Methacrylic derivatives of oligophosphazenes and their use for the modification of polymer composite materials

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The relevance of the research topic. Polymer composite materials (PCM) are increasingly used in various fields of modern technology - from mechanical engineering to medicine. A wide range of areas of their application requires the improvement of existing and the development of new PCM with the necessary properties: high-strength, non-combustible, radio-transparent, suitable for use in medical equipment, in aircraft construction and for other purposes.

One of the promising binders for PCMs are phosphazene-containing oligomers, for example, hydroxyaryloxycyclophosphazenes and their epoxy derivatives obtained in recent years, which are distinguished by increased heat resistance and fire resistance, and the ability to process by existing methods. So developed at the Department of Chemical Technology of Plastics/D.I. Mendeleev University of Chemical Technology of Russia, epoxyphosphazene oligomers have been successfully used as modifiers for industrial epoxy resins, products from which have increased fire resistance, and in some cases complete incombustibility.

The degree of its development. Methacrylic monomers, including those containing phosphazene, are often used as binders for PCM. The latter were synthesized by the interaction of hydroxyaryloxyphosphazenes with methacryloyl chloride, but this method is inconvenient due to the hydrolytic instability and high cost of the latter.

In connection with the previously revealed promise of using phosphazene-methacrylate oligomers (PMO) for modifying bisacrylate binders used in dentistry, it seemed appropriate to find other more advanced and economically applicable methods for the synthesis of PMO.

The purpose of this work. The purpose of this dissertation was to develop a new method for the synthesis of PMO by the interaction of phosphazene-epoxy oligomers (PEO) with methacrylic acid, to establish the composition and structure of the

compounds included in PMO, and to identify the possibilities of using the obtained oligomers to improve the mechanical and physico-chemical characteristics of the polymer composite materials modified by them for dental destination.

Work tasks. To achieve this goal, it was necessary to solve the following tasks:

Synthesize initial PEOs and hence PMOs with different phosphorus content;

Identify intermediates and end products using MALDI-TOF mass spectrometry, NMR spectra and epoxy number determination, etc.

To investigate the physical and mechanical properties of composite materials for dental purposes when using FMO as modifiers of the base binder.

Scientific novelty.

1. It was found that the optimal ratio of epoxyphosphazene : methacrylic acid (MAA) is a 30% molar excess of the latter with respect to epoxy groups.

2. Obtained and using NMR spectroscopy and MALDI-TOF spectrometry, a series of PMOs with different phosphorus content was obtained.

3. The ability of PMO to spontaneous polymerization during storage was evaluated and the stability of these oligomers under normal conditions for more than 8 weeks was established.

4. The possibility of using minimal amounts of PMO (~ 1 wt %) as crosslinking agents during copolymerization with methyl methacrylate has been shown.

5. It was revealed that the use of 5-10 wt. % PMO as a modifier of the base filling composition, allows a 3-4 times increase in its adhesion to tooth tissues and metals, with almost complete preservation of other necessary characteristics of the modified composite materials.

Practical significance of the results. The established fact of a significant increase in the adhesion of PCM to the tooth tissue and metal when FMO is introduced into polymer compositions expands the known theoretical position on the relationship between adhesion and the presence of phosphorus-containing components in the adhesive, including phosphazene ones.

The synthesized PMOs were tested in JSC SEZ "VladMiVa" (Belgorod) as modifiers for filling dental PCM, showed positive results and can be recommended for practical use.

Defense provisions:

1. Synthesis of initial phosphazene-epoxy oligomers with a reduced content of chlorine atoms in their molecules;

2. Synthesis of phosphazene-epoxy oligomers with spirocycles and study of their structure;

3. Synthesis of phosphazene-methacrylate oligomers; assessment of their ability to spontaneous polymerization;

4. The use of phosphazene-methacrylate oligomers as cross-linking agents in copolymerization with methyl methacrylate;

5. The use of phosphazene-methacrylate oligomers for the modification of dental composite materials.