Synthesis and properties of phosphazene-containing benzoxazine monomers and epoxy resins

Tarasov Ilia Vitalievich

Abstract

Relevance of the research. Currently, more and more work is being done on the synthesis of special monomers of phosphazene nature, primarily based on hexachlorocyclotriphosphazene, including phosphazene-containing benzoxazine monomers and epoxy resins, on the basis of which materials with high mechanical and thermal characteristics are obtained. Also, studies are being conducted on compositions based on benzoxazine monomers in combination with binders of a different nature, including epoxy, which is possible due to the structure of the resulting polybenzoxazines, which allows the formation of copolymers.

Despite the abundance of work on the synthesis of phosphazene-containing epoxy resins, now, the physical and mechanical properties of plastics based on them remain poorly understood, including for promising synthesis methods.

In combination with the current task of the Russian chemical industry to develop its own components and modifiers of binders for polymer composite materials, especially for critical areas of application, research is relevant to improve the methods for synthesizing benzoxazine monomers and epoxy resins of phosphazene nature, study their effect on the technological properties of binders and physical, mechanical, and thermal characteristics of materials obtained on their basis, with the possibility of regulating them, without deterioration of operational and technological characteristics.

The object of the study is the synthesis of modifiers and modification of epoxy and benzoxazine binders for polymeric materials.

Modified phosphazene-containing benzoxazine monomers and epoxy resins based on hexachlorocyclotriphosphazene were used in the work.

The objective of the work is to develop methods for the synthesis of phosphazene-containing epoxy and benzoxazine monomers, which will improve the technological efficiency of the process of their production, as well as regulate the

functionality of the resulting special monomers, and study the physical, mechanical and thermal properties of the obtained products.

Tasks:

1. Development of a method for the synthesis of model systems of phenoxychlorophosphazenes with the possibility of technologically obtaining hydroxyaryloxyphenoxyphosphazenes based on them;

2. Development of a method for the synthesis of model systems of hydroxyaryloxyphenoxyphosphazenes;

3. Synthesis of phosphazene-containing benzoxazine monomers (PhB) based on hydroxyaryloxyphenoxyphosphazene, bisphenol A and aniline;

4. Development of a one-stage method for the synthesis of phosphazene-containing epoxy resins based on hexachlorocyclotriphosphazene and bisphenol F in an epichlorohydrin medium;

5. Carrying out tests and analysis of rheological, thermal and other characteristics of compositions based on the obtained phosphazene-containing epoxy resins (PhER);

6. Assembly of a one-stage phosphazene-containing epoxy resins synthesis unit, development of a method scaled up to a 10 l reactor; production of a batch of modified epoxy resin for pilot testing.

Scientific novelty. When studying the composition using MALDI-TOF, PMR and ^{31}P NMR methods and the physical and mechanical properties of PhER based on bisphenol F, a correlation was found between the dynamics of changes in the composition of the obtained PhER and the properties of their cured plastics.

For the first time, PhER based on bisphenol F and benzoxazine monomers based on phenol and bisphenol A with adjustable functionality were obtained and characterized using IR, ^{1}H, ^{13}C and ^{31}P NMR, MALDI-TOF, and X-ray fluorescence spectrometry (elemental analysis for P and Cl).

Using ^{31}P NMR spectroscopy, the time of the substitution reaction in the synthesis of model systems of phenoxychlorophosphazenes and

hydroxyaryloxyphenoxyphosphazenes was determined, and a correlation was established between the experimental and calculated data.

Theoretical and practical significance. The dependence of the extreme nature of the physical and mechanical properties of the compositions on the content of PhER based on bisphenol F was found. The developed methods for synthesizing PhER and PhB allow obtaining phosphazene-modified binder components in a more technologically advanced way; at the planning stage, a raw material base was selected taking into account the availability and presence of production in Russia. Pilot samples of phosphazene-containing epoxy resins based on bisphenol A were produced and transferred for their testing in materials by the companies OJSC Komposit and National Research University of Electronic Technology (MIET). Tests were conducted and the prospects for their use in heat-resistant printed circuit boards were confirmed.

Provisions submitted for defense:

• Synthesis of phosphazene-containing epoxy resins based on bisphenol F by a single-stage method, characteristics of the obtained products and study of the mechanical properties of the cured compositions on their basis;

• Synthesis of PhER and PhB based on model systems of phenoxychlorocyclotriphosphazenes and hydroxyaryloxyphenoxycyclotriphosphazenes;

• Establishment of optimal conditions for the synthesis of model systems of phenoxychlorophosphazenes and hydroxyaryloxyphenoxyphosphazenes with the required degree of substitution.

Financial support. The work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation within the framework of the state assignment (project No. FSSM-2024-0009 "Phosphorus and silicon-containing oligomers and polymers as components of polymer composite matrices").