

## Filled Aluminosilicate of Dendrimer Morphology Used as Low Temperature Cofired Ceramic in LED Devices and Spacecraft Control Systems

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Sol-gel synthesis of filled aluminosilicates with macromolecules having a dendrimer morphology (Mcalc  $\approx$  480000) was developed. The software package Gaussian B3LYP/6-31G(d) was used to assess the possible mechanism by which nuclei of dendrimer molecules are created, with the subsequent generation of crowns of branched ensembles capable of accommodating up to 80 wt % nano-AlOOH as a filler. The data furnished by transmission electron microscopy of the samples are in agreement with the suggested mechanism of generation and growth of dendrimers. The main results were obtained on filled aluminosilicate samples that contain 80 wt % nano-AlOOH and exhibit a high wear resistance in tribological tests.

**Keywords:** Polymer composite materials, Morphology, Dendrimers, LED devices, Low-temperature ceramics, Aluminosilicates.

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### 1. INTRODUCTION

The advanced industries, especially space industry, semiconductor optoelectronics and microelectronics develop on the base of multifunctional materials. Polymer composite materials, in their turn, often play the major role in this process. Physical chemistry of high-molecular compounds is actively developing in the frame of fundamental science and different technologies. It is a new field concerned with the synthesis and investigation of the structure and properties of three-dimensional hyperbranched polymers and oligomers, the so-called dendrimers [1]. The polymers with such macromolecular ensemble 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 ensembles synthesis. As a result, the macromolecules size and shape change that leads to major physical and physicochemical properties changes such as viscosity, solubility, moisture absorption, density etc.

Some synthetic approaches allow obtaining regular dendrimer ensembles (DA), the macromolecules of which have well-defined molecular weight. 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 the spherical "macromolecules-dandelions" surface [2].

All above-mentioned arouses chemists' interest in the dendrimer macromolecules synthesis. Thus, the dendrimers based on simple and complex polyethers, polyamides, polyphenylenes, polysiloxanes, polycarbosilanes etc. have been synthesized and described in scientific literature [2]. The controlled synthesis of dendrimeraluminosilicates (AS) combined with the product forming phase (for example, coatings on a substrate) is an innovative and cost-effective way that provides the necessary properties for ceramic composites [3].

The size, phase, structural and other morphological characteristics that determine the physicochemical, physicochemical and service properties of end materials

form during the AS synthesis. The traditional techniques to obtain the nanostructured ceramic materials with the desired stoichiometry, homogeneity, high purity and specific micro- and supramolecular structures may not always lead to the goal [3, 4].

One microstructure can not determine the properties of material (physical body) consisting of macromolecules. The formation of dendrimer AS amorphous structures with the desired stoichiometry and set microstructure is an innovative approach to develop next generation multifunctional materials.

The research aim is to develop the low-temperature synthesis of amorphous AS, the macromolecules of which are the branched dendrimer ensembles capable to contain up to 80 % wt of filler nanoparticles (oxide, oxyhydroxide or aluminum nitride etc.) and form the so-called filled aluminosilicate (FAS). The materials made from such FAS correspond the technical specifications, for example have sufficient electric strength and high thermal conductivity [5, 6].

Our own technology to obtain aluminosilicates of dendrimer morphology, by which the material properties formation and modification are crucial, provides us the opportunity to develop such next generation low-temperature synthesis materials with radically new properties.

The prerequisites for such materials production technology development are as follows: 1) the possibility of preliminary quantum-chemical assessment of conformational states to predict the shapes and sizes of AS dendrimer crowns formation; 2) the capability to accommodate the maximum amount of filler nanoparticles in the branched AS dendrimer crowns.

One can obtain the dendrimer AS by a sol-gel method that include three-dimensional gel-precursor polycondensation by means of metalloxopolymer molecules crosslinking in solutions (chemically controlled polycondensation).

The monomeric or polymeric compounds and pre-composites including the products required for technological processing in end ceramic elements are used in sol-gel processes as precursors. The advantage of pre-

cursors is the opportunity to develop a wide range of nanocomposites: nanofibers and film materials, ceramic-matrix composites, ceramic binders etc.

The choice of precursors for low-temperature ceramics synthesis is based on our own structural and chemical conception of intermolecular interactions and on the structure geometrical parameters calculation. Consequently, our structural and chemical conception allows adjusting the precursors activity to their intermolecular structure applied to the sol-gel process [5].

The precursor choice for low-temperature ceramics synthesis is based on the opportunity:

- to calculate a priori the filling degree of the compounds original system with the known or simulated hypothetical molecular geometry that consists of the necessary components for the desired end product;
- to determine the quantity and types of possible intermolecular interactions;
- to choose the most prospective precursors.

