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Investigation and Optimization of Adhesive Structure Formation on Shell Limestone Surfaces

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Abstract: The article is devoted to the study of the adhesive interaction of restorative compositions with shell limestone as a highly porous material of complex structure. The key physicochemical and mechanical factors determining adhesion are analyzed, including molecular forces, hydrogen bonds, electrostatic interactions, acid-base interactions, as well as the effect of humidity on adhesion. Elements of fractal geometry are used to describe the processes of adaptation of compositions to porous surfaces, a criterion of ideal adhesive contact is introduced. Models of structure formation are considered, including the Smoluchowski equation, diffusion-limited and cluster-cluster aggregation. It is shown how optimization of the restorative composition due to the selection of the necessary fractal parameters can improve its adhesive characteristics. Recommendations are given for the use of various methods for optimizing adhesion processes in restoration. It is also possible to use the obtained results in modern additive technologies.

Keywords: adhesion; fractal dimension; porous structure; restorative compositions; shell limestone; structure formation

1 INTRODUCTION

One of the important tasks of construction materials science, especially relevant in cities - centers of historical, cultural and architectural heritage, is the production of restoration compositions with an optimal set of performance characteristics. An important property of such materials is the ability to form strong adhesive contacts with the surface of the base stone [1, 2]. When forming a contact between the adhesive and the base material (substrate), adhesive structuring occurs − special case of structuring of the adhesive composite, which occurs under conditions of strong geometric constraints specified by the porous structure of the material being restored, for example, shell limestone. In addition, the adhesive processes occurring during the formation of the "adhesive-substrate" contact are of great importance in additive technologies, widely used today in modern construction and restoration [3]. In this case, the key role in such processes is played by the coordination of the geometric characteristics of the material and the adhesive [4]. Such coordination is especially important when applying restoration compounds to complex porous surfaces, for example, fragments of historical buildings made of shell limestone [1].

Adhesion is a complex multifactorial phenomenon based on molecular, physicochemical and mechanical aspects [5, 6]. The mechanical component has a pronounced geometric-topological character associated with the complexity of the hierarchical structure of porous materials [7, 8]. Molecular forces caused by van der Waals interactions, hydrogen bonds, electrostatic and acid-base interactions determine the microscopic nature of adhesion and determine the physicochemical surface properties that form the overall picture of adhesion. At the same time, mechanical interaction, including penetration of the adhesive into the pores and microcracks of the material, forms a significant contribution to the adhesive forces, which determines the importance of studying the geometry and topology of the contact surface.

Geometrical factors play a special role in adhesion optimization and can be described through fractal regularities. The porous structure of the material being restored and the adhesive composition forms a three-dimensional structure of the adhesive contact, which in the ideal case completely fills the surface irregularities and pores. This imposes strict restrictions on the fractal properties of the adhesive material. The correspondence of the fractal dimension of the adhesive and the material being restored can be used as a criterion for the optimality of the contact.

This work is devoted to the consideration of approaches to optimization of adhesive compositions based on geometric, molecular and physicochemical factors using modeling of the structure formation of adhesives and determining their optimal fractal characteristics.

2 FACTORS AFFECTING ADHESION TO POROUS SURFACES

Adhesion (bonding) is a set of intermolecular interactions between the surfaces of different materials, leading to their holding together. For composite materials used for the restoration and reconstruction of shell limestone buildings, adhesion depends on many factors, including the type of restorative composition (e.g., silicate-based) and the physicochemical properties of the shell limestone, especially in the presence of moisture. It should be noted that the factors determining adhesive activity relate primarily to the adhesive surfaces. They can be conditionally divided into molecular, related physicochemical, mechanical and geometric-topological.

2.1 Molecular Factors of Adhesion to the Surface of Shell Limestone

The molecular theory of adhesion explains cohesion through intermolecular interactions such as Van der Waals forces, hydrogen bonds, electrostatic and acid-base interactions. The intermolecular interaction potential $V(r)$ between particles at a distance r is usually expressed as the sum of several contributions and is described by the Eq. (1) [9]:

$$V(r) = V_{\mathrm{VdW}}(r) + V_{ei}(r) + V_{\mathrm{hidrogen}}(r) + V_{\text{acid-based}}(r), \qquad (1)$$

where $V_{\text{VdW}}(r)$ − contribution of Van der Waals interactions; $V_{\text{ei}}(r)$ − electrostatic contribution; $V_{\text{hidrogen}}(r)$ − contribution of hydrogen bonds; $V_{\text{acid-based}}(r)$ − the contribution of acid-base interactions.

Let us consider in more detail the contribution of each type of interaction to the adhesion of restorative compositions that adhere to shell limestone.

