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New Thermostable Heterocyclic Binders and Environmentally Friendly Technologies of Production of Composite Materials

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Abstract—Synthesis and processing of high-strength and high-heat-resistant polymer matrices (binders) have been studied. Structural composite materials stable up to 400ºC have been developed. Processing of the binders is carried out by ecologically safe technologies.

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INTRODUCTION

At present the replacement of traditional metal materials by polymer and composite materials (CMs) is one of the basic indicators of industrial and scientific technical progress. The development of high technologies generates demands for principally new polymer and structural materials capable of preserving their high processing and performance characteristics under the action of various destructive factors. The expanding application range of polymer materials is accompanied by a strengthening of requirements to the quality of materials, their mechanical and strength parameters, and power efficiency and environmental friendliness of their processing technologies [1].

Polymer composite materials (PCMs) are finding increasing application in the designs of basic components of aerotechnics. The use of PCMs in new-generation aircrafts and engines makes it possible to radically decrease their weight, and, therefore, enhance the fuel efficiency of aircrafts and increase the useful load. To solve problems associated with the development of power heat-loaded elements of gas turbine engines (GTEs) and supersonic aircraft airframes, materials with stable performance characteristics in oxidative media up to 400°C are required. To this end, unique polymer matrices combining high physico-mechanical characteristics with maximum possible heat resistance should be created.

There are two key problems involved in the development of such binders: to choose the structure of the polymer matrix and to choose the way of processing the latter for manufacturing CMs. The polymer matrix should not soften up to 450°C, which can be reached by introducing aromatic and heterocyclic fragments into the polymer chain, i.e. by forming double-chain step structures in the chain of macromolecules to restrict mobility of the latter and enhance intermolecular interaction, crystallinity, etc.

One of the ways to produce thermoreactive binders capable of forming high-strength and high-heat-resistance matrices for PCMs with working temperatures above 170°C is polycyclotrimerization of monomers with two and more functional groups with multiple bonds with homo- and heteroatoms. The reaction forms a cross-linked three-dimensional structure with identical fragments between cross-links and stable six-membered aromatic carbo- and heterocycles as nodes of the polymer network.

Development of binders capable of forming not only a high-strength and high-heat-resistance matrix, but also ensuring realization of these properties in PCMs, calls for a nontraditional approach in view of the necessity to combine such mutually contradictive characteristics of the polymer matrix as strength, stiffness, heat resistance, plasticity and a high impact fracture toughness.

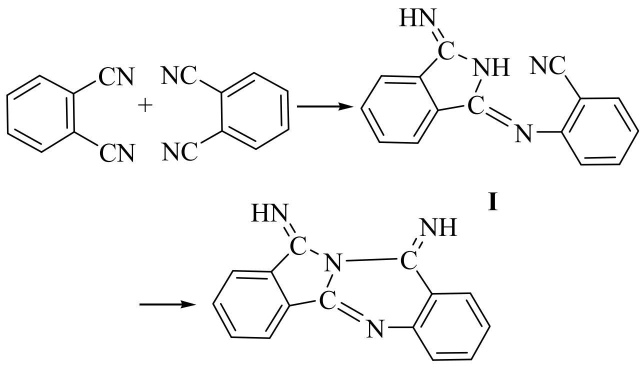
Heterocyclic Binders for Thermostable PCMs

Composite materials with working temperatures of up to 400°C are produced by the reactive molding technology. The molding process involves the intramolecular isomerization polycyclization reaction without evolution of low-molecular volatile products, which occurs in the preliminarily synthesized low-melting soluble oligomer (binder) on thermal treatment directly on the filler. The cyclizations forms a monolithic, high-strength, and high-heat-resistance polymer matrix of a step macroheterocyclic structure. Step polymers possess the highest, among organic polymers, thermooxidative stability and deformative thermostability [2]. Thus, the task of creation of a polymer matrix stable at temperatures of up to 400°C comes down to development of a method of synthesis ща polyfunctional oligomers (binders) whose high-temperature transformations form high strength and high heat resistance macroheterocyclic structures of the step type.

