

Dielectric layer of printed circuit boards formation using dendrimer morphology polyaluminosilicates

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Abstract. Aluminosilicates with different molecular weights have been synthesized. A composite material based on aluminosilicates and highly dispersed filler powders with various filling degrees has been obtained. Viscosity values of the aluminosilicates with different molecular weights and composites based on them with highly dispersed AlO(OH) powders have been studied. The processes of mechanochemical mixing of the aluminosilicates with fillers have been studied. The interrelation between the molecular architecture of branched polyaluminosilicates functionalized by reactive groups and their self-organization in thin films and layers has been revealed. Samples with applied dielectric layers and coatings on aluminum bases have been produced. Thermal conductivity of the developed dielectric layers used in printed circuit boards on metal bases has been measured.

1. Introduction

Non-metallic coatings commonly used as dielectric layers for printed circuit boards on aluminum bases have largely reached their parametric improvement limit. At the same time, the up-to-date microelectronics industry development requires reliable materials that work in various operating conditions, including outer space. This problem can be solved by using new materials in combination with the traditional ones.

Currently, a new field of high-molecular compound chemistry concerned with the synthesis and research of the functional inorganic polymer material properties of various structures, namely polyaluminosilicates, is rapidly developing. 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 polyaluminosilicate systems allow obtaining highly ordered systems with a specified chemical structure and reactivity in solvents of various chemical nature, which have a number of special properties that differ from currently known inorganic polymers [1, 2].

Thin (including multilayer) coatings and layers of the mentioned polyaluminosilicate oligomers and polymers are of particular interest. The research relevance of such coatings and layers is currently connected with the rapid development of inorganic microelectronics, an interdisciplinary science field aimed at obtaining lightweight, cheap, and reliable working in extreme operating conditions printed



circuit boards on metal substrates, as well as products and devices with dielectric coatings with improved thermophysical and mechanical properties.

One of the key parameters of dendrimer morphology polyaluminosilicates is the system viscosity and ability to contain a large number of highly dispersed fillers in their interdomain and intercrown spaces. It is known that the larger amount of the filler is injected into a polymer matrix, the lower is the viscosity of a polymer-filler system. The filler amount directly affects the properties of the finished composite material. Moreover, the highly filled material should be capable of forming aerosol for its subsequent application on aluminum substrates by 3D aerosol printing. In this case, a defect-free monolayer with good adhesion to the aluminum base, i.e. good chemical affinity, should be formed. In addition, the physical and physicochemical properties mainly depend on the presence of certain terminal groups in the medium composition, in which they are located. It allows using them in various microelectronic products and devices.

Thin films and layers of dendrimer morphology polyaluminosilicates functionalized by mesogenic and reactive groups can be used in microelectronic devices, semiconductor optoelectronics, and power electronics as inactive layers for various purposes, especially dielectric or protective ones [2]. The problem of controlling such film and layer properties is reduced to solving fundamental interdisciplinary tasks of the influence of functionalized polyaluminosilicate individual elements (in particular, a functional group structure, an end fragment length, and a molecule branching degree) on self-organization processes in thin film layers and on their properties dependent from their application method and also is reduced to determining their molecular architectures as the most promising for specific application. The development of technological methods to manufacture highly organized thin films and layers (including multilayer ones) with a specific structure, morphology, and dielectric and thermophysical properties is an actual applied problem.

The research aim is to find the fundamental interrelations between the molecular architecture of the branched polyaluminosilicates functionalized by reactive groups and their self-organization in thin films and layers and to estimate the possibility of their use as printed circuit board dielectric layers applied by 3D aerosol printing.

2. Experiment

It has already been mentioned that the motivation to develop a new integrated technology to manufacture the dielectric ceramic coatings and layers based on filled polyaluminosilicates and their application on aluminum surfaces is that the problem of creating new special-purpose coatings is perceived as dual. The dialectical problem duality and unity lies in the fact that the first complex issue requiring thorough research is to develop a new method to apply coatings to obtain dielectric layers with the defect-free structure. The second issue is to develop sol-gel synthesis of dendrimer morphology polyaluminosilicates capable of containing up to 80 % wt of highly dispersed filler powders, since a larger filling entails the formation of a loose structure. In other words, it is necessary to study how to produce defect-free dielectric coatings with high thermal conductivity for printed circuit boards and to synthesize aluminosilicates with a high crown formation degree. Such coatings and aluminosilicates can then be technologically applied on these surfaces and used as a polymer matrix for highly dispersed filler powders.

