair composition. As a binder, methyl methacrylate curable with benzoyl peroxide in the presence of a catalyst - dimethylaniline and a modifier - polymethylphenylsiloxane resin would be used. The filler was finely ground quartz sand. The operational and physicomechanical properties of the resulting compositions were studied: photoabsorption, compressive strength, and tensile strength. Experimentally, the optimal ratio of polymethylphenylsiloxane resin in the composition was found to be 2.5 mass. parts of the modifier per 100 mass. parts including a binder. It was found that the introduction of polymethylphenylsiloxane resin does not significantly affect the adhesion characteristics, the tensile strength is reduced to a small extent. Moreover, the water absorption of the cured composition with a modifier content of 3 mass. parts compared with unmodified resin is reduced four times.

1. Introduction

At present, for repairing concrete and reinforced concrete structures [1, 2] for repairing cracks, chips, and internal cavities, repair compositions based on various polymer compositions have become widespread [3-7]. In particular, compositions based on epoxy resins are widely used [8–13]. However, the main disadvantage of these formulations is the increased viscosity of the epoxy binder. It is possible to eliminate it by introducing diluents, including active ones [14-18]. However, in general, this does not solve this problem. The same applies to repair compositions based on unsaturated polyester resins and other polymer binders [19, 20]. The viscosity of the composition can be reduced by using the low viscosity methyl methacrylate monomer (MMA). Due to their low viscosity, they easily penetrate the porous structure of building materials, providing them with increased water resistance and high strength characteristics [21, 22]. Currently, a number of formulations based on MMA are known. Known composition based on MMA, tertiary amine and polyisocyanate, cured at room temperature with benzoyl peroxide. However, as practice has shown, the composition has several disadvantages. This is, in particular, increased water absorption and moisture absorption and,
in connection with this, possible foaming of the binder, accompanied by a corresponding increase in the porosity of the system and a decrease in strength characteristics.

The aim of the presented work was to obtain a binder material for repair compositions and concrete polymers free from the above disadvantages. The goal was supposed to be solved by introducing organosilicon polymer compounds into the composition.

2. Methods

For the study, the following initial components were taken:
- methyl methacrylate (methyl ester of methacrylic acid, MMA) – produced by Transaction LLC, Dzerzhinsk, Nizhny Novgorod Region;
- PMPhS polymethylphenylsiloxane resin – produced at PJSC Khimprom Novocheboksarsk;
- polyisocyanate (PIC) polymethanepolyphenyl isocyanate, CAS No. 9016-87-9 – production of KurskChemProm LLC;
- dimethylaniline CAS 121-69-7 – production of Chemical Line LLC;
- benzoyl peroxide – production of LLC Kama Chemical Company.

As objects of study, a cold curing binder of the following composition was used:
- MMA – 100 mass. parts;
- polyisocyanate – 10 mass. parts;
- dimethylaniline – 7 mass. parts;
- benzoyl peroxide – 5 mass. parts.

Fine filler quartz sand with a particle size of 10-40 microns was used as a filler. The repair composition was prepared by mixing 100 mass. parts of a binder with a given amount of modifier and 300 mass. parts of filler. After loading the pasty mass into the mold and subsequent vibration compaction at a temperature of 20 ºC, the curing process of the samples at a temperature of 20 ºC took place. The resulting samples were tested in accordance with standard methods.

Methods of research of compressive strength are selected as standard according to the standards "Concretes. Methods for determining the strength of control samples".

The tensile strength was determined according to the standards "Protection against corrosion in construction. Concrete and reinforced concrete structures. Test methods for the adhesion of protective coatings".

Water absorption was determined according to the standards "Concretes. Method for the determination of water absorption".

