Synthesis and research of polyaluminosilicate chemical structure influence on properties of dielectric layers received by 3D aerosol printing

A A Ivanov¹, V A Polyushko² and A Yu Khomyakov¹

¹Tomsk State University of Control Systems and Radioelectronics, Tomsk, 634050, Russia
²Tomsk State University, Tomsk, 634050, Russia

E-mail: alexchemtsu@rambler.ru

Abstract. Polyaluminosilicates with different chemical structures have been synthesized. They have been experimentally studied and a priori estimated. Dielectric ceramic layers have been obtained by means of 3D aerosol printing and studied with the use of synthesized polyaluminosilicates and highly dispersed powder of Al₂O₃ ceramic filler.

1. Introduction

The advanced industries, especially microelectronics, develop on the base of multifunctional materials. Inorganic polymer composites, in their turn, often play the major role in this process. For example, the Bergquist Company (USA), a well-known manufacturer of thermal-conducting electrically insulating materials, produces the printed circuit boards on a metal base Thermal Clad IMS (Insulated Metal Substrate) that consist of a metal substrate, a dielectric thermal-conducting layer, and a metallization layer. The dielectric layer is a key element of Thermal Clad IMS. It is a special chemically resistant polymer structure with a ceramic filler. Such a material called Bond Ply has high adhesion to a metal surface, mechanical and thermomechanical strength. Its breakdown voltage is not lower than 6 kV of an alternating current at a surface and volume resistance of 10¹³ Ohm/square and 10¹⁴ Ohm·m with a thickness of 75 micron. Consequently, the thermal conductivity is not lower than 1.3 W/m·K. Such dielectric layer parameters do not allow using Thermal Clad IMS in power electronics where more efficient heat removal is required. Such heat removal is impossible due to the limited thermal conductivity of the Thermal Clad IMS dielectric layer.

Using nothing but polymers to produce microelectronic products and devices for various purposes is often ineffective. One may improve the polymer material properties, such as thermophysical, physicomechanical, and physicochemical, using the dispersed filler powders that differ in their chemical nature and set the necessary properties of the finished composites.

Physical chemistry of high-molecular compounds is rapidly developing in the frame of fundamental science and different technologies. It is a new field concerned with the synthesis and study of the structure and properties of three-dimensional hyperbranched polymers and oligomers, the so-called dendrimers (fractals). The polymers with such macromolecular assembly morphology of both organic and inorganic compounds attract our attention because the number of branches increases exponentially by each chain growth act in three-dimensional macromolecular assembly synthesis. As a
result, the macromolecule size and shape change that leads to major physical and physicochemical properties change, such as viscosity, solubility, moisture absorption, density etc.

Some synthetic approaches allow obtaining regular dendrimer assemblies, the macromolecules of which have well-defined molecular mass. Furthermore, it should be noted that a lot of physical and physicochemical properties of dendrimer materials such as glass transition temperature mainly depend on the chemical nature of the terminal groups located on spherical macromolecules.

All of the above-mentioned arouses chemists' interest in the dendrimer macromolecule synthesis. Thus, the dendrimers based on simple and complex polyethers, polyamides, polyphenylenes, polysiloxanes, polycarbosilanes etc. have been synthesized and described in the scientific literature [1-4]. The controlled synthesis of polyaluminosilicates combined with the product forming phase by means of 3D aerosol printing of the dielectric ceramic layers of printed circuit boards is an innovative and cost-effective way that provides the necessary properties for printed layers.

Consequently, the size, phase, structural, and other morphological characteristics that determine the physicomechanical, physicochemical, and service properties of the end dielectric layers of printed circuit boards form during the synthesis of polyaluminosilicates. The traditional techniques to obtain the nanostructured ceramic material with the desired stoichiometry, homogeneity, high purity, and specific micro- and supramolecular structures may not always lead to the goal. Taking into account the fact that it is possible to control the supramolecular structure of polyaluminosilicates in the synthesis phase, one should not forget about its interaction with the dispersed filler powders that have their own phase and structural features. In this case, the material properties depend on functional additives and are predetermined by such characteristics as the type of supramolecular formations, uniform distribution of components, specific surface area, porosity, and phase composition etc.