The argumentation for this problem in relation to the task to develop the polymer matrix based on the dendrimer morphology polyaluminosilicates filled with highly dispersed fillers applied on aluminum surfaces is the following:

- A dendrimer morphology aluminosilicate, the macromolecules of which can be of various sizes and shapes: linear, crosslinked, stair, parquet, dendrimer (fractal), etc. is the basis (binder) of a target material for coatings;
- The macromolecule shape and size are the factors that determine the basic physical, physicochemical, and operational properties of the coatings, in the first place, the ability to contain the required amount of fillers. Hydroxides, oxides, and nitrides of Al, B, and other compounds are used as fillers for heat-conducting coatings in most cases.

– Varying the parameters of these factors, one can purposefully change the coating properties on metal surfaces and predict the technology development of both surfaces and applied coatings.

The task is to develop the synthesis of amorphous aluminosilicates, the macromolecules of which are branched dendrimer assemblies capable of containing up to 80 % wt of filler nanoparticles (oxide, oxyhydroxide, and aluminum nitride and/or boron nitride, etc.), and to produce original coatings on aluminum surfaces from the filled polyaluminosilicates that meet high performance specifications, for example, have chemical, electrical, and wear resistance, high thermal conductivity and adhesive power, is the next most important task in the present research.

As the coating basis, the aluminosilicate meets the requirements for heat-resistant and wear-resistant coatings with high thermal conductivity, provided that the macromolecules form such supramolecular formations that form hollow (interdomain) areas capable of containing a large number of filler micro and nanoparticles between them. As the binder coating component, dendrimer aluminosilicate macromolecules with branched crown formation contain the maximum amount of fillers. In addition, the coating is capable of intense heat dissipating emitted in operating microelectronic and LED devices.

Morphological studies are an extremely time-consuming activity, if one takes into account the synthesis of macromolecules with a certain microstructure and the study of supramolecular formations, into which they are combined.

We have previously carried out a computer experiment to form the aluminosilicate segments from silicic acids and aluminum nitrate by the $\text{pH} > 7$ in the framework of the well-known sol-gel synthesis method to avoid unforeseen labor costs. A conformational state of the aluminosilicate segments has been estimated *a priori* by the quantum-chemical method with the available *GAUSSIAN'03W B3LYP/6-31G(d)* software package. The aluminosilicate samples experimentally obtained by polycondensation have been studied by various methods, including transmission electron microscopy. This method has clearly shown the dendrimer morphology of aluminosilicate macromolecules, the formation possibility of them has *a priori* been shown by the quantum-chemical method [3].

2.1. Synthesis and study of the structure polyaluminosilicate.

The synthesis of dendrimer morphology polyaluminosilicates has been carried out in four stages in our research:

- I stage: Silicic acid dissolution (35.7 g of $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ in 70 ml of water containing 5.8 g of NaOH) by the $\text{pH} > 7$;
- II stage: Aluminum nitrate dissolution followed by hydrolysis;
- III stage: Light polycondensation with aluminosilicate sol formation from oligomer molecules;
- IV stage: Intense sol polycondensation is carried out at 20-140 °C [4].

The formation of aluminosilicate macromolecules begins with the formation of a dendrimer nucleus, on which other arcuate oligomer segments are grown in spatially accessible OH-groups. As a result, *macromolecules-dandelions* form, i.e. the dendrimers that are clearly visible in microphotographs. Indeed, the dendrimer macromolecules form, when macromolecular cross-linking or linear macromolecules cannot occur. It is appropriate to mention that the rigidity of aluminosilicate macromolecules prevents their linearization.

One controls the dendrimer assembly morphology by regulating the quantitative characteristics defining their microstructure and size according to certain parameters, such as the number of spatial segments of branches from generations or crowns (N_c), the number of branches formed by each spatial segment or the branching index of links (N_b), the number of terminal groups (Z), the number of generations (G).

