Basic laws of filled polyaluminosilicate polycondensation used in printed circuit boards of power electronic spacecraft devices

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Abstract. Filled fractal aluminosilicates have been synthesized by a sol-gel method. Optimal conditions to obtain aluminosilicate gels have been determined. The obtained samples have been studied by IR spectroscopy, X-ray phase analysis, transmission electron microscopy, and the du Nouy method. The studies have shown the presence of chemically unbound –OH groups in the aluminosilicates. The effect of the amount of polymer matrix filled with highly dispersed filler powder and medium acidity on the adhesive strength of the dielectric layers applied on aluminum bases by 3D aerosol printing used in printed circuit boards of power electronic spacecraft devices has been studied by means of the du Nouy method.

1. Introduction

The modern development of electronic and space industries along with the advanced nano and microtechnologies sets the task to develop new highly efficient composite materials that meet high operational requirements and are competitive with traditional materials. The composite materials based on sol-gel systems with highly dispersed filler powders, the surface of which is modified in various ways and has an adjustable microstructure, are of particular interest in recent years.

There is sol-gel technology [1] associated with the rapidly developing field of physical chemistry of high-molecular compounds concerned with the synthesis and study of functional inorganic polymer material properties of various structure, namely polyaluminosilicates, among the promising methods to develop composite materials.

According to the modern concepts, gel formation begins with the fractal sol structure formation and fractal aggregate growth. Then they begin to collide and interlock with each other, as the percolation theory describes. Randomly located neighboring clusters, which consist of polymers or particle aggregates, join together to form a single structural network near the gel formation point. When a single tightening cluster forms as if expanding throughout the entire sol volume, the gel point corresponds to a percolation threshold. The sol loses mobility and stiffens after passing the gel formation point and converts into the so-called wet gel. The wet gel usually takes the form of a vessel, in which the sol is located. Gel formation does not stop at the gel formation point. One usually says that the gel ages during aging. This fairly scientific term (gel aging) refers to the structural change processes that occur after the gel formation point in the wet gel. In the formed wet gel a single cluster coexists with the sol that contains many small clusters. At the same time, these small clusters are continuously joining to a common body.
(a continuous giant cluster). In addition, condensation reactions, which have not been fully completed in sols, can continue in gels. Moreover, the reprecipitation of monomers or oligomers occurs, and solid→liquid phase transitions occur.

The interest in this class of inorganic polymers is caused by a large set of synthetic capabilities that provide a big suite of developed chemical structures, high resistance to aggressive environments, high vacuum, and high pressures and temperatures. Functional groups of various purposes introduced into the polyaluminosilicate systems allow obtaining highly ordered systems with a specified chemical structure and reactivity in solvents of various chemical nature. These systems have a number of special properties that differ from the currently known inorganic polymers. Thus, modified highly dispersed filler powders can act as the functional groups. These powders are embedded into the polyaluminosilicate polymer matrix microstructure by molecular or ionic layering. Due to colloidal treatment of dispersed fillers in the sol, uniform distribution of one or several substances along their surface in a thin layer is achieved. As a result, it is possible to form materials with an adjustable homogeneous microstructure that cannot be achieved by the traditional ceramic technology method (mechanical mixing of components). In this case, the materials of various nature, for example metals, their oxides, and carbon materials (nanodiamonds, carbon nanotubes, etc.), can be used as initial highly dispersed filler powders [2-7].

The study aim is to establish the basic physicochemical and technological polycondensation laws (the formation of heterogeneous sol-gel systems) of the filled polyaluminosilicate used in printed circuit boards for power electronic spacecraft devices.

The following main objectives have been set to achieve this aim:

- to study the technological aspects of synthesis, structure formation, and stability of the silicasols based on silicic acids hydrolyzed in an acidic environment in modifying inorganic substances, which are aluminum nitrate and highly dispersed filler powders;
- to study the effect of the sol-gel system structure formation on the properties of the dielectric layers on an aluminum base obtained by 3D aerosol printing based on the synthesized filled polyaluminosilicates with different contents of highly dispersed fillers.