The dendrimer AS provide the polymer materials with the controlled properties as their formation process is accompanied by three-dimensional branches growth. The macromolecules shape and rigidity change simultaneously with the molecular weight (MW) increase. This process is accompanied by the physicochemical properties change of the bodies consisting of dendrimer AS: phase state, viscosity, solubility, density etc.

## 2. THE DENDRIMER AS SOL-GEL SYNTHESIS

Many studies on the amorphous and crystalline AS and aluminophosphates synthesis have been published [1-3, 7-20]. This synthesis products are used as catalysts, adsorbents, dielectrics, structural materials and in other fields of science and technology including medical supplies. Silicic acid and aluminum nitrate have been chosen as starting reagents to form the dendrimer AS ensembles for the synthesis of dendrimer AS to obtain the filled tailored materials. The formation was carried out in three stages:

- I stage: The silicic acid dissolution by the  $\text{pH} > 7$ ;
- II stage: The aluminum nitrate hydrolysis;
- III stage: Light polycondensation with gel-precursor formation from oligosilicic acids and  $\text{O}_3\text{N-Al}(\text{OH})_2$ .

One interrupt stage III to obtain the FAS samples so that the well-proportioned and adequate dendrimer crowns form to inject the nanoparticles of monomeric precursor- powders by the mechanochemical mixing method with the simultaneous ultrasonic machining. In such a way one can obtain the FAS containing different quantities of fillers.

The AS sample TEM photo displays the clearly structured picture of the AS dendrimer macromolecular ensembles obtained by the polycondensation (Fig. 2).

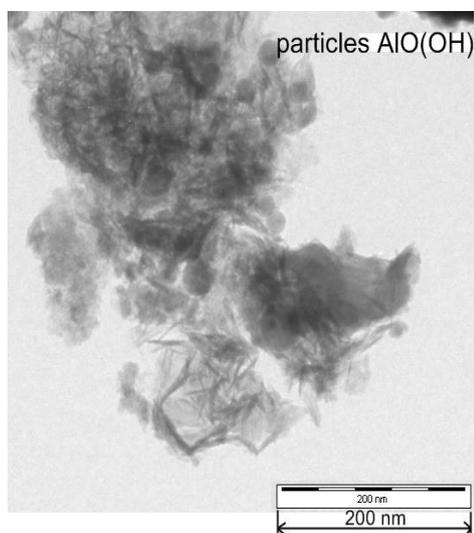
## 3. ALUMINOSILICATE MORPHOLOGY COMPUTER VISUALIZATION

Computer simulation is the only approach for the a priori research of gel-precursors microstructure in our study. The influence of the polymer molecule segments conformational states on the polymer chain rigidity was estimated by the geometrical optimization using the

conformation computer calculation method (method B3LYP with basis set 6-31G).

Stepwise polycondensation illustrating the aluminosilicate fragment formation provides the computer simulation for aluminosilicate segments of the most probable conformations that counteract the intermolecular crosslinking and contribute to the oligomer dendrimerization with crown formation. Indeed, the OH-groups steric accessibility on the apices of the arcuate oligomer segments implies the great probability of chemical bonds between the arcuate segments that results in the formation of dendrimer morphological units, generations or crowns. Any conformer (I), (II), (III) or (IV) can serve as a center or nucleus to start the polycondensation processes (Fig. 3). That results in intensive crown formation because the unbound OH-groups included into the ( $=\text{Al-OH}$ ) ensembles enter into the condensation reaction with OH-groups bound to the ( $\equiv\text{Si-OH}$ )-groups. As already mentioned, both types of OH-groups are located on the arcuate segment apices and that is why they are dimensionally accessible. It is easy to notice that such polycondensation results in macromolecule formation in the form of DA (Fig. 2).