The collaborative research of the RIAM and Institute of Organoelement Compounds of the Russian Academy of Sciences (IOEC) showed that unique and the most promising polymer matrices for PCMs with working temperatures of up to 400°C are systems on the basis of tetranils derived from aromatic tetracarboxylic acids and bis(*o*-cyanamines) [3]. In view of the chemical structure of tetrafunctional monomers, it was suggested the half-step macroheterocyclic structure formed by their reaction would contain condensed isoindole and quinazoline rings conjugated with aromatic fragments.

To check this suggestion, a model reaction of anthranitrile with phthalodinitrile in melt at a stoichiometric reagent ratio was studied (Scheme 1).

Scheme 1.

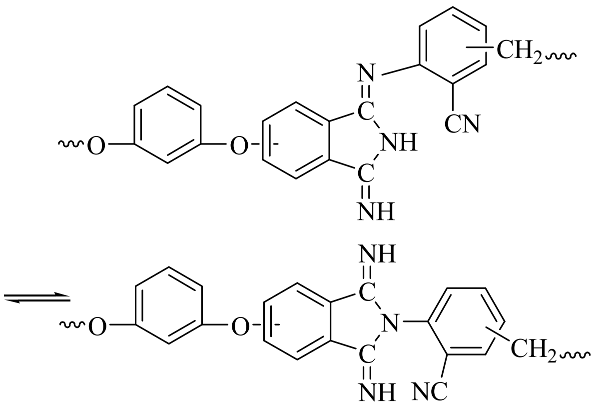


I

II

It was found that the reaction at 250°C for 5 h gives compound **I** with a yield of no less than 80%. The mass spectrum of compound **I** contains a molecular ion peak at *m/e* 246. The IR spectrum of the product chows absorption bands at 3200 (NH) and 1627 cm^{-1} ($C=N$), as well as a $C\equiv N$ absorption band at 2233 cm^{-1}. The spectral data provide evidence for the suggested structure of compound **I**. Further heating results in isothermal cyclizations of product **I** to form isomer **II** containing condensed isoindole and quinazoline rings.

It was shown that the polycondensation in melt of stoichiometric amounts of tetrafunctional monomers: 3,3'-diamino-4,4'-dicyanodiphenylmethane and 4,4'-(*m*-phenylenedioxy)diphthalonitrile forms an oligomer (binder). The structure of its two possible isomers was confirmed by elemental analysis, IR spectroscopy, and thin-layer chromatography [4, 5]:



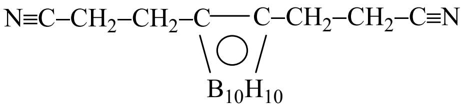
After grinding on a ball mill and acetone extraction of admixtures and unreacted monomers, the resulting oligomer is a fine cream-colored power readily soluble in amide solvents and *N*-methylpyrrolidone. At 100–130°C the oligomer forms a low-viscous mobile melt whose formation occurs at 200°C within 15–25 min. This binder can be applied on fillers from solutions, melts, or by electrostatic sputtering to obtain prepregs with almost indefinite pot lives. Intermediate products and CMs on their basis were produced by a safe and waste-free technology.

New Thermostabilizers

The service of organic polymeric matrices in an oxidative medium at 400°C, i.e. under a very severe exposure, is impossible without high-temperature thermostabilizers (antioxidants). Research on the thermo-oxidative stability of polymer matrices in the presence of common antioxidants (sterically hindered phenols, amines, phosphites, metal carbonyls, etc.)

showed that, irrespective of the chemical nature of the antioxidant, stabilization is largely observed in the temperature range 200–250°C. Raising the temperature of isothermal testing to 350–400°C offsets completely the contribution of antioxidants into the thermo-oxidative destruction of binders.

