Formation of the Properties of High Strength Building Quasi-Structure Polymer Composites

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***Abstract* – The main requirements and conditions for the formation of the physical and physicomechanical properties of high-strength quasi-nanostructural polymer composites are given. Methods for reducing porosity and increasing the density of the polymer composite structure have been studied. Cement stone is considered as the main link in the structure formation of high-strength polymer construction composites. Considered the porous structure of concrete, which has its own characteristics. It has been established that a dense structure can have a contact and "floating" arrangement of the aggregate. The properties important for research in the process of forming the structure of high-strength polymer composites are determined.**

***Keywords* – monomer; polymerisation; polymercomposite; aggregate; hydrosilicate; microstructure; adsorption; hydration; anisotropy; gas permeability; wear resistance; resilience; abrasion.**

I. INTRODUCTION

When choosing concrete to obtain a quasi-structural high-strength polymer polymer composite, it is necessary to consider:

-the technology of polymer composites from the point of view of production of polymer concrete products;

- features of the structure that determine the final properties of the new composite building material - nanostructured polymer composite.

These conditions require a new assessment of several properties of concrete, and properties that are less important for conventional concrete and reinforced concrete products [1, 2] are of great importance.

It should be specially emphasized that essentially all concretes can be impregnated, although different concretes may require different processing conditions. However, the technology for producing high-strength polymer construction composites allows a new approach to concrete technology. On the one hand, in order to obtain optimal results, for example, in terms of strength or other properties, it will be necessary to use concrete of appropriate structure and properties; on the other hand, when using special post-processing, it is possible to simplify the production of concrete and reinforced concrete structures, with extensive use of injection molding technology, and to use concrete and materials that cannot be used under normal conditions, for example, concrete with increased dosages of calcium chloride, concrete on gypsum cement, concrete with alkali-resistant glass or stone fiber and a number of similar materials [5,8].

This is due to the fact that during the impregnation of the monomer with the subsequent polymerization, many defects of concrete are “healed” and its structure is monolithic and stabilized and thus becomes inaccessible for many factors and processes that adversely affect the strength and durability of high-strength concrete and determine the requirements for its composition, properties and starting materials.

II. Methods and materials

Cement stone is a complex heterogeneous system, in which hydrosilicates, hydroaluminates, hydroaluminous ferrites, hydrosulfoaluminous ferrites, calcium hydroxide and clinker relics are represented. With the introduction of finely ground mineral or special chemical additives in cements, small amounts of other minerals and substances can be found in the cement stone. The formation of the properties of concrete polymers will be greatly influenced by those components that form the basis of the structure of the cement stone [9,10].

The main component of the cement stone are calcium hydrosilicates, which create a certain spatial structure in the form of a system of globules, which includes the unreacted part of the cement grains with the envelope of new growths and the intergranular space filled to one degree or another with nanostructure new growths. Calcium hydrosilicates have a crystalline, semi-crystalline or amorphous structure. Crystalline products with different crystallite sizes appear more often during thermal, especially autoclave, processing and during crystallization of new growths in intergranular space and pores. In the cement stone of normal hardening and in the shell of tumors near the border with the source material, where the possibilities of crystal growth are limited, gel-like submicrocrystalline quasi-nano-products of hydration prevail.

The composition and structure of hydrosilicates depend on the CaO / SiO_2 (C / S) ratio. Calcium hydrosilicates of tobermorite group are most common.

The hydration products of alite, the main mineral of cement stone, form, according to modern views, two shells: the “outer” crystalline and the “inner” amorphous. The outer shell is composed of crystals of various minerals, depending on hardening conditions and other factors, and may contain materials with a less formed structure, especially if the pore space is limited. The inner shell contains slightly crystallized hydration products of variable composition, approaching the starting material in terms of C / S ratio.

The border between the residual C3S grain and the inner shell is clear, and the boundary between the inner and outer shell is blurry. In this zone microcracks may occur from shrinkage, heating and other types of effects.