Van der Waals forces include dispersion forces, orientation and induction interactions. They are universal and act between all molecules. Dispersion forces play an important role in the adhesion of restorative compositions to inorganic surfaces. These forces depend on the polarizability of the molecules, which in the case of wet shell limestone can be increased due to the presence of water. The Lennard-Jones potential (2) is the most often used to describe Van der Waals forces:

$$V_{\text{vdW}}(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right), \tag{2}$$

where ε − the depth of the potential well, which characterizes the strength of interaction; σ − effective diameter of the molecule.

This potential describes the balance between attraction at large distances (dispersion forces) and repulsion at short distances (Pauli repulsion). In [10], a type of potential for silicates and aluminosilicates is proposed that describes the interaction between oxygen and silicon atoms in the structure of zeolite-like materials, as well as with a correction of the value taking into account ions such as sodium and calcium. For the materials under consideration, typical values are $\varepsilon \approx$ 0.4 - 0.5 kcal/mol and $\sigma \approx 3.0$ Å for interactions between oxygen and silicon atoms. Similar parameters are used for calcite, the main mineral in shell limestone. According to [11], the Lennard-Jones potential for Ca-O interactions is used to model limestone bases, with constant values of $\varepsilon \approx$ 0.32 kcal/mol and $\sigma \approx 3.9$ Å. This potential allows us to consider the interactions of carbonates with silicate and aluminosilicate bonds in the presence of moisture.

Electrostatic interactions can be significant for materials with opposite charges. Aluminosilicate materials can have a surface charge that contributes to their attraction to the carbonate matrix of the shell limestone, especially under high humidity conditions. The electrostatic interaction potential between two charged particles q_i and q_j at a distance r is expressed by the Eq. (3):

$$V_{\text{ei}}(r) = \frac{q_i q_j}{4\pi\varepsilon_0 r}, \tag{3}$$

where ε_0 − dielectric constant.

The electrostatic contribution is significant when taking into account the interaction with silicate restorative compositions, since such materials can have local charges that interact with charged or polarizable groups on the surface of the shell limestone.

Hydrogen bonds are especially important for adhesion in the presence of physically bound water. Water molecules can form bridges between the surface groups of silicate and aluminosilicate composition and the surface of the shell limestone, strengthening the adhesion. This contribution increases under humid conditions, since water is capable of forming hydrogen bonds with –OH groups that may be present on the surface of the adhesive and substrate. Water molecules present in the porous structure create additional hydrogen bonds. Water acts as an intermediate agent that forms hydrogen bond bridges, increasing the adhesive force. In addition, the presence of water reduces the rigidity and increases the mobility of molecules on the surface of the aluminosilicate composition, facilitating their interaction with the shell limestone. Thus, in [12] it is shown that cooperative tridentate hydrogen-bonding interactions significantly enhance underwater adhesion, which can be relevant for understanding the role of water in the adhesion mechanisms of mineral materials. This is especially important when restoring wet shell limestone, since physically bound water not only increases adhesion, but also promotes the diffusion of the restorative composition into the pores of the shell limestone, improving its penetration and fixation.

The hydrogen bond potential can be expressed in terms of empirical potentials, for example using Eq. (4):

$$V_{\text{hydrogen}}(r) = D_{\text{e}}\left(\text{e}^{-a(r-r_0)} - 2\text{e}^{-a(r-r_0)/2}\right), \tag{4}$$

where D_{e} is the bond energy, usually about 5-10 kcal/mol; r_0 is the equilibrium bond distance; a α − rigidity parameter. This potential is used to model water adsorption on the surface of carbonates, which is confirmed by a study of the effect of moisture on adhesive forces.

Acid-base interaction is determined by the ability of surface groups to act as acids or bases. The surface of shell limestone can exhibit weakly acidic properties, and some surface groups of lime-silicate material can be alkaline, which leads to additional adhesion at the level of surface layers [13].

Acid-base interactions are often modeled using the donor-acceptor interaction approach, which can be expressed through the acid-base affinity parameter based on the Lewis donor-acceptor theory method. Acid-base interactions can be modeled using energy contributions to potential functions that account for the donor-acceptor behavior of particles. The Lewis potential is described through the interaction energy E_{AB} (5):

$$E_{\text{AB}} = C \cdot \frac{\alpha_{\text{A}} \cdot \beta_{\text{B}}}{r^2}, \tag{5}$$

where α_{A} − acceptor capacity (acid strength); β_{B} − donor capacity (main force); C − empirical constant depending on the specifics of the materials.