The method of mixing (injection) of the dispersed filler with the polymer matrix also influences on the properties of the finished composites. In the present research we have injected the Al2O3 dispersed powder into the polymer polyaluminosilicate matrix by mechanochemical mixing with subsequent ultrasonic deagglomeration.

The study objective is to synthesize the polyaluminosilicate chemical structure and research its influence on the properties of the dielectric ceramic layers of printed circuit boards based on the polyaluminosilicates filled with highly dispersed fillers applied on aluminium bases by 3D aerosol printing.

This study continues a series of our articles on the problem of dielectric ceramic layers forming on an aluminum base by means of 3D aerosol printing. The main results have been obtained for the samples of the polyaluminosilicates filled with highly dispersed Al2O3 filler with 65 % wt.

2. Experiment

The polyaluminosilicate macromolecules have the peculiarity to accept various sizes and shapes in the synthesis: linear, cross-linked, ladder, parquet, dendrimeric etc. [5, 6]. The polyaluminosilicate macromolecules shape, size, and geometry determine the basic physicomechanical, physicochemical, and service properties of dielectric ceramic layers. For example, their tendency to form three-dimensional hyperbranched macromolecules containing the maximum possible quantity of filler nano- and microparticles (Al2O3 in this case) in the space between the branches (crowns) under certain conditions allows obtaining high-strength ceramic materials with superior thermal conductivity. The polyaluminosilicates with branched crowns formation contain the maximum filler quantity. These layers (the coating) made of this composite can intensify heat dissipation during the operation of microelectronic products and devices.

One can purposefully change the properties of the coatings applied on metal surfaces and forecast their properties dependence on the operating conditions and run time by varying the structural and morphological parameters of the components for producing composites.

It is possible to control the supramolecular structure of the polyaluminosilicates depending on their synthesis conditions. It is well known that the viscosity of linear polymers increases with molecular mass increasing according to the Mark-Kuhn-Houwink equation \( [\eta] = K M^\alpha \), where \([\eta]\) is the polymer
characteristic viscosity, $M$ is the average molecular weight, and $K$ and $\alpha$ are constants. Unlike all the other macromolecules including branched and star-shaped, dendrimeric polymers do not suit this equation after reaching a certain $M$. For example, $[\eta]$ of dendrimeric polyesters decreases with further growth of $M$ after reaching $M \approx 5000$ that is anomalous for the corresponding linear polyesters. This paradoxical effect can be explained by the following fact. As the generation number increases, the dendritic macromolecule volume increases in proportion to the third degree of a linear size ($V = 4/3 \pi r^3$) while its mass increases exponentially ($\sim 2^{G-1}$, where $G$ is the number of branch generation). Such dependence is not appropriate for linear polymers [7, 8].

The unusual relationships between $[\eta]$ and $M$ of dendrimers are associated with the globular macromolecule shape (as opposed to loose skeins). The dendritic macromolecule interior has a unique microenvironment that turns the macromolecule into a globule (dense skeins) [9, 10].

The polyaluminosilicates of various structures with various supramolecular formations and having different molecular masses have been obtained during the research. Silicic acids have been chosen as starting reagents (figure 1). The synthesis of polyaluminosilicates carries out in three stages:

*I stage:* the silicic acid dissolution by the pH $> 7$

\[
\text{HO-Si-O-Si-OH} + \text{NaOH} \rightleftharpoons \text{HO-Si-O-Si-ONa} + \text{H}_2\text{O}
\]

*II stage:* the aluminum nitrate hydrolysis

\[
\text{O}_3\text{N-Al(NO}_3\text{)}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{O}_3\text{N-Al(OH)}_2 + 2\text{HN}_3\text{O}_3
\]