2. Experiment

Modern nanotechnology development should be considered in the first place as a task to create new functional and smart materials. A major breakthrough in this field is associated with the development of mass nanomaterial synthesis methods that have the properties necessary for practical application. As it has already been mentioned, sol-gel technology is the most interesting and promising approach to create functional and smart materials. This technology is based on hydrolysis, homo and heteropolynuclear complexation, polymerization, and polycondensation reactions in solutions with a sol system formation and its subsequent transition to the gel. However, despite the fact that the sol-gel technology is a fairly simple method to produce nanomaterials, the classic sol-gel approach is insufficient to obtain products for practical application.

Let us consider in detail the functionalization of the sol-gel material based on the polyaluminosilicate filled with a highly dispersed filler powder to give it a set of properties necessary for practical application.

It is possible to obtain materials with different chemical structures during the polyaluminosilicates obtained by the sol-gel synthesis. For example, to obtain a composite material used as a dielectric coating for a printed circuit board on an aluminum base we have chosen a fractal polyaluminosilicate structure, which forms under certain physical conditions that have not been completely studied.

The fractal polyaluminosilicate structure formation is described by the following process. Let us assume that a limited two-dimensional space is divided into many square cells. A particle is placed in one of the cells, it serves as a fractal structure nucleus. Mathematically this is a point; physically this is an atom, molecule or cluster consisting of $10^{2}$-$10^{4}$ atoms. Then another particle is placed in a randomly chosen cell that begins to move along the cells in a random way. If the particle reaches the space
boundary during its movement, it is reflected from it and continues to move until it is close to the first particle. In this case it stops and is fixed in this cell, and the next particle is launched into the space. The structure shown in figure 1 forms after constant repetition of the described process, where each particle has found its neighbor after such a walk. Such a branched structure consisting of the particles is called a fractal aggregate. The model has brilliantly been confirmed experimentally (figure 1).

![Image](image_url)

**Figure 1.** TEM photograph of dendrimers of PAS macromolecular assemblies. (200 nm scale, Philips CM 30 transmission electron microscope).

The fractal polyaluminosilicate macromolecule is a microscopic solid body consisting of interconnected microparticles that form a rigid framework, which occupies about half of the total volume and has a low specific density.

A silicic acid and aluminum nitrate have been chosen as starting reagents to form the fractal polyaluminosilicate assemblies for the fractal polyaluminosilicate synthesis to obtain filled tailored materials. The formation has been carried out in three stages: I stage: the silicic acid dissolution by the pH > 7; II stage: the aluminum nitrate hydrolysis; III stage: the light polycondensation with gel-precursor formation from oligosilicic acids and $O_3N$-$Al$-(OH)$_2$ [8].

The gel forms as follows. SiO$_2$ is released from the solution into the solid phase in the form of microscopic particles at many condensation centers at the first stage. The diameter of such microparticles is sequence larger and more than the diameter of the molecules included in its composition. The growing microparticle should acquire charge. SiO$_2$ prevents attaching of the charged molecules to it. Such process is possible in a small range of the solution acidity. We have varied the range during the experimental production of polyaluminosilicates. The molecules that constitute the particles are firmly bound, while they are in the form of ions or molecules in the solution. This occurs under the condition that the molecules appear in the solution as a result of slow chemical processes. A microscopic particle forms as a result of the chemical interaction of individual molecules.

Individual particles combine in the solution as the particles form. It determines the polyaluminosilicate structure. This occurs very slowly, because it depends on microparticle diffusion in
the solution. The last stage of the polyaluminosilicate fractal morphology formation is of great importance and associated with fluid removal in its interfractal and interdomain voids.

The samples with different pH values have been studied to obtain a defect-free polyaluminosilicate microstructure.

The structural arrangement of fractal polyaluminosilicate aggregates is due to diffusion, chemical interaction, and adhesion of the individual microparticles that move in the solution. Figure 1 shows that the fractal aggregate consists of curved spiral branches, some of which end in the form of a fan.

3. Results and discussion

The dependence of acid-base surface properties on the medium pH has been studied in relation to the apparent effect of the surface polyaluminosilicate state on its adsorption properties in this research.

A series of the polyaluminosilicate samples synthesized at pH = 4, 6, 7, 8, and 10 has been obtained as a result of the experiments. The most stable aluminosilicate gels have formed at pH from 6 to 8. The gel has not formed at pH <6 and pH> 8 due to the incomplete precipitation of silicon ions in an acidic medium and the aluminum hydroxide dissolution in an alkaline medium.