Typical values of the constants depend on the nature of the materials: for aluminosilicates and calcite under humid

conditions, it is proposed to use the value α_A = 0.6 - 0.8 and β_B = 0.4 - 0.6 in approaches based on measurements of surface tension and Hamaker energy.

2.2 Physicochemical Factors and Parameters of Adhesion to Shell Limestone

The interaction potential (1) is the basis for the transition from adhesive molecular interactions to a comprehensive physicochemical description and thermodynamic theory of adhesion. The general expression of surface energy through intermolecular interactions (e.g., Van der Waals forces) can be represented by the integral of the intermolecular potential $\varphi(r)$ over the entire space above the surface (6):

$$\gamma = \int_h^\infty \varphi(r)\mathrm{d}r\,, \tag{6}$$

where h is the distance between molecules on the surface; r is the intermolecular distance.

This formula shows that the surface energy depends on the attractive force of molecules at the phase boundary.

Thermodynamic theory describes adhesion through changes in free energy at the interface between two phases [14]. According to this theory, adhesion is characterized by the work of adhesion W_{adh}, which is defined as the energy required to separate two surfaces in accordance with the Eq. (7):

$$W_{adh} = \gamma_1 + \gamma_2 - \gamma_{12}\,, \tag{7}$$

The work of adhesion is positive for spontaneous adhesion of surfaces, and the higher the W_{adh}, the stronger the adhesion.

Adhesive interactions are closely related to the contact angles formed at the contact of three phases, as well as to the flow and inflow angles. The contact angle θ describes the contact of a liquid with a solid surface and is determined by Young's Eq. (8):

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta\,, \tag{8}$$

where γ_{SV}, γ_{SL} and γ_{LV} − surface tension at the interface between a solid, liquid and air.

Angles of runoff and wetting θ_A, θ_R describe the dynamic behavior of a liquid on an inclined surface. The angle of runoff θ_A − this is the maximum angle of inclination at which the drop begins to flow down, and the angle of wetting θ_R − the angle at which the drop stops on the surface. The difference $\Delta\theta = \theta_A - \theta_R$ is called contact hysteresis and is related to adhesion: a large hysteresis indicates high adhesion of the liquid to the surface. A significant hysteresis indicates strong cohesive forces holding the liquid and preventing its movement.

The work of adhesion can also be expressed in terms of the runoff and wetting angles using the relation [15] (9):

$$W_{adh} = \gamma_{LV}(1 + cos\,\theta_{avg})\,, \tag{9}$$

where θ_{avg} − average contact angle, defined as (10):

$$\theta_{avg} = \frac{\theta_A + \theta_R}{2}\,, \tag{10}$$

Thus, the work of adhesion depends on the average value of the runoff and wetting angles, as well as on the surface tension of the liquid $\gamma_{LV.}$ Changing the runoff and wetting angles, for example, by chemically modifying the surface, allows one to regulate the adhesive properties of the system, which is important for practical applications in hydrophobic and hydrophilic coatings.

2.3 Effect of Surface Geometry on Adhesive Interaction. Fractal Analysis of Geometric Parameters

The mechanical theory of adhesion [16] is based on the fact that adhesion is achieved by the penetration of the material into the microroughness and pores of the base surface. For shell rock, with its high porosity and microcracks, the lime-silicate composition penetrates the structure, providing reliable adhesion. The adhesion force can be described by the Eq. (11) [17]:

$$F_{adh} = kA\gamma\left(1 - E^{-\beta P}\right), \tag{11}$$

where F_{adh} is the adhesion force; k is the coefficient of adhesion strength; A is the contact area; γ - surface tension at the interface between the adhesive and the base; β - penetration coefficient; P - pressure when applying the composition.

It is important to note that A is the "real" area of adhesive contact, the accounting of which is complicated by the complex relief of the base surface.

A powerful tool for describing complex surfaces such as shell limestone and other porous materials that are often encountered in adhesive joints is fractal geometry. Traditional models based on Euclidean geometry are often insufficient to adequately describe such structures. The fractal approach allows one to take into account the hierarchical structure and partial ordering characteristic of many natural and artificial surfaces. The main concepts of the fractal theory of adhesion are the fractal dimension D and lacunarity Λ [18, 19]. The fractal dimension characterizes the degree to which the space is filled by the fractal object. For surfaces, D ranges from 2 (smooth surface) to 3 (completely filled space). The higher D, the more developed the surface. Lacunarity Λ describes the "emptiness" or "perforation" of the fractal object. High lacunarity corresponds to a large number of voids or pores. Lacunarity is often associated with the distribution of pore sizes and shape.