Cement stone contains areas with different structure, composed of different minerals. Its structure is characterized by complexity, diversity and heterogeneity.

The heterogeneity of the structure is because the cement stone consists of globules of cement grains with density gradually decreasing to the surface, the contact zone between the globules consisting of various neoplasms, and also includes pores, leaks and structural defects. It is also necessary to take into account the chemical heterogeneity of the cement stone, that is, the fact that certain areas consist of minerals differing from one another and in some places a significant increase in the content of individual components is possible compared to their average value determined by physicochemical analysis.

The microstructure and heterogeneity of cement stone significantly affect its strength and other properties that are essential for polymer composite technology [6].

In general, the chemical and mineralogical composition of cement stone and concrete determines its high sorption properties, which has a positive effect on the properties of polymer composites. However, it must be borne in mind that the nature of this effect will be determined by the type of impregnating material. For example, you can recall the known facts from the theory of building materials. For example, the use of cement or ground limestone provides a higher strength of asphalt concrete than the use of ground quartz. When producing polymer composites on several resins, the effect of quartz sand turns out to be positive.

SV Shestoperov investigated the adsorption of cement stone minerals, which showed that C3A has the highest adsorption with respect to the sulfite-alcohol mash, adsorption on C3S is small, on C2S it is very small [1]. Based on studying the adsorption of cement stone resins used as an additive to concrete, O.S. neoplasms, and non-hydrated grains practically do not adsorb them; another group (urea, melamine-formaldehyde, shale, etc.) is practically not adsorbed by cement neoplasms. These resins improve the wettability of the pore space of the cement stone.

In the production of high-strength polymer composites, it is also necessary to consider the influence of the chemical and mineralogical compositions of the cement stone and aggregate on the polymerization process. The alkaline environment of the cement stone creates specific conditions that can affect both the duration of the polymerization process and the properties of the final product.

The structure of the solid phase of hydrated cement is very complex. Only one product of hydration - calcium hydroxide, or portlandite - forms crystals of relatively large sizes; the crystallites of all other hydration products have a colloidal dispersion, that is, at least one measurement of them is less than 1000 nm. Fibrous calcium hydrosilicates, formed in the early stages of hardening (up to 1 day), have a length of 500–1000 nm and a diameter of 100–200 nm. At late stages of hydration, the sizes of such fibers are 10–100 times smaller. Of greatest interest is the study of aggregates of primary particles. Such aggregates form the structural elements of the cement stone, which determine its technical properties. Contacts between them are formed not only as a result of chemical interaction. Having colloidal dimensions and a developed surface, calcium hydrosilicates, the main product of Portland cement hydration, interact with neighboring particles due to adhesion forces, or van der Waals forces.

A detailed study of the aggregates of primary particles was made possible by the development of scanning (or scanning) electron microscopy and small-angle X-ray diffraction. Cement stone, as well as hardened dough C3S, is characterized by the presence of cigar-shaped and globular particles. The texture of the surface of these particles indicates that they are aggregates of thin leaves and fibers. The largest diameter of the aggregates is 300 nm. Porous areas of cement paste contain disordered needle tumors of the substituted C – S – H gel. Sometimes needles branch and become tree-like (the so-called dendritic forms), also take the form of wheat sheaves. Hexagonal plates C4AN13 and C4ASH12 and prisms of ettringite are observed. The width of the plates is about 5–15 μm, the thickness is less than 50 nm, the prism length reaches 30 μm, but the thickness is not more than 50 nm. Of course, various hydrated neoplasms in varying degrees are responsible for the formation of the technical properties of a portland cement stone. The main structural elements of the solid phase of the hardened cement paste are C – S – H gel, calcium oxide hydrate crystals and clinker relics. Naturally, such a heterogeneous, chaotic structure is by nature porous.

In fig. 1 shows some types of cement stone microstructures obtained with an electron scanning microscope [1]. These photographs illustrate a wide variety of the pore structure of cement stone, which can be very conventionally attributed to a system of pores of different sizes.