3. Results and discussion

The ability to cure the studied composition for polymerization at room temperature is due to the presence of a tertiary amine catalyst [23, 24]. The role of the tertiary amine is dimethylaniline. As the studies showed, the pot life of the composition before it transitions to a solid state does not exceed two hours, and the curing process is accompanied by a strong exothermic effect (table 1).

| The content of PMPhS, mass. parts per 100 mass. parts of binder | Initial viscosity, s | Gelation start time, min |
|---------------------------------------------------------------|----------------------|--------------------------|
|                                                               | at 15 ºC | at 25 ºC | at 15 ºC | at 25 ºC |
| 0                                                             | 11       | 9        | 86       | 74       |
| 1.0                                                           | 12       | 10       | 74       | 67       |
| 2.5                                                           | 14       | 12       | 69       | 60       |
| 5.0                                                           | 17       | 15       | 60       | 52       |

A subsequent set of strength characteristics is observed over the next three weeks. This is apparently explained by the slowly proceeding processes of anionic polymerization of methyl
methacrylate. The introduction of a small amount of organosilicon modifiers in the first stage leads to a significant increase in the compressive strength of the cured composition.

Considering the lines of equal levels (Figure 1), it can be noted that the maximum strength characteristics occur when the content is 1.5-3.0 mass. parts of PMPhS per 100 mass.

![Figure 1. The dependence of the compressive strength on the content of PMPhS and the exposure time](image)

Parts of binder [25]. The appearance of the maximum is apparently associated with a partial crosslinking of the polymer matrix due to the presence of a significant amount of reactive groups in the organosilicon resins used. In addition, an increase in strength is also manifested due to the sizing effect achieved by the interaction of silanol groups on the surface of quartz sand with hydroxyl groups of a polyphenylsiloxane resin. However, with a further increase in the concentration of organosilicon resins, a decrease in the strength characteristics of the cured compositions is observed. This should be due to the fact that when the content of PMPhS is exceeded more than 3 hours, the excess of unreacted resin begins to act as an independent binder. And since the physicochemical properties of PMPhS are extremely low, it should be expected that a further increase in the content of organosilicon resin in the binder will lead to a significant deterioration in the physicochemical characteristics of the composition.

With the introduction of PMPhS in the composition, as expected, a decrease in water absorption is observed (Figure 2). Introduction 3 mass. parts PMPhS per 100 mass. parts a binder leads to a decrease in water absorption by almost 4 times compared with a composition without an organosilicon resin (curve 1). For comparison, we studied the water absorption of the same repair composition, but with the addition of an industrial water repellent GKZh-94 (curve 2). In this case, water absorption is reduced by only 15-20 % compared with the modification of PMPhS with the same ratio of modifiers. Therefore, we can assume that PMPhS is also a water repellent for the formulation in question.

At the same time, an increase in strength characteristics due to the introduction of a hydrophobizing organosilicon liquid into the repair composition was not observed.

The adhesion characteristics (tensile strength) to various building materials were determined by applying a thin layer of the repair composition to the appropriate substrate, glued after 30 days to the cured composition with cyanoacrylate adhesive [26, 27] steel fungi and their subsequent separation. Studies have shown that the effect of PMPhS in the given range of studies is negligible (table 2).
Figure 2. The dependence of water absorption on the content of the modifier: 1 - PMPhS modifier; 2 - GKZH-94

Table 2. The results of the study of the viability of the composition.

| The content of PMPS in the composition, mass. parts | Tensile strength, MPa |
|-----------------------------------------------|----------------------|
|                                               | concrete substrate   | marble substrate | steel substrate | aluminum substrate | glass substrate |
| 0                                             | 12.8                | 4.3              | 9.7             | 3.8                | 4.0             |
| 2                                             | 12.5                | 4.0              | 8.2             | 3.8                | 4.5             |
| 5                                             | 10.4                | 3.7              | 7.1             | 3.0                | 3.7             |

Thus, the studies showed that the introduction of a small amount of organosilicon modifier can significantly improve the operational characteristics of repair compositions based on MMA.

4. Conclusions
Based on the results of the study, it is fashionable to draw the following conclusions:
1. The use of polymethylphenylsiloxane leads to a partial increase in compressive strength with a modifier content in the range of 2-3 mass. parts.
2. Modification with polymethylphenylsiloxane in an amount of 3 mass. parts reduces the water absorption of the repair composition by four times compared with the unmodified formulation.
3. The addition of polymethylphenylsiloxane in the range of 2-3 mass. parts, does not significantly affect the adhesive characteristics of the repair composition.

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