One of the most significant in the mechanical theory of adhesion, which is geometric in nature, is the relationship between the fractal dimensions of the base material and the adhesive restorative composition. Let the first surface (shell

limestone) be characterized by fractal dimension D_1, the second surface (adhesive restorative composition) by fractal dimension D_2. Fractal dimension D_1 characterizes the complexity of the shell limestone surface. The greater D_1, the more "rugged" the surface. Fractal dimension D_2 characterizes the complexity of the cluster structure of the adhesive. The greater D_2, the more branched the cluster. Contact occurs in three-dimensional Euclidean space (the embedding dimension $D_E = 3$). Ideal adhesive contact is achieved when the adhesive completely fills all the irregularities and pores on the shell limestone surface. In this case, from the geometric point of view, one can imagine that the adhesive surface is "superimposed" on the shell limestone surface, completely repeating its structure as its negative imprint. In the ideal case, one can assume that the "sum" of their fractal dimensions should be related to the dimension of the space in which the contact occurs.

Let us consider the mutual dimension of two fractal sets. The Minkowski-Buligand dimension [18-20] (or box-counting dimension) is defined by the following Eq. (12):

$$D = \lim_{\varepsilon \to 0} \frac{\log N(\varepsilon)}{\log(1/\varepsilon)}, \tag{12}$$

where $N_A(\varepsilon)$ - the minimum number of cubes (or "boxes") of size ε, required to cover the set.

Next, we will consider two fractal sets A and B with dimensions D_1 and D_2 respectively. Let $N_A(\varepsilon)$ and $N_B(\varepsilon)$ - number of boxes of size ε, required to cover the sets A and B respectively. Then the Eqs. (13) and (14) are fulfilled:

$$N_A(\varepsilon) \sim \varepsilon^{-D_1}, \tag{13}$$

$$N_B(\varepsilon) \sim \varepsilon^{-D_2}, \tag{14}$$

To describe the "mutual arrangement" of sets A and B Let's introduce the concept of Minkowski product $A \oplus B$ (15):

$$A \oplus B = \{a + b \mid a \in A, b \in B\}, \tag{15}$$

Dimension of the Minkowski product $D(A \oplus B)$ related to dimensions D_1 and D_2 the following inequality (16):

$$\max(D_1, D_2) \le D(A \oplus B) \le D_1 + D_2, \tag{16}$$

In the case of ideal contact, when the adhesive completely fills all the irregularities of the shell limestone, it can be assumed that the Minkowski product $A \oplus B$ "fills" all the space near the surface of the shell limestone. In the limiting case, when the adhesive perfectly repeats the structure of the shell limestone, the dimension of the Minkowski product should be related to the dimension of the space D_E. In the case of ideal contact, the dimension of the Minkowski product is approximately equal to $2D_E - 1$. Thus, in the three-dimensional case, if one of the sets is a "plane" ($D_1 = 2$), and the other - a "ragged" surface ($D_2 > 2$), then when they are "superimposed" one can expect that the dimension of the Minkowski product will approach $2D_E - 1 = 5$. This assumption is based on heuristic considerations, acknowledging that when fully filled, the 'interaction' of two fractal sets effectively results in an increase in dimensionality. Thus, for an ideal contact we obtain the approximate relation (17):

$$D_1 + D_2 \approx 2D_E - 1, \tag{17}$$

In three-dimensional space ($D_E = 3$) is performed (18):

$$D_1 + D_2 \approx 2 \cdot 3 - 1 = 5, \tag{18}$$

Expression $5 - D_1 - D_2 \approx 0$ is a criterion for the ideality of adhesive contact within the framework of this theory. The obtained criterion is key for this work.

3 MODEL REPRESENTATIONS OF ADHESIVE STRUCTURE FORMATION IN RESTORATIVE COMPOSITIONS

The structural and geometric properties of the restorative composition are formed in the process of spatially limited structure formation. The process of pore filling and subsequent hardening can be described as aggregation of particles of the restorative composition. In the simplest case, the diffusion-limited aggregation (DLA) model can be used [21]. The cluster-cluster aggregation (CCA) model [21] describes the aggregation of already formed clusters. It leads to the formation of looser and more branched structures than DLA. The fractal dimension of CCA clusters is lower than that of DLA clusters. This model may be relevant if the adhesive consists of already aggregated particles or if the process of its application and hardening promotes aggregation.

To describe more general processes of structure formation, the Smoluchowski equation [22] is applicable, which describes the change in the concentration of clusters of different sizes over time in accordance with Eq. (19):

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} K(i,j) c_i c_j - c_k \sum_{j=1}^{\infty} K(k,j) c_j, \tag{19}$$

where is c_k - concentration of clusters of size k; $K(i,j)$ - kinetic coefficient describing the rate of adhesion of clusters of sizes i and j.