The sample structure and phase composition have been studied by X-ray phase analysis. The physical configuration of the obtained diffraction patterns shows that all the samples have an X-ray amorphous structure regardless of the synthesis pH (figure 2). It does not allow identifying them by this method.

![Figure 2. Microdiffraction pattern of X-ray amorphous phase of fractal aluminosilicate.](image)

IR spectroscopy method has been used to study the sample composition (figure 3).

The IR spectra of the aluminosilicate samples (figure 3) show the presence of all expected characteristic bands according to the polycondensation product structure. One can identify a stretching vibration area 3950-2200 cm\(^{-1}\) and bending vibration area 2200-450 cm\(^{-1}\) in the IR spectra of the synthesized samples regardless of the medium pH. The IR spectra of the samples synthesized at various pH values have a similar physical configuration. According to the published data, the functional polyaluminosilicate composition is characterized by the following set of absorption bands: \(\nu_{\text{Al-O}}\) 469 cm\(^{-1}\), \(\nu_{\text{Si-O}}\) 1102.0 cm\(^{-1}\), \(\nu_{\text{Si=O}}\) 1637 cm\(^{-1}\), O-H stretching vibrations with an unbound hydrogen bond are characterized by vibrations \(\nu_{\text{O-H}}\) 3688.0 cm\(^{-1}\), water dimerically bound by hydrogen bonds is characterized by antisymmetric and symmetric H-O-H vibrations in crystallization water \(\nu_{\text{H-O-H}}\) at \(\nu\) 3307.0 cm\(^{-1}\), oligomeric associates are \(\nu_{\text{O-H}}\) 3140.0 cm\(^{-1}\), H-O-H deformation vibrations in crystallization water are \(\nu_{\text{O-H}}\) 1630.0 cm\(^{-1}\), deformation vibrations of H-O- bound water are \(\nu_{\text{H-O}}\) 1527.0 cm\(^{-1}\), deformation vibrations of -OH hydroxyls are \(\nu_{\text{O-H}}\) 1396.0 cm\(^{-1}\), H\(_2\)O vibrations in aquacomplexes \(\nu_{\text{H-O-H}}\) at 854.0-570.0 cm\(^{-1}\).

The IR spectra analysis has shown the presence of chemically and physically bound water and hydroxide ions.
The deep sol polycondensation with the injected in advance nanoparticles of the AlO(OH) highly dispersed filler of amorphous structure (figure 4 and 5) results in the target product formation, i.e. a filled fractal polyaluminosilicate (figure 6). It is carried out in the aluminosilicate sol phase directly on an aluminum product surface (by 3D aerosol material application on an aluminum base) at 20-140 °C. Figure 6 illustrates the possibility to increase the polycondensation degree during heating. Water release occurs in two stages with maxima at 100 and 136 °C. At a temperature of 67-124 °C the sample loses six times more water than in the range of 129-147 °C, when all available OH-groups have already reacted.

**Figure 3.** IR spectra of SiO$_2$·nH$_2$O samples synthesized at various reaction medium pH.

**Figure 4.** Microphotograph of AlO(OH) nano and microparticles located in crowns of fractal aluminosilicate ensembles.
Considering the second objective described in this article, we have applied the filled polyalumino-silicate samples with different content of highly dispersed fillers obtained at pH = 6, 7, and 8 on aluminum substrates using the Aerosol Jet 15EX 3D printer of Neotech AMT company equipped with a pneumatic aerosol generator.

We have estimated adhesive strength to study the structure formation effect of the sol-gel system on the dielectric layer properties obtained by 3D aerosol printing on an aluminum base.

Figure 5. Microdiffraction pattern of AlO(OH) nano and microparticles.

Figure 6. Microphotograph (transmission electron microscopy) of filled fractal aluminosilicate.
Adhesion is a consequence of intermolecular interactions that occur between the surfaces of contacting heterogeneous multilayer bodies. It is a thermodynamic work that needs to be done to separate two contacting bodies under equilibrium conditions.

When adhesion occurs between the Al surface and highly viscous sol of the filled fractal aluminosilicate (FFAS) at the very beginning of coating formation and then between the Al surface and solid-phase gel layer after the gel formation, one new interface occurs between these bodies instead of two interfaces of the contacting bodies. Consequently, the surface energy of two bodies transforms into the energy of the newly formed surface. The adhesion equilibrium work is calculated according to the body surface tension based on the energy conservation law.