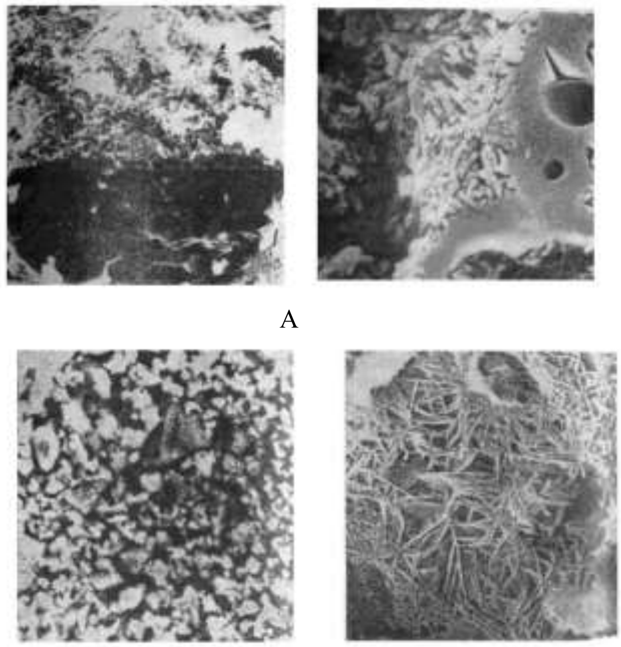
The actual geometry of the microstructure has a great variety and micro-inhomogeneity. As a rule, it is mixed and includes both cellular elements and linear and bead capillaries.

The sizes of pores and capillaries are very different and depend on the type of binder and hardening conditions. The pore size distribution in a normal setting hardening cement stone is characterized by two maxima - in the region of about 10 nm and in the region of 60-70 nm. Pores over 100 nm are relatively rare.

The first maximum corresponds to the prevailing pore size of the hydrosilicate gel. The porosity of a hydrosilicate gel can reach (by volume) 28%.

Larger pores are formed as a result of evaporation of the mixing water, air entrainment, contraction and insufficient compaction. It should be noted that the porosity of cement materials can vary significantly as a result of changes in temperature and humidity of the hardening environment and water-cement ratio.

The porosity of cement mortars is of a slightly different nature. The maxima of the pore size distribution curve characteristic of the cement stone are clearly visible. At the same time, the third peak is also observed - in the region of 1000 nm. Its existence is explained by a significant increase in the macroporosity of the cement stone in the solution. With equal energy spent on compaction, the degree of compaction of the solution is less than the cement stone. The nature of the porosity of the solutions is also influenced by the presence of a contact zone between the aggregate and the cement stone. In the area of the contact zone, a local increase in the water-cement ratio is observed, as a result of which the sizes of hydrate neoplasms increase, their packing is loosened and, naturally, the porosity increases.



A

Б

Fig. 1. Different types of cement stone microstructure (A) and contact zone of cement stone and aggregate (B)

The porous structure of concrete has its own characteristics. It is a system of randomly distributed pores with a size of from 0.01 or less to 100 microns. Large pores are formed mainly as a result of air entrainment in the concrete mix during its laying and mixing. There may be a discontinuity in the concrete in the contact zone of the mortar part and coarse aggregate as a result of insufficient adhesion. Under all these circumstances, the total porosity of good dense concrete varies between 6–20%, and the pore volume with a diameter of more than 1000 nm rarely exceeds 2–3%.

It should be noted that the value of the porosity of the material in some cases depends on the method of measurement used. When drying possible destruction of the microstructure of the cement stone, which affects its permeability and porosity. Several researchers distinguish between the internal porosity of the gel and the crystal structure and the external interglobular porosity. To obtain polymer composite, not only the volume of porosity and the transverse dimensions of capillaries and pores, but also the surface area of the solid phase, which characterizes its roughness, reactivity, total sorption and other properties, are essential.