*III stage:* polycondensation with gel formation from oligosilicic acids and $\text{O}_3\text{N-Al(OH)}_2$

\[
\text{HO-Si-O-Si-O-Si-OH} \rightleftharpoons \text{Si-O-Si-O-Si-OH}
\]
One initially interrupts stage III at the initial phase of the sol transition into the gel in order to inject later the dispersed Al₂O₃ powder by mechanochemical mixing with subsequent ultrasonic deagglomeration. Then one continues stage III, and the dielectric layers of printed circuit boards are formed by 3D aerosol printing.

The necessary data for the a priori research of the polyaluminosilicate microstructure have been obtained after the viscosity characteristics of the polyaluminosilicate samples synthesized under various conditions have been studied.

Computer simulation is the only approach to the a priori study of the polyaluminosilicate gel microstructure in this research. The influence of the conformational states of the polymer molecule segments on the polymer chain rigidity has been estimated by their geometric optimization by means of the computer-aided calculation of conformations (the B3LYP method with the 6-31G basic set). It is shown that the polymer chain rigidity depends on the polyaluminosilicate gel microstructure. The oligomer segment conformations change depending on the freedom degree of Si-O-Al-O-Si rotational oscillations. The conformer population levels also depend on the atomic radii and charges of Si and Al atoms. The Si charge varies from 1.201 to 1.305 and Al charge varies from 0.973 to 0.986. The Al atom presents less steric difficulties. The most appropriate conformation, which prevents the long-range order formation in the arrangement of structural elements, is the conformation shown in figure 2a. In other words, it is those conformations that form the dendritic supramolecular structures that, in their turn, form amorphous polyaluminosilicates (Fig. 2a).

Other conformations shown in figures 2b, 3a, and 3b are less prone to form the dendritic supramolecular structures since the levels of conformer populations are arranged in such a way that the charges between silicon and aluminum atoms promote their repulsion that arranges the structural elements of long-range order polyaluminosilicate macromolecules.

Figure 1. Diagram of structural configuration of silicic acids.
The ability of the obtained polyaluminosilicates to contain a large amount of the dispersed filler, which specifies the necessary thermophysical parameters of the end dielectric layers, is very important to use and apply them on aluminium bases by 3D aerosol printing as the dielectric layers of printed circuit boards.

To obtain an aerosol in a 3D printer (the Aerosol Jet 15EX 3D printer of Neotech AMT Company) using a pneumatic generator it is necessary that the viscosity of the polyaluminosilicate filled with the dispersed $\text{Al}_2\text{O}_3$ powder does not exceed the limit values allowed for the aerosol pneumatic generation from the composite material.

For example, the sample with a dendrimeric structure (figure 2a) is the most preferable by 65 % wt. filling with the dispersed $\text{Al}_2\text{O}_3$ powder of polyaluminosilicate of different structure (figures 2a, 2b, 3a, and 3b) (the most preferable structures for the dispersed filler powder injection) because the obtained system viscosity (composite material) is suitable for its pneumatic generation after the mechanochemical mixing of the polyaluminosilicate polymeric matrix with the dispersed $\text{Al}_2\text{O}_3$ powder has been carried out with subsequent ultrasonic deagglomeration.
3. Results and discussion

The samples of the dielectric ceramic layers of printed circuit boards have been obtained by means of 3D aerosol printing (figure 6) with the use of the obtained composite material based on the dendrimeric morphology polyaluminosilicate and dispersed filler Al₂O₃ powder (figure 5). The thermal conductivity of the obtained dielectric layers has been measured (the LFA 667 device of NETZSCH Company) by means of the laser flash method (the Parker method).

![Particles Al₂O₃](image)

**Figure 5.** Microphotographs of dendrimeric morphology polyaluminosilicate and dispersed filler Al₂O₃ powder (in upper-right corner) obtained by transmission electron microscopy (TEM).

