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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Thermal Aging of Carbon- and Glass-Reinforced Plastics Based on Heat-Resistant Polyimide Binders

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Abstract—A series of fibrous composites, carbon- and glass-reinforced plastics based on heat-resistant polyimide binders, were prepared. The viscoelastic and strength properties of the composites obtained confirm the enhanced heat resistance of the binders.

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Among polymeric materials commercially produced today, polyimides are the most heat-resistant [1]. They exhibit dielectric properties, high mechanical characteristics, and good chemical and radiation resistance. Therefore, they are demanded by various branches of industry such as aviation and aerospace industry, ship building, electronics, and instrument making. Virtually all the kinds of technical materials capable of prolonged service in articles at temperatures of 300°C and above, including composite materials, are based on polyimides. At the same time, the problem of modifying the structure and properties of composites based on polyimide binders and extending the fields of their application remains topical. Therefore, it seems appropriate to study thermal aging of fibrous composites based on heat-resistant polyimide binders.

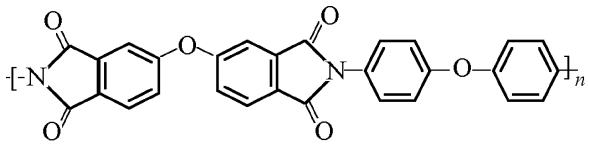
The goal of this study was to choose the optimal composition of the polyimide binder and to prepare on its basis a composite material preserving the viscoelastic and strength characteristics after keeping in air at 350°C for 100 h.

EXPERIMENTAL

As starting compounds for preparing binders we used commercially available monomers widely used in industry in production of polyimides: *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (NA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BZP), 3,3',4,4'-(diphenyl oxide)tetracarboxylic dianhydride (DPO), 4,4'-diaminodiphenyl ether (DADPE), and 1,3-phenylenediamine (*m*-PDA), without additional purification.

To prepare composite materials, we synthesized three types of binders.

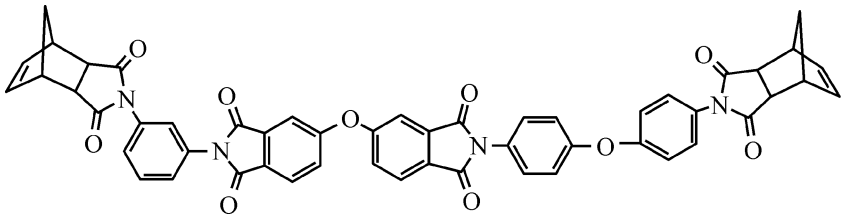
(1) Imide binder (IDA) of the composition DPO–DADPE was prepared by the reaction of 3,3',4,4'-(diphenyl oxide)tetracarboxylic dianhydride with bis(4-acetamido)diphenyl oxide in the melt at 280–290°C, with the removal of 10% volatiles. According to the reaction mechanism [2], initially a set of oligomers containing anhydride and N-acylamino groups are formed in the melt. This melt with a viscosity of about 100 Pa s at 270°C was used as prepolymer for impregnation of carbon or glass fabric. Further heat treatment at 350°C for 1–2 h leads to the formation of a polyimide:



IDA (DPO–DADPE)

(2) Imide polymerizable oligomer (IPO) with terminal norbornene groups of the composition NA–(*m*-PDA–DPO–DADPE)–NA based on 3,3',4,4'-(diphenyl oxide)tetracarboxylic dianhydride, 4,4'-diaminodiphenyl ether, and 1,3-phenylenediamine was prepared by

Scheme.

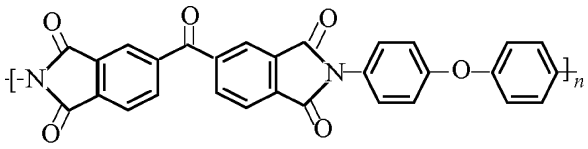


IPO [NA–(*m*-PDA–DPO–DADPE)–NA]

acylation of diamines with acidic diesters in alcoholic solutions. The process involves formation of H complexes [3] which can be considered as pseudo-prepolymers. The heat treatment of the H complexes at 100–150°C yields fusible imide-containing oligomers with terminal norbornene groups, which are used for impregnation of carbon or glass fabric (Scheme 1).