Eq. (19) allows us to determine how the particle size distribution changes over time as a result of their collisions and associations. The first term of Eq. (19) $\frac{1}{2} \sum_{i+j=k} K(i,j) c_i c_j$ describes the formation of clusters of size k because of collisions and mergers of clusters of sizes i and j, where $i + j = k$. The coefficient $\frac{1}{2}$ takes into account that each collision is counted twice in the sum (for example, the collision of cluster i with cluster j and the collision of cluster

j with cluster i). The second term $-c_k \sum_{j=1}^{\infty} K(k,j)c_j$ describes the loss of clusters of size k as a result of their collisions and mergers with other clusters of any size j. The coagulation coefficient for diffusion-limited aggregation (DLA): In this case, the coefficient depends on the diffusion coefficients of clusters i and j (20):

$$K(i,j) \sim (D_i + D_j)(R_i + R_j), \tag{20}$$

where D_i and D_j – diffusion coefficients; R_i and R_j – radii of gyration of clusters i and j, respectively.

The kinetic coefficient $K(i,j)$ in the general case depends on the physicochemical factors discussed above, such as the forces of intermolecular Van der Waals interaction, electrostatic forces, hydrogen bond forces and acid-base interactions, as well as on the temperature and viscosity of the medium.

The processes of structure formation in a limited pore space can be considered from several other positions, according to which in the considered material, as a result of a number of physical and chemical processes occurring at the micro level, the fractal dimension changes. For cluster systems, to which the considered composition also belongs, the fractal dimension D_f connects the number of particles N in the cluster with its characteristic size R based on the relation (21):

$$N \sim R^{D_f}, \tag{21}$$

For clusters formed in the DLA process in $2D - D_f \approx 1.7$, in $3D - D_f \approx 2.5$ the kinetics of fractal dimension growth is complicated (it involves solving the Smoluchowski equations). However, approximations can be made, for example, by assuming that the average cluster size grows in a power-law manner with time (22):

$$R(t) \sim t^z, \tag{22}$$

where z is a dynamic indicator.

Then, if we assume that the number of particles in a cluster is proportional to time, then the fractal dimension does not change (23):

$$D_f(t) \approx \frac{\ln(t)}{\ln(R(t))} \sim \frac{\ln(t)}{z\ln(t)} = \frac{1}{z}, \tag{23}$$

This is a very simplified argument, but it shows that the growth of fractal dimension is related to the dynamics of cluster growth.

In an idealized case, if the adhesive simply fills the existing pores without changing its internal structure or forming new fractal elements, its fractal dimension does not change. It "copies" the fractal structure of the pore space. However, this is a rather theoretical case. In most real situations, the hardening of the adhesive is accompanied by a change in its structure, which leads to a change in the fractal dimension. Let's consider several possible scenarios:

1) *Polymerization and gelation.* During the solidification process, polymerization may occur, leading to the formation of a three-dimensional network, for example, of an aluminosilicate nature. This network may have a fractal structure. At the initial moment, when the polymer is still liquid, its fractal dimension is close to 3 (volume filling). As polymerization and network formation proceed, the fractal dimension may decrease, approaching values characteristic of percolation clusters (about 2.5) or even lower, depending on the degree of network branching.
2) *Crystallization.* If crystallization of new formations is possible in the adhesive and the resulting crystals can have different shapes and orientations, then the formation of a fractal structure is also possible. The fractal dimension will depend on the crystallization conditions (temperature, cooling rate, presence of impurities).
3) *Particle aggregation.* Since the adhesive is a dispersed system, the particles can aggregate during the hardening process, forming clusters. The considered DLA and CCA models describe this process and lead to the formation of fractal structures with dimensions of about 2.5 (DLA) and lower (CCA). During the hardening process, the mobility of the particles decreases, which can "fix" the formed structure.
4) *Capillary forces and wetting.* Capillary forces and wetting play an important role in the process of filling the pores. If the adhesive wets the surface of the material well, it will tend to fill all the smallest pores and cracks, which can lead to an increase in fractal dimension. On the contrary, poor wetting can lead to the formation of voids and a decrease in fractal dimension.

The fractal dimension of the cured adhesive also depends on the initial pore structure of the material. If the pores are small and numerous, the adhesive will be forced to form a more branched structure to fill them all. This may lead to an increase in the fractal dimension. If the pores are large and few in number, the adhesive can fill them without forming complex fractal structures. In this case, the fractal dimension may be lower. The connectivity of the pores also plays an important role. If the pores are interconnected, the adhesive can move freely and fill them, which contributes to the formation of a more uniform structure. If the pores are isolated, the adhesive will fill them independently, which may lead to the formation of a more heterogeneous and possibly more branched structure.