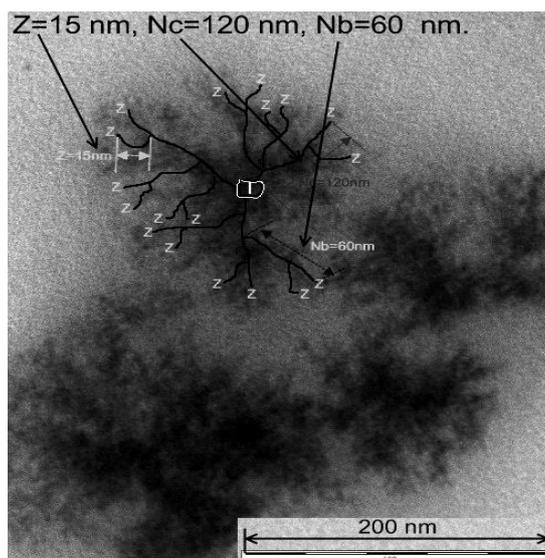
Possible conformers (I)-(IV) (Fig. 3) formed from metadysilicic (MDS), orthosilicic (OS), metasilicic (MS) acid,  $\text{AlOOH}$  (Fig. 1) form at stage III as a result of polycondensation. Conformer (I) consisting of comonomers MDS, Al, OS and MS is represented by twelve simulated monomer units as a sequence of abbreviations MDS-Al-OS-MS-MDS-Al-OS-MS-MDS-Al-OS-MS and as a visualized model in Fig. 3.



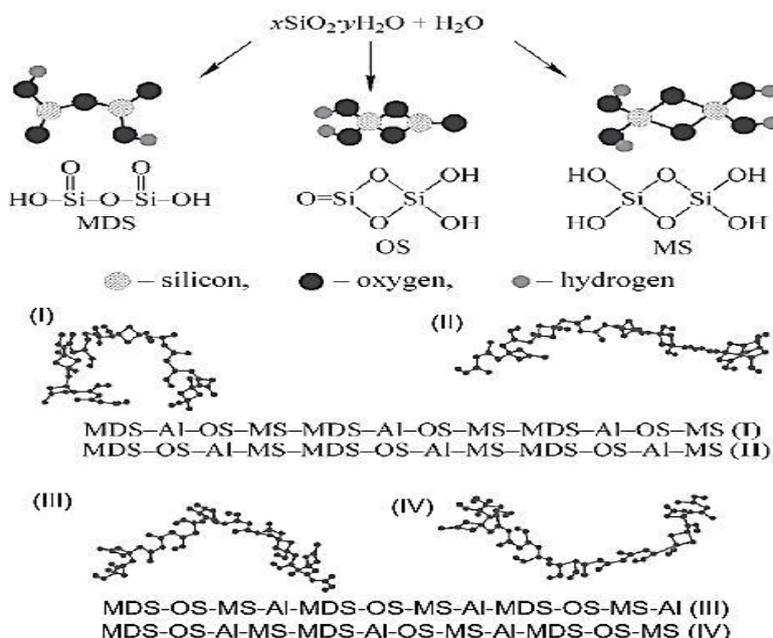
**Fig. 1** – The micrograph of  $\text{AlO}(\text{OH})$ , the nanoparticles of which are located in the dendrimer ensembles crowns (the upper right figure).

## 4. CONCLUSIONS

A simple comparison between the visualized models (calculated by the quantum-chemical method) (Fig. 3) and the micrograph of AS dendrimer ensemble obtained by means of TEM (Fig. 2) leads to the conclusion about the identity between the AS morphological picture obtained by TEM and the idea of oligomer segments participating in crown formation. In other words, the AS macromolecule formation starts with the



**Fig. 2** – The TEM photos of the aluminosilicate and aluminioxyhydroxidedendrimer macromolecular ensembles. There are dendrimer design parameters on the upper left crown



**Fig. 3** – The oligomer AS conformer model capable of playing the role of DA nucleus and participating in crown formation visualized by a computer program Gaussian

dendrimer nucleus formation. Other arcuate oligomer segments grow on the nucleus around the dimensionally accessible OH-groups that results in "macromolecules-dandelions" formation, i.e. the dendrimers, which are clearly visible in the TEM photos (Fig. 2).

It is also shown that the polymer chain rigidity depends on the gel-precursor microstructure. The oligomer segment conformations change depending on the degree of Si-O-Al-O-Si rotational oscillations freedom. Conformer population levels also depend on atomic radii and charges of Si and Al: Si charge varies from 1.201 to 1.305, Al from 0.973 to 0.986. Al atom provides less steric hindrance. The most adequate conformation preventing the long-range order formation in structural elements is the conformation shown in Fig. 3 (IV). In other words, precisely these conformations participate

in dendritic supramolecular structure formation, which in its turn form dendrimeraluminosilicates (Fig. 2).

The quantitative parameters that determine the dendrimer AS macromolecular structure and sizes are the quantity of crowns (Nc) and the quantity of branches (Nb) that are formed by every dimensional segment (Z) (element branching index) as well as by the quantity of generations (G) (Fig. 2).

The synthesized dendrimer AS samples have crowns (Nc = 3) and branches (Nb = 3) that are well-defined by the TEM method (Fig. 2).

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