The double bond in the norbornene group is opened at temperatures above 300°C, which allows these systems, whose melt has a viscosity of up to 1000 Pa s at 270°C, to be used as thermosetting binders [4].

(3) Imide binder (ITA) of the composition BZP–DADPE was prepared by the reaction of tetra(4-acetamido)diphenyl oxide with 3,3',4,4'-benzophenonetetracarboxylic dianhydride in the melt [5]. Keeping the reactants at 270°C leads to the formation of a prepolymer with a viscosity of about 100 Pa s [3]. Curing of the prepolymer at 300–350°C yields an imide polymer [6]:



ITA (BZP–DADPE)

In our study ITA imide binder was compounded with carbon pitch in 60 : 40 ratio [7].

The process for preparing the composites can be conventionally divided in two parts.

(1) The prepreg was prepared by impregnating a fabric with a melt of a polyimide binder. We used ELUR-0.08P carbon fabric, T15(P) glass fabric, and three types of polyimide binders: IDA, IPO, and ITA–carbon pitch.

To prepare a prepreg, the binder powder was distributed between two layers of a fabric. Then the fabric with the applied powder was rolled on rollers at 240–260°C for several seconds for uniform distribution of the polymer melt throughout the volume. In preparing prepregs, the fabric : binder weight ratio was 50 : 50. The ready prepreg was a flexible material with uniform content of the fiber and matrix, suitable for placing in a mold.

(2) Preparation of plastics by hot pressing. Ready prepregs were piled, placed in a mold, and pressed at 350°C for 1 h at a pressure of 1600 atm.

Strength tests were performed by the three-point bending procedure with a 1958U-10-1 tensile-testing machine (Russia). The distance between the bearings was 30 mm, and the rate of sample loading, 5 mm min^{-1}. The shear elastic modulus *G*' was determined with an MK-003 torsion pendulum (developed by the Institute of Macromolecular Compounds, Russian Academy of Sciences), by the method of freely attenuating torsion oscillations at room temperature. The natural oscillation frequency was 0.4–0.5 Hz, and the amplitude, 1%. Thermal gravimetric analysis (TGA) of carbon and glass fabrics was performed on a TG 209 F1 thermal microbalance (Netzsch) in an inert atmosphere (Ar) at a heating rate of 10 deg min^{-1}.

Traditional procedure for preparing polyimide composites involves impregnation of a filler with a solution of a polyamido acid, followed by its imidizatiojn in the course of pressing. However, many linear aromatic polyimides are infusible, which restricts the range of polymers suitable as binders for preparing reinforced plastics.

In this study we used nontraditional approaches to the synthesis of polyimides. Initially, by fusion of the starting monomers, we prepared prepolymers. Stable prepolymer melts formed in this step were used for preparing prepregs by the melt technology. Further heat treatment of prepregs leads to formation of infusible polyimides DPO–DADPE and BZP–DADPE directly in composite materials. The imide binders used in this study have low viscosity (100–1000 Pa s) at 270°C and melt life of up to 30 min, which allows high-quality impregnation in the course of preparing prepregs based on carbon and glass fabrics.

We prepared a series of samples of carbon- and glass-reinforced plastics and determined the weight and volume fractions of fibers. The results are given in Table 1. The weight fractions of fibers were determined as the ratio of the fiber weight to the weight of the matrix in the sample. To calculate the volume fraction of fiber ν (%), we used the formula

$$\nu = \frac{1}{1 + \frac{\rho_f}{\rho_m}\frac{1}{\omega}} \times 100,$$

where ρ_f is the fiber density; ρ_m, binder density; and ω, weight fraction of fiber in the composite.

The following values were taken in the calculations: carbon fiber density 1.7 g cm^{-3}, glass fiber density 2.5 g cm^{-3}, and polyimide binder density ~1.4 g cm^{-3}.

Table 1 shows that treatment of carbon and glass fabrics with polyimide binder melts allows preparation of composites with a high (73–87 wt %) content of reinforcing fibers.