4 METHODS OF OPTIMIZING GEOMETRICAL PARAMETERS TO IMPROVE THE ADHESION PROPERTIES OF RESTORATION COMPOSITIONS

Based on the above analysis, several methods for optimizing adhesive compositions can be proposed. Due to the multifactorial nature of the structure formation process, determining the fractal dimension of the clusters formed in the adhesive restorative composition requires empirical

methods. Therefore, the initial selection of the composition can be guided by the structural-geometric criterion.

The main optimization problem is characterized by the objective function Eq. (24):

$$F(w_1, w_2,\ldots, w_n) = \left|D_1 + D_A(w_1, w_2,\ldots, w_n) - 5\right| \to \min, \quad (24)$$

where D_1 - fractal dimension of the shell limestone surface (known); $D_A(w_1, w_2,\ldots, w_n)$ - fractal dimension of adhesive clusters, depending on both the granulometric composition (w_1, w_2,…, w_n, w_i – volume fraction of fraction i) and its structure formation processes occurring inside the pore space. Limitations are represented by the conditions (25, 26):

$$\sum_{i=1}^{n} w_i = 1, \quad (25)$$

$$w_i \geq 0, \quad (26)$$

This task is aimed at minimizing the deviation from the ideal contact criterion. $D_1 + D_2 - 5 = 0$. Additional criteria may include minimizing lacunarity in the contact zone (27):

$$F(w_1, w_2,\ldots, w_n) = \Lambda(w_1, w_2,\ldots, w_n) \to \min, \quad (27)$$

It should be noted that minimization $|D_1 + D_2 - 5|$ already indirectly contributes to the minimization of lacunarity, since complete filling implies a reduction in voids. The Richardson curve fit criterion (a plot of $\log(N(\varepsilon)$ versus $\log(1/\varepsilon)$), where ε defines the "scale" of the measurement, [19]) can also be useful, especially if the behavior of the contact at different scales needs to be considered (28):

$$F_{\text{add2}}(w_1, w_2,\ldots, w_n) = \\ = \int_{r_{\min}}^{r_{\max}} \left|L_{\text{shell}}(r) - L_{\text{adh}}(r, w_1, w_2,\ldots, w_n)\right| \mathrm{d}r \to \min, \quad (28)$$

However, this criterion is also partially accounted for by the main criterion, as the fractal dimension is linked to the behavior of the Richardson curves.

4.1 Determination of Geometric Characteristics of the Material and Composition of the Restoration Using Image Processing

The initial data for optimization according to criterion (18) is the fractal dimension of the base material (shell limestone), which can be realized by processing images of the material surface using the box counting method. When implementing it, a grayscale image can be represented as a three-dimensional surface, where x and y are the pixel coordinates, and z is the gray intensity (from 0 to 255), each pixel becomes a point in three-dimensional space. The space in which this surface is located is covered with a grid of cubes of size ε (epsilon). The size ε determines the "scale" of the measurement. The number of cubes $N(\varepsilon)$ that intersect or contain at least one point (pixel) of the surface is counted. The size of the cubes ε is reduced (for example, by 2 times), and the procedure for counting filled cubes is repeated, a new pair of values (ε, $N(\varepsilon)$) is constructed. A graph of the dependence of $\log(N(\varepsilon)$ on $\log(1/\varepsilon)$ is plotted. The slope of the resulting line is the fractal dimension D.

The method was implemented using the *FDim* software tool [23] for different shell limestone samples. The measurement results are given in Tab. 1.

Table 1 Fractal characteristics of typical shell limestone samples

Number	Samples	Fractal dimension D_f	Lacunarity Λ
1		2.557	0.259
2		2.454	0.210
3		2.357	0.282

It should be noted that the shell limestone structure is variable, which is reflected in the fractal characteristics of the corresponding images. As a result, it is proposed to perform the corresponding measurements separately for each restoration project.

Let us calculate fractal dimension of the adhesive composition surface (Tab. 1) according to the relation (18) for ideal adhesive contact. The results are shown in Tab. 2.

The obtained data (fractal dimension $D_2 \approx 2.5$) indicate that the DLA mechanism (and even more so CCA) can ensure the formation of a non-ideal cluster system, and the composition must be designed taking into account the formation of fine-crystalline products in contact with the pore material.