The average thermal conductivity of the dielectric ceramic layers on aluminum bases obtained by means of 3D aerosol printing is 21 W/(m·K). Taking into account that the amount of the dispersed Al₂O₃ filler in the polymer matrix of the dendrimeric morphology polyaluminosilicate does not exceed 65 % wt., one can assume that a new structure, which can be considered as a completely new material with fundamentally new properties, appears by mechanochemical mixing of the system components. The research of the obtained system structure has to be continued and the results will be presented in our future works.

The mass loss of the samples of the dielectric ceramic layers of printed circuit boards on aluminum bases obtained by 3D aerosol printing (figure 6) has been estimated by thermogravimetry and mass spectrometry.

The first two peaks show the water desorption in figure 7. The desorption of physically adsorbed water (moisture) usually occurs at a temperature not lower than the adsorbate boiling point (in this case 100 °C). The fact that a desorption peak can be observed at 60 °C may indicate polycondensation processes occurring with water exudation in the sample. Consequently, there are no volatile substances in the insulation coating after the heat treatment at a temperature of more than 100 °C. This fact proves the shrinkage absence of the dielectric ceramic
layer after drying even at room temperature. This favorably affects the choice of microelectronic products and devices, which the obtained dielectric layers can be applied for.

![Image of dielectric ceramic layer samples on aluminum bases obtained by 3D aerosol printing.](image)

**Figure 6.** Photograph of dielectric ceramic layer samples on aluminum bases obtained by 3D aerosol printing.

![Graph of DSC and TG curves for dielectric ceramic layer sample.](image)

**Figure 7.** Curves of differential scanning calorimetry (DSC) and thermogravimetry (TG) of sample 9 (figure 6) of dielectric ceramic layer on aluminum base after it has been kept in vacuum desiccator above P2O5 for 3 days at T_room (STA 449 F1 device of Netzsch Company) combined with quadrupole QMS 403 D Aeolos mass spectrometer (of Netzsch Company). Al is crucible material. Measurement conditions are following: heating at rate of 10 °C/min, medium is Ar (99.999, flow 50 ml/min.) Baseline has been corrected before measurements.
4. Conclusion
In conclusion, the polyaluminosilicates with different chemical structure have been synthesized in the work. The experimental study and a priori assessment of the obtained polyaluminosilicates allow selecting several samples for their further use as a polymer matrix for the highly dispersed powder of the ceramic filler. The ceramic dielectric layers on an aluminum base have been obtained with the use of the system based on the dendrimeric morphology polyaluminosilicate and highly dispersed ceramic powder of Al₂O₃ filler. Their thermal conductivity is 21 W/(m·K). The obtained samples study by TG and DSC methods has shown no shrinkage and degassing by heat treatment over 100 °C that significantly expands the scope of their application.

Acknowledgements
The reported study was funded by RFBR according to the research project № 18-29-11018/18.

References
[1] Tomalia D A and Durst H D 1993 Top. Curr. Chem. 165 193–313
[2] Tomalia D A, Naylor A M and Goddard W A 1990 Angew Chem. 102 119–57
[3] Tomalia D A et.al. 1986 Macromolecules 19 2466–8
[4] Newkome G R et. al. 1985 J. Org. Chem. 50 2003–4
[5] Takahashi K et. al. 2006 Int. J. of Adhesion and Adhesives 26 639–43
[6] Uchida H. et. al. J. Am. Chem. Soc. 112 7077–9
[7] Lambert J B, Pflug J L and C L Angew 1995 Chem., Int. Ed. Engl 34 98–9
[8] Suzuki H et. al. 1995 A. Chem. Lett. 293
[9] Caminade A M and Majoral J P 2004 II Accounts of chemical research 37(6) 341–8
[10] Phair J W, Smith J D and Van Deventer J S J 2003 Materials Letters - MATER LETT., 57(28) 4356-67