The problem to stabilize organic polymers at 350–400°C has raised demand for the development of special compounds capable of building-in into the polymer chain during binder synthesis. The collaborative research of the RIAM and IOEC resulted in the development of high-temperature antioxidants: thermostabilizers on the basis of *o*-carborane, specifically 1,2-bis(cyanoethyl)-*o*-carborane:



$$N{\equiv}C{-}CH_2{-}CH_2{-}C{-}C{-}CH_2{-}CH_2{-}C{\equiv}N \quad B_{10}H_{10}$$

The compound builds-in into the main polymer chain during binder synthesis and fulfills the role of termostabilizer in the polymer matrix. The effect of *closo*-12-carboranes is explained by the active reaction of the icosahedron BH groups with air oxygen and boron-centered radicals with free radicals formed due to thermo-oxidative destruction of the main polymer chain. This prevents degenerative chain branching, realizing in part the "non-chain" inhibition principle, specifically, deactivation of compounds involved in any reactions leading to polymer destruction. The introduction into monomers at the stage of binder synthesis of 10–20 wt % of 1,2-bis(cyanoethyl)-*o*-carborane allowed preparation of a thermostabilized carborane-containing polymer matrix with a covalently bound antioxidant. Thus stabilizer is easier to introduce into polymer, an ideal molecular distribution is reached, and antioxidant losses due to diffusion and evaporation are excluded.

Structure of Stabilizers and Thermal Stability of Composite Materials

The presence of free–C≡N groups imparts to the oligomer the ability to undergo intramolecular polycyclization on heating to form a half-step macroheterocyclic structure containing condensed isoindole and quinazoline rings. The binder curing process was followed by IR spectroscopy by the decrease of the relative intensity of the–C≡N absorption band over the course of thermal treatment. On heating in the range 170–400°C, the –C≡N bands at 2213 and 2233 cm^{-1} are decreasing, implying consumption of the –C≡N groups during structuring of the oligomer. The spectra provide evidence for the occurrence of intramolecular isomerization polycyclization at the final stage of formation of the polymer matrix. The binder curing process was also studied by differential scanning calori-metry (DSC) and IR spectroscopy to establish the temperature and time parameters for the attainment of a virtually 100% conversion of the functional groups.

The optimal curing regime was established by studying the dependence of glass transition point on temperature and of the physicochemical properties of the matrix on thermal treatment conditions. The formation of the polymer matrix with high physico-mechanical characteristics is almost complete after thermal treatment at 200–250°C. Further heating at 300–400°C is needed to complete formation of the polymer matrix and to reach the maximum possible for this type of binders resistance to heat and thermal oxidation.

It should be noted that the polymer matrix (unmelting and insoluble) after thermal treatment is formally not a cross-linked 3D polymer. The properties characteristic of a cured thermoreactive binder sre formed during formation of tightly packed super-rigid half-step structure of regularly alternating aromatic and heterocyclic fragments with a strong intermolecular interaction. Such polymers exhibit quite high heat resistance, nearly maximum possible for organic polymers.

Effect of Curing conditions on the Properties of Composite Materials

The fact that the developed binders are suitable for manufacturing on their basis heat-loaded PCMs was established by the results of thermomechanical analysis (TMA) of cured polymer matrices. Such tests allow us to determine a real working temperature range for structural PCMs. The TMA was used to measure the dependence of the glass transition point of the binder cured at 200, 250, and 350°C (Fig. 1).