Table 2 Determination of the required fractal dimension of the adhesive composition

Number	1	2	3
Fractal dimension D_1 shell limestone	2.557	2.454	2.357
Required fractal dimension D_2 of the adhesive composition surface	2.443	2.546	2.643

Often the granulometric distribution of dispersed materials is described by a power law, which is an indication of its fractal structure. A special case of a power distribution is the Richardson-Kolmogorov distribution, which is often observed in crushing and grinding processes. The general form of a power distribution (cumulative) (29):

$$N(r) \sim r^{-D_2}, \tag{29}$$

where d - particle size (diameter, linear size, etc.); $N(d)$ - number of particles with size greater than d; D_2 - exponent, which can be interpreted as fractal dimension (Tab. 2).

This ratio allows a rough estimate of the required particle distribution in the adhesive restorative composition. To obtain the size distribution, it is necessary to differentiate expression (29) and obtain the Eq. (30):

$$\frac{\mathrm{d}N(r)}{\mathrm{d}r} - Dr^{-D-1}, \tag{30}$$

To obtain a normalized distribution describing the probability of finding a particle of size r, it is necessary to integrate expression (29) within the range from $r_{\min}$ up to $r_{\max}$ and divide by the obtained result (31):

$$P(r) = \frac{(D+1)r^{-D-1}}{r_{\min}^{-D} - r_{\max}^{-D}}, \tag{31}$$

where $P(r)$ is the probability density of the particle size distribution ($P(r)$ is normalized, $\int_{r_{\min}}^{r_{\max}} P(r)\mathrm{d}r = 1$; $r_{\min}$ - minimum particle size; $r_{\max}$ - maximum particle size; D - fractal dimension.

Let us consider the problem of selecting particle sizes, assuming that there are several fractions with known particle size distributions $P_i(r)$ (e.g., unimodal, such as normal or lognormal distribution) and weighted fractions w_i. Then the overall distribution of the mixture will be (32):

$$P_{\text{mix}}(r) = \sum_{i=1}^{n} w_i P_i(r), \tag{32}$$

where n is the number of fractions, $\sum_{i=1}^{n} w_i = 1$.

To solve the problem of selecting a composition, one can use methods known in mathematical statistics [24, 25]:

1) *Kolmogorov-Smirnov criterion*. This criterion is based on the comparison of the maximum discrepancy between the cumulative distribution functions (33):

$$D_{\text{KS}} = \sup_r \left| F_{\text{mix}}(r) - F_{\text{target}}(r) \right|, \tag{33}$$

where is $f_{\text{mix}}(r)$ and $F_{\text{target}}(r)$ - cumulative distribution functions for the mixture and target distribution, respectively ($F(r) = \int_{r_{\min}}^{r} P(r')\mathrm{d}r'$). Minimizing D_{KS} is a useful way to ensure good distribution fit.

2) *The chi-square test* is represented by Eq. (34):

$$\chi^2 = \sum_{j=1}^{m} \frac{(O_j - E_j)^2}{E_j}, \tag{34}$$

where Oj – observed frequency in the j^{th} interval; Ej - expected frequency in the j^{th} interval, m - number of intervals.

Minimizing χ^2 also allows one to achieve a good fit, especially when the amount of data is large.

3) *Minimizing Kullback-Leibler entropy* (Relative Entropy): This criterion, also known as the Kullback-Leibler divergence, measures the "distance" between two probability distributions according to Eq. (35).

$$D_{\text{KL}} = \int_{r_{\min}}^{r_{\max}} P_{\text{target}}(r) \log \frac{P_{\text{target}}(r)}{P_{\text{mix}}(r)} \mathrm{d}r. \tag{35}$$

Minimizing D_{KL} is aimed at making $P_{\text{mix}}(r)$ approximated P_{target} as accurately as possible, especially in areas where $P_{\text{target}}(r)$ large.

Let's consider an example of calculations. Let's assume that we need to select a granulometric composition with a fractal dimension $D = 2.5$ in the size range from $r_{\min} = 1$ μm to $r_{\max} = 100$ μm. We have two fractions with normal distributions: fraction 1 – average size $\mu_1 = 1.5739$ μm, standard deviation $\sigma_1 = 0.6653$ μm; fraction 2 – average size $\mu_2 = 20$ μm, standard deviation $\sigma_2 = 14.6942$ μm.

The target distribution is given by Eq. (36):

$$P_{\text{target}}(r) = \frac{3.5r^{-3.5}}{1^{-2.5} - 100^{-2.5}}, \tag{36}$$

The probability density of the normal distribution for fractions is given by the Eqs. (37)-(38):

$$P_1(r) = \frac{1}{\sigma_1\sqrt{2\pi}} \mathrm{e}^{-\frac{(r-\mu_1)^2}{2\sigma_1^2}}, \tag{37}$$

$$P_2(r) = \frac{1}{\sigma_2\sqrt{2\pi}} \mathrm{e}^{-\frac{(r-\mu_2)^2}{2\sigma_2^2}}, \tag{38}$$

Now we need to find weight fractions w_1 and w_2 such that the equality (39):

$$P_{\text{mix}}(r) = w_1 P_1(r) + w_2 P_2(r), \tag{39}$$

best matched $P_{\text{target}}(r)$. For example, we use the Kullback-Leibler divergence D_{KL}. Minimum value f Kullback-Leibler divergence: $D_{\text{KL}} = 4.0644$. The corresponding weights are $w_1 = 0.8789$, $w_2 = 0.1211$. The degree of correspondence

between the mixture and target distributions is shown in Fig. 1.