The surface of the internal space of the tumors is about 670 m2 / g, including about 49 m2 / g on the outer surface of the grains and 621 m2 / g on the intralayer space. However, it must be borne in mind that the availability of the pore space for impregnation will depend on the size of the molecules of the impregnating composition.

The properties of cement stone, mortar and concrete to a greater extent will be determined by the volume and nature of porosity. The great influence of porosity on the properties of cement stone and concrete has caused numerous studies in this direction. As a result, various dependencies and formulas have been proposed, most of which are empirical or semi-empirical.

Essential is the factor that the strength of the material is influenced not only by the size of the voids, but also by their shape and nature of the relationship. Depending on the nature of the porosity of the concrete structure is dense, with a porous filler, cellular (Fig. 2).

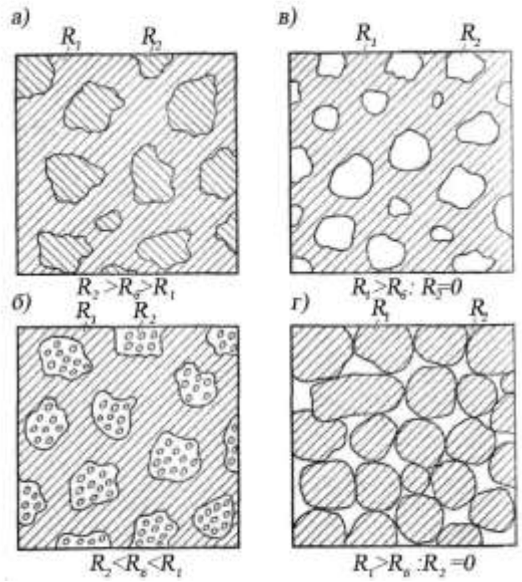


Fig. 2. Main types of concrete structure a - dense; b - dense with cellular aggregate; c - cellular; g– granular; Rb is the average strength of the structure; R1 and R2 - strength of the constituent concretes

A dense structure can have a contact arrangement of the aggregate, when its grains contact one another through a thin layer of cement stone, and a “floating” arrangement of the aggregate, when its grains are located at a considerable distance from one another. A dense structure consists of a solid matrix of solid material (for example, cement stone) in which the grains of another solid material (aggregate) are embedded, which are strongly associated with the matrix material. The cellular structure is distinguished by the fact that in a continuous medium of a solid material pores of various sizes are distributed as separate conditionally closed cells [1].

The porous structure of cement stone and concrete, as a rule, is isotropic, that is, its properties in different directions are approximately the same. However, by special molding techniques or the introduction of special structure-forming elements, the structure of concrete can be given anisotropy, that is, its properties in one direction will differ markedly from properties in another direction. Examples include obtaining directional porosity when evacuating a concrete mixture or electroosmotic exposure to it, or concrete containing needle-like or fibrous elements oriented in a direction.

Of course, the division into the given types of structures is conditional. In fact, the structure of concrete is very complex: for example, in the dense structure of heavy concrete, cement stone has numerous pores, in a dense structure of lightweight concrete, pores are present not only in the cement stone, but also in the aggregate grains; etc.

However, an understanding of the types of structures and the associated properties of the properties allows a more accurate assessment of the effect of the concrete matrix on the structure and properties, which is important when developing CAD systems in 3-d dimensions [3, 4].

The structure of concrete is heterogeneous, which has a significant impact on the properties of the material. Not only cement stone and aggregate can differ in properties, but also separate kernels of aggregate one from another, and separate microvolumes of cement stone.

As already noted, near the core grains in the contact zone, the microstructure of the cement stone differs somewhat from the bulk structure, but the contact zone itself, like the main body, is heterogeneous, it has more or less defective places, unreacted grains, microcracks and other elements reducing the homogeneity of the material. Therefore, the strength, permeability and other properties of materials in micro-volumes differ from one another, which significantly affects the processes of obtaining concrete polymer and its final properties. In addition, the structure and properties of concrete can vary slightly in different products and samples, even if the latter have the same composition and are made in the same way.