It is difficult to measure the surface tension of a solid body and the interfacial tension between liquid and solid bodies. In this case, the adhesion is evaluated according to the wetting value.

Thus, if the liquid surface tension is known, it is sufficient to measure the wetting angle of a solid partner surface by that liquid to determine the adhesion work $A_{ad}$ of this liquid on the solid body surface. This angle is 180° for highly viscous FFAS sols after 3D aerosol application, i.e. the Al surface is completely wetted after 3D printing. It is practically impossible to determine directly the adhesion thermodynamic work of a very viscous FFAS on a solid surface. Therefore, other approaches have been developed for such systems, for example, they do not determine adhesion but adhesive strength, which is measured as the specific work or specific strength of the adhesion fracture between the adhesive (FFAS) and substrate (Al).

In the adhesive bonding mechanical destruction the work to peel two bodies is spent not only for the adhesion overcoming, but also for other processes not related to the adhesion: the studied coating deformation, mechanical interlocking force overcoming in the coating, etc. It is obvious that the concepts of adhesion and adhesive strength, as well as the values characterizing them, are not identical. Therefore, we have taken this into account when comparing the methods to estimate the adhesive strength.

We have varied the amount of highly dispersed filler powder in the fractal aluminosilicate polymer matrix from 60 to 80 % wt, since such an amount of the filler in the polymer matrix makes it possible to provide the necessary thermophysical characteristics of the finished dielectric layers on an aluminum base.

The experimental estimation of the FFAS adhesion strength on aluminum bases applied by 3D aerosol printing has been carried out by the du Nouy method with the K20 digital tensiometer in a measurement range of 1-999 mN/m and the operating temperature adjustment from 10 to 100 °C. The du Nouy method consists in measuring the interfacial (surface) tension $\sigma$ by the du Nouy type tensiometer. The essence of the du Nouy method or ring tearing is to calculate $\sigma$ according to the force required to tear off the ring of the known radius from the polyalumino-silicate coating surface applied on an aluminum base. A platinum rhodium ring has been used, where the ring wire radius $R_1$ is 0.2 mm and the ring radius $R_2$ is 19.09 mm.

**Table 1.** Adhesive strength parameters of aluminosilicate samples with different content of highly dispersed filler powder (60, 70, and 80 % wt) determined by du Nouy method obtained at pH = 6, 7, and 8.

| Parameter | Sample № |
|-----------|----------|
|           | (content of filler micro and nanoparticles, % wt) | (60) | (70) | (80) |
| Adhesive strength – adhesion work $A_{ad}$ at pH=6, mN·m⁻¹ | 1949 | 3211 | 2890 |
| Adhesive strength – adhesion work $A_{ad}$ at pH=7, mN·m⁻¹ | 3781 | 4915 | 4567 |
| Adhesive strength – adhesion work $A_{ad}$ at pH=8, mN·m⁻¹ | 4530 | 6380 | 5917 |
Basing on the obtained results presented in table 1, we can conclude that the obtained filled polyaluminosilicate samples have better adhesive strength to an aluminum base at pH = 8, since not only the adsorption and diffusion interaction between the adhesive and substrate occurs, but also chemical bonds form that leads to the additional adhesion.

The difference in the adhesion strength values at different aluminosilicate matrix filling is due to the intermolecular interactions between the filler and matrix, namely due to the presence of the fractal aluminosilicate domains of unbound –OH groups at the branch ends, which in their turn enter into chemical interaction with the oxidized surface of the aluminum base.

4. Conclusion

The developed method to synthesize filled aluminosilicates by sol-gel synthesis allows obtaining defect-free dielectric layers on aluminum bases in the course of the research. The conditions for the highest stability of the synthesized FFAS have been determined. The most stable gels have formed at pH from 6 to 8. By means of IR spectroscopy it is possible to find the presence of unbound –OH groups that are involved in the formation of chemical bonds with the oxidized aluminum base surface.

According to the research results of the samples obtained by the du Nouy method, change patterns of the filled fractal aluminosilicate adhesive strength to the aluminum base surface have been found. They show that the sample with the highly dispersed filler with 70% mass filling of the aluminosilicate matrix obtained at pH = 8 has the highest effective $A_{ad}$ value.

The samples of dielectric ceramic layers on aluminum bases have been obtained that are used in printed circuit boards of power electronic spacecraft devices.

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