Dendrimer Polyaluminosilicates as a Matrix for Filled Coatings

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Abstract—Sol-gel synthesis of filled polyaluminosilicates with macromolecules having a dendrimer morphology ($M_{\text{calc}} \approx 480\,000$) 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 70 wt % nano-$\text{Al}_2\text{O}_3$ 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 70 wt % nano-$\text{Al}_2\text{O}_3$ and exhibit a high wear resistance in tribological tests.

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Modern branches of technology, and primarily the industry of light-emitting diodes and microelectronics, are developed on the basis of polyfunctional materials, with the principal role frequently played by inorganic polymeric composites. A new area of research in the physical chemistry of macromolecular compounds has been evolving in the field of fundamental science and various technologies. It is associated with synthesis and studies of the structure and properties of 3D superbranched polymers and oligomers, the so-called dendrimers [1]. Polymers with this morphology of macromolecular ensembles of both organic and inorganic compounds attract researchers’ attention because the number of branches increases exponentially with each chain-growth event in the course of synthesis of 3D macromolecular ensembles. As a result, both the size and shape of macromolecules change, which is accompanied by a profound modification of their physical and physicochemical properties, such as viscosity, solubility, moisture absorption, density, etc.

Some synthetic approaches can produce regular dendrimer ensembles (DEs) whose macromolecules have a rather well-defined molecular weight. It should be noted, in addition, that many physical and physicochemical properties of dendrimer materials, e.g., their glass transition temperature, mostly depend on the chemical nature of terminal groups situated on the surface of spherical “macromolecules-dandelions” of this kind.

All the aforesaid arouses chemists’ interest in syntheses of dendrimer macromolecules. For example, dendrimers based on polyethers and polyesters, polyamides, polyphenylenes, polysiloxanes, polycarbosilanes, etc. have been synthesized and described in the literature [2]. Combining the controlled synthesis of dendrimer polyaluminosilicates (PASs) with the stage of technological molding of articles (e.g., formation of coatings on a substrate with a developed surface) is an original and economically advantageous procedure that imparts required properties to ceramic composites.

The dimensional, phase, structural, and other morphological characteristics responsible for the physicomechanical, physicochemical, and service properties of finished coatings are set already in the course of PAS synthesis. Use of classical methods for synthesis of nanostructured ceramic materials with a required stoichiometry, homogeneity, high purity, and certain micro- and supramolecular properties fails to always yield desired results [3, 4].

The goal of the present study was to develop a method for synthesis of amorphous PASs whose macromolecules have the form of branched dendrimer ensembles that can accommodate up to 70% filler nanoparticles (aluminum oxide or nitride, zirconium dioxide, etc.) and form the so-called filled polyaluminosilicates (FPASs) whose
coatings on metallic surfaces satisfy technical specifications, e.g., have a sufficient adhesion strength and high heat conductivity [5, 6].

The study proceeds with the earlier research into the problem of formation of multilayer coatings on rough surfaces. The main results were obtained with FPAS samples containing 70 wt % Al₂O₃ (FPAS-70).

There are the following prerequisites for development of a technique for deposition of coatings of this kind: (i) possibility of a preliminary quantum-mechanical assessment of conformational states for prognosticating the shape and size of the crown-formation in PAS dendrimers; (ii) capacity to accommodate the maximum amount of filler particles in the branched “crowns” of the PAS dendrimers; and (iii) possibility to form a superdeveloped surface in aluminum articles, with a surface profile of certain configuration and strong roughness [7].

SOL-GEL SYNTHESIS OF SUPERBRANCHED PAS DENDRIMERS OF SiO₂ : Al₂O₃ = 40 COMPOSITION

There have been numerous published reports devoted to syntheses of amorphous and crystalline PASs and polyphosphates [8–12]. Products of these syntheses find use as catalysts, adsorbents, insulators, construction materials, and in other fields of science and technology, including those related to medicine [13–15]. Silicic acids and aluminum nitrate were chosen as starting reagents from which dendrimer PAS ensembles can be formed in order to synthesize amorphous dendrimer PASs for special-purpose filled coatings. The ensembles were formed in three stages. In some experiments, H₃PO₄ was added to control the dendrimer crown branching.

Stage I. Dissolution of silicic acids (35.7 g of SiO₂ₙH₂O) in 70 mL of water containing 5.8 g NaOH at pH > 7:

The resulting homogeneous solution is mixed with a solution of 5.52 g of NH₄HCO₃ in 120 mL of water.

Stage II. Dissolution of aluminum nitrate, accompanied by its hydrolysis:

\[
\text{O}_3\text{N} \rightarrow \text{Al} \xrightarrow{\text{NO}_3} + 2\text{H}_2\text{O} \quad \Rightarrow \quad \text{O}_3\text{N} \rightarrow \text{Al} \xrightarrow{\text{OH}} + 2\text{HNO}_3.
\]

A 9.0-g portion of Al(NO₃)₃ preliminarily dissolved in 120 mL of water is added to the mixture obtained in stage I.

Stage III. Weak polycondensation to give a PAS sol composed of oligomer molecules.

To obtain FPAS samples, stage III is interrupted so that proportioned and adequate crowns of dendrimers are formed and Al₂O₃ nanoparticles can be introduced into these crowns by ultrasonic dispersion. This yields FPASs containing different amounts of fillers. The IR spectra of PAS samples in Fig. 1 show all the characteristic bands expected in accordance with the structure of polycondensation products (Scheme 1).

A transmission electron microscopic (TEM) image of a PAS sample shows a clearly structured pattern of the dendrimer macromolecular PAS ensembles produced in the course of polycondensation (Fig. 2a).

Stage IV. Deep polycondensation of the sol containing Al₂O₃ nanoparticles ends in that the target product, FPAS, is formed. This stage is performed in the sol phase of PAS directly on the surface of an aluminum article at 20–140°C. Figure 3 illustrates the possibility of raising the degree of polycondensation by heating, with the release of water occurring in two stages, with peaks at 100 and 136°C. At temperatures of 67–124°C, a sample gives off a six times larger amount of water, compared with the interval 129–147°C in which all the available OH groups have already reacted.