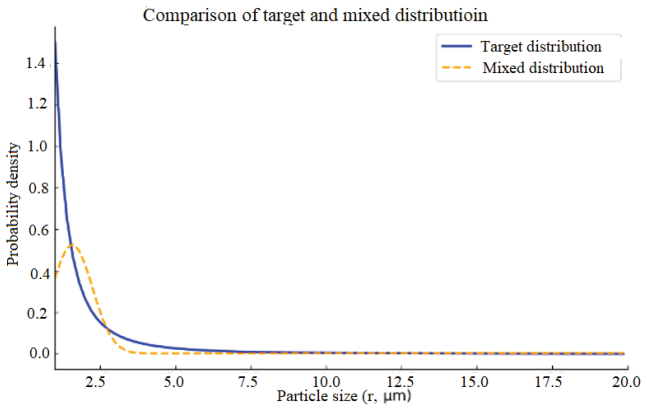

Figure 1 The result of selecting the distribution that best matches the target

Based on the above analysis of adhesion processes and optimization of adhesive interactions using fractal geometry methods, it is possible to evaluate the substrate surface for further selection of the optimal adhesive composition, taking into account the adaptive nature of the ongoing structure formation processes. The restorative material must be able to take the "shape" of pores and the fractal dimension dictated by the relationship (18) for the porous structure during the structure formation process. The adhesive material system adapts to the substrate system, which ensures the integrity and functionality of the resulting adhesive contact system.

Thus, one of the effective concepts for optimizing restorative compositions is the use of fractal patterns that link adhesive interaction with the geometric structure of materials. Fractal dimension D_f is a parameter characterizing the complexity of a surface. In restoration work, she describes how "rugged" the surface of a material, such as stone or limestone, is used in historic buildings. In the case of additive technologies, ideal adhesive contact assumes that the applied composition (adhesive) repeats the surface structure of the restored material as a negative imprint, minimizing voids and improving adhesion. This is only possible by matching the fractal dimension of the adhesive D_2 with a base surface dimension of D_1. The adhesive composition must have the required fluidity and rheological characteristics to ensure uniform distribution over the surface and filling of all voids. Fractal optimization is especially important when using 3D-printing with restoration compositions. Printing allows you to control the micro- and macrostructure of the material, adapting it to complex surfaces. This technology guarantees accurate reproduction of the structural features of a historical building, minimizing the risk of destruction. Moreover, the use of fractal optimization improves the durability of adhesion, reduces the likelihood of delamination and increases resistance to changes in humidity and temperature fluctuations.

5 CONCLUSIONS

The presented work examines theoretical and applied aspects of adhesive structuring of restorative compositions intended for interaction with porous materials such as shell limestone. It is shown that adhesion is a multifactorial phenomenon, including molecular, physicochemical and mechanical components, and the mechanical component has a pronounced geometric-topological character and can be described through fractal parameters. The main approaches to improving adhesive properties are proposed: fractal matching of the surface dimensions of the material and adhesive to achieve ideal contact, optimization of the physicochemical characteristics of the composition by adding nanoparticles and chemical surface treatment. The results of the study showed that successful adhesion is achieved with a comprehensive consideration of molecular, physicochemical and geometric factors. The use of fractal geometry made it possible to quantitatively describe the porosity and texture of the material, as well as to propose criteria for optimizing the composition, including minimizing lacunarity and designing the granulometric distribution of adhesive particles. The practical significance lies in the application of these approaches in additive technologies for restoring historical buildings, where the precise application of compositions, considering the local fractal parameters of the surface, ensures improved adhesion and durability of restoration work. Further research in this area may focus on developing methods to control the structure of adhesives during application and hardening, refining models of structure formation by accounting for temperature and humidity conditions, and utilizing fractal approaches to describe the dynamic properties of adhesive contacts under external influences. Thus, the obtained results emphasize the importance of an integrated approach to the design of adhesive materials based on the coordination of their physicochemical and geometric characteristics with the restored material, which opens up prospects for creating more sustainable and durable technologies in construction and restoration.

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