It was found that curing at 160–350°C leads to a rigid macroheterocyclic half-step structure whose transition from the rigid to highly elastic state is not seen in the TMA curves up to 550–600°C, when thermal oxidation of the polymer commences. Under TMA conditions, no α-transitions, viz. the deformation of the polymer matrix, associated with the segmental mobility of macromolecules on polymer devitrification, are not detected. Such behavior is characteristic

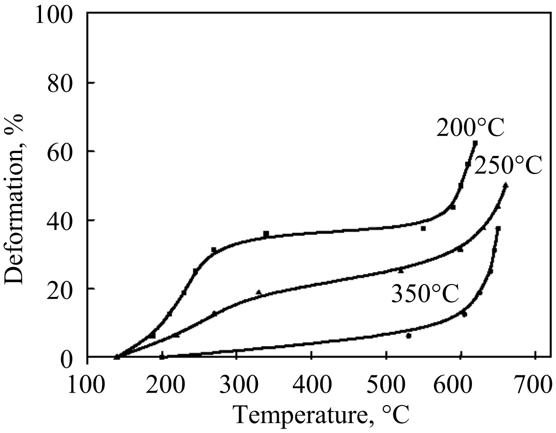


Fig. 1. Thermomechanical curve of a polymer matrix cured at various temperatures.

of rigid-chain fully aromatic step polymers whose mechanical loading induces no other deformations but an elastic (Hookean) deformation associated with changes in the average interatomic and intermolecular distances, as well as valence angles in the macromolecule. The lack in the developed polymer matrix, up to 600°C, of a reversible highly elastic and an irreversible viscoelastic deformation points to an extremely high deformation heat resistance, additionally contributed by the thermostabilizer.

The weight loss initiation temperature of thermostabilized polymer matrices in an oxidative medium is 500–600°C. The optimal quantity of stabilizers, as found by the DTG analysis of cured samples in air, is 10–20 wt %. If the fraction of antioxidants is higher than 20 wt %, the degradation initiation temperature is sometimes increases by 20°–30°, but the physicochemical properties of the polymer are much deteriorated because of essential impact of the thermostabilizing system on the binder curing process and, as a consequence, violation of the optimal regime of formation of the polymer matrix. The long-term thermostability of cured polymer matrices was studied under isothermal aging conditions in an oxidative medium for 50 h at 400°C and for 10 h at 450°C, which is quite a severe test for any organic polymers. The binder samples comprising the carborane-containing antioxidant showed a 20% weight loss at 450°C, whereas those containing no antioxidant completely burned out under these conditions.

Prepregs on the basis of the thermostable heterocyclic binder are produced by electrostatic powder sputtering on a moving carbon tape [6]. The installation for prepreg production comprises a feeding drum, alignment cage, fusion cage, heated setting rollers, and a drawing drum (Fig. 2).