The heterogeneity of the structure and properties requires the application of probabilistic-statistical methods to the assessment of concrete. However, in most of these methods, concrete strength is used as a criterion, which is an integral characteristic. To produce concrete polymer, differential methods for evaluating heterogeneity, especially its porosity and structure imperfection, are essential. After all, when concrete is impregnated, a small microcrack, which has little effect on the strength of concrete, can significantly change the impregnation rate, the distribution of the liquid phase and the subsequent polymerization conditions, which will directly affect both the process itself and the final properties of the product.

Information about pore sizes and their availability to liquid media determines the choice of impregnating compositions and processing modes, since for each porous structure an individual approach is advisable in order to get the best results, using low-viscous impregnating compositions it is difficult to ensure common pores and defects; materials. On the contrary, the latter, as a rule, cannot penetrate the thin pores and capillaries and do not ensure their homonolation.

III. CONCLUSION

The study of chemical interactions in the production of high-strength polymer composites, the influence of surface forces, sorption, adhesive and capillary phenomena on these processes began at the end of the last century. A deeper study of these issues will improve the quality and effectiveness of polymer composites.

Porosity largely determines such important deformative properties of cement stone, mortar and concrete, such as shrinkage and creep. At the same time, the humidity of the material is extremely important. The change in the moisture content in the pores determines the capillary pressure forces that tighten the skeleton of the cement stone.

With an increase in humidity, these forces weaken, and the cement stone expands, with a decrease in humidity, the capillary pressure increases, which results in compression deformation - shrinkage. Osmotic phenomena occurring in porous media saturated with liquids also have a certain influence on these processes. The creep of mortars and concretes depends mainly on the creep of cement stone. The latter, in turn, is largely determined by the degree of pore filling with moisture.

The permeability of high-strength concrete is determined by molecular diffusion, viscosity and molecular flows. Molecular diffusion of gases is observed if the pores of the concrete are filled with a liquid (for example, water) or a solid (for example, an organic polymer).

If the pores of the concrete are completely or partially free from liquid or solid phase, molecular micropores ($r \leq 10–5$ cm) are observed, and viscous flows occur in macropores ($r \geq 10–5$ cm).

The transfer of fluids through concrete is also characterized by three main modes. With a radius of capillaries of $r \leq 10–5$ cm and slight evaporation of fluid from the capillaries, diffusion transfer is possible in accordance with Fick's law. There is also a two-phase transfer of fluids through the concrete: first in the form of a liquid, and then in the form of its vapor. Capillary transfer largely depends on the intensity of evaporation of liquid from the capillaries.

Stresses arising in concrete in the presence of overpressure lead to microfracture of the material, which accumulate under cyclic exposure and cause destruction of the material. When alternately freezing and thawing in concrete, osmotic phenomena also occur that affect the process of destruction.

The wear resistance of high-strength concrete is of great importance when it is used in hydraulic engineering, road, airfield and some industrial facilities, the destruction of concrete as a result of wear is caused by mechanical abrasion or cavitation erosion, which is specific for hydraulic structures [7]. The resistance of concrete to abrasion increases as its strength increases, especially in tension. Abrasion largely depends not only on the strength, but also on the specific content of mortar and cement stone in concrete, on the type and particle size distribution of the aggregates, on the state of the aggregate contact zone and on the cement stone. The most abrasive component of concrete is cement stone. Increasing its solidity should be given special attention [2].

To ensure the wear resistance of high-strength concrete, increasing its strength and density is of great importance. These studies are currently engaged in the department of technology of binders and concretes of the Institute of Construction and Architecture of the National Research Moscow State University of Construction (NRU MGSU, Moscow) in conjunction with the materials science department of the Integrated Research Institute named after. H.I. Ibragimova of the Russian Academy of Sciences (Grozny).

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