ABSTRACT

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SYNTHESIS OF PHOSPHAZENE-CONTAINING BENZOXAZINE MONOMERS AND POLYMERS

Dibenzoxazines are heterocyclic compounds capable of curing without the release of low-molecular by-products by opening the ring with minor shrinkage and the formation of non-melting insoluble polymers with high strength and elastic modulus. Polybenzoxazines are characterized by high thermal and chemical properties, low moisture absorption, good fire resistance, and release a small volume of non-toxic smoke when in contact with flame. Due to this combination of qualities, they are a promising alternative to materials based on phenol-formaldehyde and epoxy resins.

Although polybenzoxazines are less flammable than epoxy resins, many of them do not meet the highest V-0 fire resistance class according to the UL-94 standard without modification. Since epoxides are often added to benzoxazine-based binders in practice to control processability, this further worsens fire resistance. One way to compensate for this undesirable consequence is to use phosphorus-containing compounds, which, given the context of use mainly in aviation and transport, are practically the only acceptable class of flame retardants. Phosphazenes, which have the highest heat resistance compared to other phosphorus-containing flame retardants, are the most promising modifiers for obtaining non-flammable polymers. However, for critical structures, long-term stability of properties is necessary and a decrease in mechanical characteristics is unacceptable, which is possible only with covalent bonding of the flame retardant to the matrix. With regard to benzoxazine, the problem of creating such phosphazene-based flame retardants has not yet been solved and is relevant.

The aim of the work is to synthesize phosphazene-containing benzoxazine monomers, oligomers and polymers for use in the composition of low-flammability polymer binders.

Research objectives:

1. Synthesize benzoxazine monomers based on diphenols and aromatic amines (aniline, toluidine);

2. Develop methods for synthesizing initial hydroxyaryloxycyclophosphazenes (HArP) and phosphazene-containing benzoxazines based on them;

3. Identify the possibilities of using arylaminophosphazenes as modifiers with the function of a flame retardant and a catalyst for the polymerization of benzoxazines;

4. Evaluate the applicability of the synthesized compounds and compositions based on them as components of binders for polymer composite materials with reduced flammability.

The scientific novelty of the work is that previously undescribed benzoxazines based on bisphenol A and aniline with a controlled content of the benzoxazine-phosphazene component have been synthesized. The catalytic activity of chloro- and arylaminophosphazenes in the polymerization processes of benzoxazines has been discovered for the first time, the two-stage nature of curing has been established, and its temperature-time characteristics have been determined. Completely non-flammable phosphazene-containing benzoxazine compositions have been obtained that are not inferior to basic polybenzoxazines in thermal and mechanical properties.

The theoretical and practical significance of the work lies in the synthesis of benzoxazine-phosphazenes based on bisphenol A and the establishment of the catalytic activity of arylaminophosphazenes in the polymerization of benzoxazines, and their applicability as a basis for two- (benzoxazine-arylaminophosphazene) and three-component (benzoxazine-arylaminophosphazene-epoxide) compositions has been confirmed, which provides more means for regulating the polymerization processes of benzoxazines, which is necessary to expand the range of binders for polymer composite materials based on them.

Thesis submitted for defense:

1. Synthesis of new phosphazene-containing benzoxazines by interaction of previously obtained hydroxyaryloxyphosphazenes based on bisphenol A and hexachlorocyclotriphosphazene.

2. Features of polymerization of benzoxazines in the presence of arylaminophosphazenes.

3. Properties of phosphazene-containing epoxy compositions.