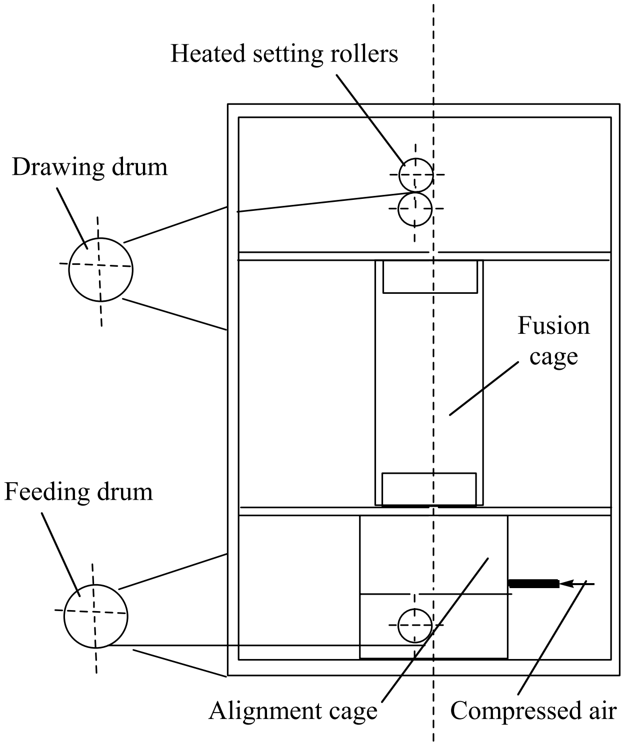


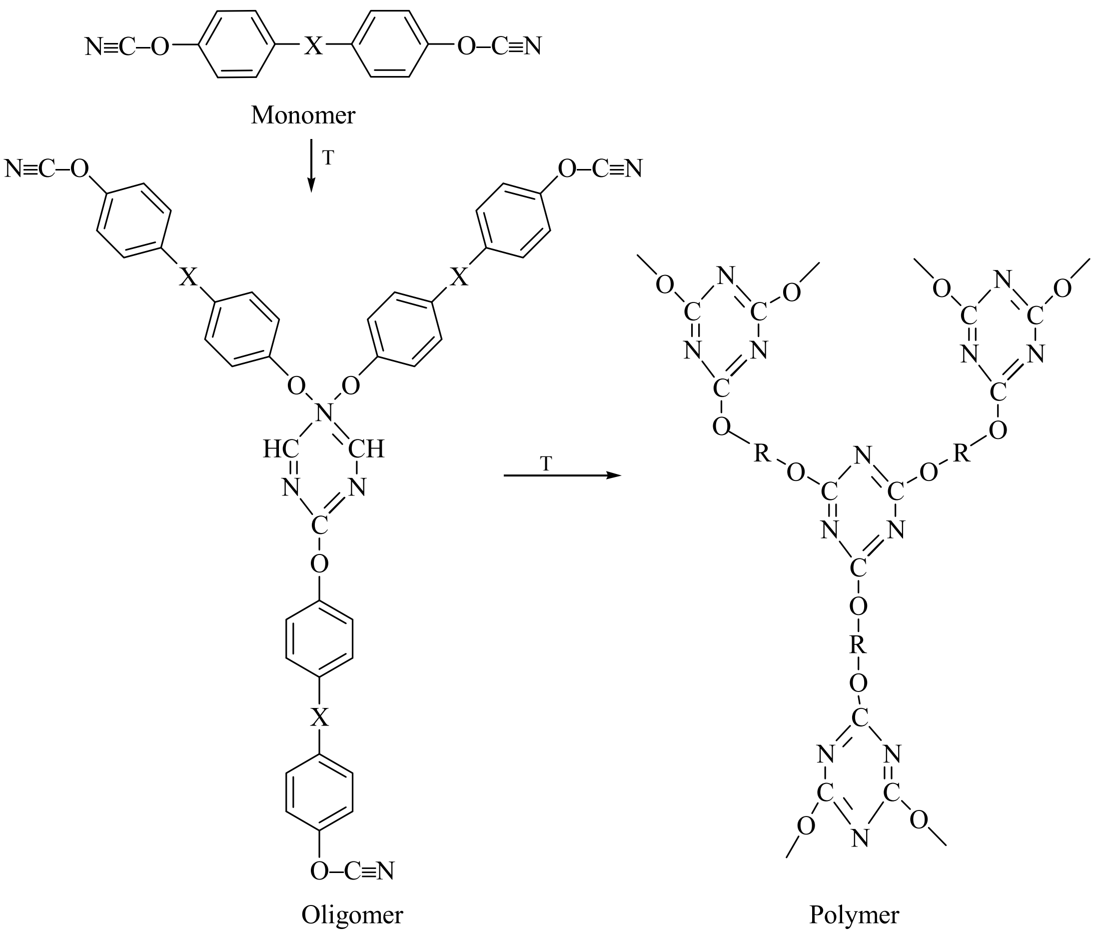
Fig. 2. Scheme of the electrostatic powder spraying system.

An environmentally friendly melt powder techology for applying low-melting binders on fillers to produce prepregs with an almost indefinite pot life was developed. Since binders are cured by the mechanism of multistage step isomerization polycyclization without evolution of volatile products, a simplified molding process can be used, which involves molding at temperatures of up to 200°C in tooling, followed by thermal treatment in the free state.