We have analyzed the dendrimer assemblies of the synthesized aluminosilicates and have calculated the polymerization degree (P), N_c , N_b , and G . A conformer that allows synthesizing an amorphous polyaluminosilicate has been taken as the assembly nucleus (Figure 1); $N_c = 3$, $N_b = 3$, and $G = 3$. The polymerization degree P or number of repeating units with $N_c = 3$, $N_b = 3$, and $G = 3$ are 120

($P=120$). The number of terminal groups is 81 ($Z = 81$). The molecular weight of the amorphous polyaluminosilicate M is $\sim 480\,000$.

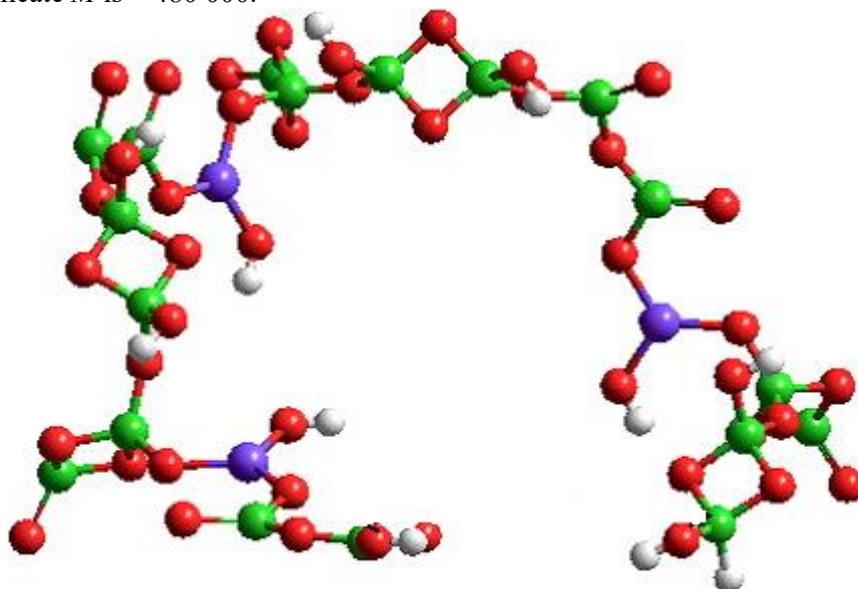


Figure 1. Model of oligomer polyaluminosilicate conformer that is dendrimer macromolecule nucleus visualized by GAUSSIAN computer program.

We have analyzed the elemental composition of the dendrimer polyaluminosilicate assemblies by X-ray fluorescence spectroscopy to confirm quantitatively the calculated polymerization degree P and molecular weight. The content of O and Si elements in the model visualized aluminosilicate samples is close to the experimental values. The difference in Al content is by a factor of 1.5. Perhaps, it can be explained by the discrepancy in this element weights in the experimental and theoretical samples.

It should be emphasized that the principal objective of the research practical orientation is to develop the physicochemical principles to create coatings from filled polyaluminosilicates with enhanced consumer parameters.

3. Results and discussion

AlO(OH) nano and microparticles have been chosen as a highly dispersed filler to obtain dendrimer polyaluminosilicates filled with the latter. The nano and microparticle sizes are comparable to the voids between the aluminosilicate crown branches that allow placing a large number of filler particles in the crowns.

The AlO(OH) nano and microparticles have been injected into the polymer matrix of the dendrimer aluminosilicate by means of the *Emax* ball mill of *Retsch* company by mechanochemical mixing. Thus, mechanochemical processes in a mixed system inevitably result in high shear stresses in macromolecules. Some crowns of the aluminosilicate macromolecules are under the load exceeding the strength of chemical bonds. Moreover, some terminal groups break and react with the highly dispersed filler particles, and new compounds form.

We control the speed of molecular weight decrease varying the mechanochemical mixing intensity. This speed is mainly determined by the shear stress and amount of highly dispersed filler affecting a new compound formation.