Network Polymers on the Basis of Dicyanate Esters for High-Strength Heat-Resistant Polymer Composites

Epoxy oligomers are most frequently thermoreactive polymers used as binders for high-strength composites with working temperatures of up to 170°C. However, the chemical structure of network polymers on the basis of epoxy oligomers does not allow to raise substantially the working temperature of polymer composites, thereby preserving their high mechanical properties. The chemical structures of epoxy oligomers

Scheme 2.



and their hardeners are quite diverse, but the thermal characteristics of network polymers on their basis are defined by the presence in the starting oligomers of high concentrations of α-oxide rings, since the aliphatic and heterochain fragments formed in the polymers by α-oxide ring opening are fairly thermally unstable.

To enhance the heat resistance of network polymers, systems whose intercross-links are formed by rigid aromatic, heterocyclic, or organoelement radicals, whereas thermally unstable groups are almost or completely lacking.

One of the most promising synthetic approaches to a new generation of polymer matrices for PCMs with working temperatures above 170°C is a polycyclotrimerization reaction of monomers containing two or more functional groups with multiple bonds between homo- and heteroatoms, which leads eventually to poly(1,3,5-triazine) structures with thermostable aromatic S-triazine structures as polymer network cross-links [7]. Such requirements are largely met by the polycyclotrimerization of aryl dicyanates, specifically dicyanate esters of bisphenols of various chemical structure. The reaction involves no evolution of volatile products and features a high selective cyclotrimerization of N≡C–O groups and their almost complete conversion (Scheme 2).

The polycyclotrimerization of the diacyanate ester of bisphenol A is performed in the presence of minor amounts (about 1%) of ionic catalysts. The resulting regular narrow-meshed network polycyanurates [poly (1,3,5-triazines) exhibit a complex of valuable properties: thermal and chemical stability, high dielectric and adhesion parameters, resistance to ionizing radiation, low gas permeability, and other properties which radically distinguish them from other cross-linked polymer systems. The cyclotrimerization reaction can be stopped at the stage of formation of a low-melting soluble resin-like oligomer whose

Comparative characteristics of polymer matrices

Parameter	Epoxy matrix	Polyimide matrix		Polycyanurate matrix		Binder IP-5[a]
		PMR-15	bismaleimides	BCT-1210[b]	HexPly 954-3A	
Density, g cm^{-3}	1.23–1.30	1.32	1.25–1.35	1.23	1.19	1.24
Tensile strength σ^+, MPa	60–120	48–56	40–80	80–90	56	85
Tensile elastic modulus E^+, GPa	2.6–3.6	3.9–4.5	4.2–4.9	3.17	3.3	4.5
Relative elongation ε, %	2.8–5.0	1.4	1.5–2.5	3.2	1.9	2.3
Crack resistance G_{1C}, J m^{-2}	130–150	230–280	34–260	140	170	400
Glass transition temperature, °C	100–200	330–370	250–350	240	197	400–450

[a] Heterocyclic binder developed at the RIAM, Technical Specifications 1-595-12-881-2005. [b] Polycyanurate binder developed at the RIAM, Technical Specifications 1-595-12-1042-2008.

solution or melt is a binder which can be processed by different methods.

The cyclotrimerization of aryl dicyanate was performed in melt at 140–150°C under vigorous stirring. The IR spectra of samples taken from the reaction mixture showed gradually decreasing N≡C–O stretching vibration bands at 2236–2272 cm^{-1}; therewith, strong bands characteristic of the S-triazine ring appear at 1570 and 1370 cm^{-1}. The stretching absorption of the ether C–O–C stretching absorption band appears at 1235–1160 cm^{-1}. The resulting evidence allowed us to assess the dependence of the conversion of aryl dicyanate N≡C–O groups on the time of isothermal oligocyclotrimerization (Fig. 3).

The kinetic curve is evidently S-shaped, implying an autocatalytic reaction which is strongly accelerated with increasing concentration of aryl dicyanate cyclotrimerization products in the reaction mixture; therewith, the maximum acceleration is already observed at a 10% conversion of N≡C–O groups.

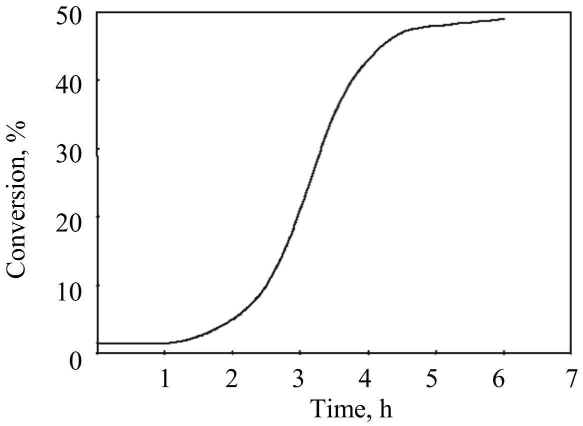


Fig. 3. Dependence of oligomer (binder) N≡C–O group conversion on heating time.

Starting from 2,2-bis(4-cyanatophenyl)propane, a poly(1,3,5-triazine)-containing binder was synthesized for further production of an oligocyanurate meeting engineering requirements to binders suitable for processing by the resin transfer molding (RTM) technology. The developed synthesis gives the product as a low-viscosity resin-like material readily soluble in ketones, esters, alcohols, and aromatic hydrocarbons.

The binder is cured as a result of further cyclotrimerization of N≡C groups and followed by IR spectroscopy by the decreasing N≡C–O stretching vibration bands at 2236–2272 cm^{-1} and increasing absorption bands at 1570 and 1370 cm^{-1}, characteristic of stretching vibrations of the 1,3,5-triazine ring. The N≡C–O band disappears almost completely, when the samples are heated at 200°C, and the yield of the gel fraction is 98–100%. It should be noted that the binder is cured without release of any low-molecular reaction products, which makes it possible to obtain monolithic matrix and PCMs on its basis and simplify the technology of composite molding at 160–180°C in a tooling, followed by thermal treatment at 200–220°C in the free state. Post-curing of the material at 200°C remains almost unaffected its deformation heat resistance, but it is necessary to rearrange the supramolecular structure of the matrix, i.e. to realize transition from the globular structure to fibril-like formations favoring relaxation processes and relieving internal strain [8].

The curing of the polycyanurate binder involves no release of any low-molecular reaction products, which allows this binder to be processed by the RTM technology to obtain monolithic matrix and PCMs on its basis. The PCMs produced by the RTM technology from a polycyanurate network polymer are suitable for manufacturing various components of aircraft equipment with working temperatures of up to 200°C.

Optimization of the technologies of synthesis and curing of thermostable binders opened the way to unique polymer matrices combining the physico-mechanical characteristics of the best epoxy matrices with the deformation heat resistance and having no analogs among organic polymer matrices (see table).

CONCLUSIONS

Scientific basis for the synthesis and processing of high-strength and high-heat-resistance polymer matrices (binders) for structural composite materials with working temperatures of up to 400°C is developed. The choice of polyfunctional monomers is substantiated, and the method of production on their basis of oligomers (binders) capable of forming directly in the filler at high temperatures highly thermo-stable half-step fmacroheterocyclic structures is developed, investigated, and optimized.

The binder curing process is studied by IR spectroscopy. Parameters for complete curing are established. The possibility was demonstrated of additional thermostabilization of binders with boron-containing polymers, viz. oligoarylenecarboranes, capable of building-in into the chemical structure of binders on their synthesis and curing. Heterocyclic binders are applied on fillers by the environmentally friendly melt or power technologies, and the resulting prepregs have a virtually indefinite pot life. Due to the fact that binders are cured by the mechanism of multistage step isomerization polycyclization without release of volatile products, a simplified molding process, including molding at temperatures of up to 200°C in a tooling and subsequent thermal treatment in the free state.

A method of synthesis of a thermoreactive poly (1,3,5-triazine) binder for high-strength and heat resistant composite materials with working temperatures of up to 200°C is developed.

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