It has experimentally been determined that prolonged mixing for 15-20 minutes results in a significant decrease in the aluminosilicate molecular weight and its operational properties loss at very high shear stresses of aluminosilicate dendrimer morphology macromolecules (approximately $1.2 \cdot 10^8$ Pa). Mechanodestructive processes in the aluminosilicate practically do not develop at a shear

stress of less than $1.4 \cdot 10^8$ Pa. Since the viscosity decreases with a decrease in the polymer molecular weight, the mechanodestruction continues up to a certain limit value of the molecular weight.

To control the aluminosilicate destruction it is necessary to know the shear stress and be able to control it during the mechanochemical processes. It has been found in the experimental studies that it is possible to reduce the aluminosilicate destruction degree by decreasing the shear rate and temperature. However, the shear rate decrease is less effective than the temperature increase, since the shear rate decrease is accompanied by the aluminosilicate viscosity increase.

The aluminosilicate viscosity has been measured by the *Brookfield DV2TRV* viscometer.

The research on the physicochemical regularities in the synthesis of the polyaluminosilicates with different molecular weights and the composite material preparation based on them with different content of highly dispersed filler particles will be presented in our subsequent articles. The oligoaluminosilicate binder viscosity is in the range of 0.26 ± 0.01 Pa·s. The viscosity of AlO(OH) oligoaluminosilicate filled by 80 % wt highly dispersed powder is in the range of 2 ± 0.02 Pa·s.

A large amount of highly dispersed filler injected in the aluminosilicate polymer matrix dramatically increases the mixture viscosity and causes the mechanochemical processes to occur more intensively. Therefore, it is necessary to take into account the molecular weight decrease of the polymer binder in case of the system high filling.

Thus, the shear stress increase, on the one hand, improves the filler dispersion degree, but on the other hand, causes an undesirable process of the polymer mechanodestruction. Therefore, it is necessary to carry out the mixing under the optimal technological conditions (temperature, shear rate, filler concentration, and time) to obtain the filled polyaluminosilicate with adequate properties.

During the research, we have managed to choose the optimal conditions for the mechanochemical mixing by the dispersed filler different contents in the system (up to 80 % wt). It has been found that this method allows achieving the maximum distribution of filler particles in the crowns and intercrown spaces of the dendrimer morphology aluminosilicate. It also contributes to degassing processes occurring as a result of chemical interaction of the polymer-filler system components.

The obtained composite material has been subjected to additional ultrasonic deagglomeration in the *LABORETTE 17* ultrasonic bath after mixing.

We have used the synthesized polyaluminosilicate filled with a highly dispersed filler and the *Aerosol Jet 15EX 3D* printer of *Neotech AMT* Company to obtain ceramic layers and topologies on aluminum bases by 3D aerosol printing with the help of the pneumatic method.

A series of samples has been obtained from the filled dendrimer morphology polyaluminosilicates to measure thermal conductivity using a laser flash method (Parker method).

Table 1. Thermal conductivity parameters for aluminosilicate samples with different filler contents (20, 30, 40, 50, 60, 70, and 80 % wt) determined by Parker method.

Parameter	Sample №						
	(content of filler micro and nanoparticles, % wt)						
	1 (20)	2 (30)	3 (40)	4 (50)	5 (60)	6 (70)	7 (80)
λ (W/m·K)	9.31	17.27	24.67	81.35	106.14	123.73	141.25

Bearing in mind the maximum thermal conductivity (141.25 W/m·K) of sample 7 (Table 1), the aluminosilicate filling with aluminum oxyhydroxide in an amount of 80 % wt is optimal. Other required parameters for the filled dendrimer morphology polyaluminosilicates, which are stable by aerosol formation and their application on an aluminum base, should be taken into account.

4. Conclusion

The aluminosilicate viscosity values with different molecular weights and composites based on them with highly dispersed AlO(OH) powders have been studied. The processes during the

mechanochemical mixing of the aluminosilicates with fillers have been studied. The interrelation between the molecular architecture of the branched polyaluminosilicates functionalized by reactive groups and their self-organization in thin films and layers has been revealed. The samples with applied dielectric layers and coatings on aluminum bases have been produced. The thermal conductivity of the developed dielectric layers used in printed circuit boards as heat-conducting dielectric layers on metal bases has been measured.

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