Then we prepared a series of samples for thermal aging experiments. Carbon- and glass-reinforced plastics with 12 and 8 fabric layers, respectively (sample thickness about 1 mm) were cut into 4 × 45 mm plates. Then the samples were placed in an oven and kept there at 350°C for 20, 40, 60, 80, and 100 h. Some of the samples based on IPO and ITA–carbon pitch binders split after heating in the oven.

The shear elastic moduli *G*' of carbon- and glass-reinforced plastics are given in Table 2. As seen from these data, samples based on ITA–carbon pitch binder start to split after annealing at 350°C for 40–60 h. Samples based on IDA binder demonstrate the best *G*' values compared to similar samples based on IPO and ITA–carbon pitch binders and preserve about 40% of the initial value of *G*'.

It should be noted that, with IDA binder, polycondensation can be accompanied by processes leading to the formation of a loosely cross-linked branched system. Formation of a cross-linked structure may be due to trimerization of acetyl groups [7]. In addition, the cross-linking mechanism involving formation of phenylenephthalimide structures is possible [8]. Such system may be more resistant to thermal aging than the linear polymer.

With IPO binder, deterioration of the properties of plastics upon thermal aging is apparently due to thermal instability of terminal aliphatic norbornene groups in the course of prolonged heat treatment at 350°C.

When assessing the application prospects of ITA–carbon pitch binder, it should be noted that ITA binder

Table 1. Weight (ω) and volume (ν) fractions of fibers in carbon- and glass-reinforced plastics

Plastic composition	Thickness, mm	ω, wt %	ν, vol %
ELUR-0.08P–IDA	0.62	85	82
T15(P)–IDA	0.7	83	73
ELUR-0.08P–IPO	0.65	74	70
T15(P)–IPO	0.7	87	79
ELUR-0.08P–(ITA–carbon pitch)	0.75	73	69
T15(P)–(ITA–carbon pitch)	0.73	78	66

Table 2. Results of testing carbon- and glass-reinforced plastics based on polyimide binders IDA, IPO, and ITA–carbon pitch on an MK-003 torsion pendulum at room temperature

Time of annealing at 350°C, h	Shear elastic modulus G', GPa					
	IDA		IPO		ITA–carbon pitch	
	ELUR-0.08P carbon fabric	T15(P) glass fabric	ELUR-0.08P carbon fabric	T15(P) glass fabric	ELUR-0.08P carbon fabric	T15(P) glass fabric
Initial	5.35	5.17	3.75	3.08	5.15	4.17
20	4.40	5.12	3.0	2.5	4.14	2.31
40	4.12	3.44	1.90	1.02	0.81	0.9
60	3.83	2.89	0.89	0.40	0.73	–
80	3.72	1.96	0.65	–	–	–
100	3.18	0.75	0.35	–	–	–

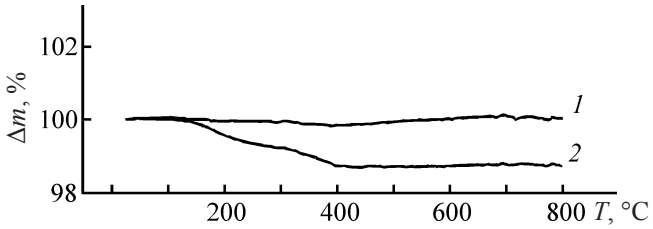


Fig. 1. TGA curves of carbon and glass fabrics in an inert atmosphere (AR) at a heating rate of 10 deg min^{-1}. (Δm) Weight loss and (T) temperature. (*1*) ELUR-0.08P carbon fabric and (*2*) T15(P) glass fabric.

is a promising polymeric material for preparing carbon–carbon composites. It is known [9] that addition of mesomorphic carbon pitch to a polymeric matrix favors formation of a uniform carbon structure in the course of carbonization (650–700°C). However, as follows from our experimental data (Table 2), specifically addition of carbon pitch to ITA polymeric binder decreases the heat resistance of the composites at 350°C. In this case, carbon pitch does not form a carbonized matrix, and its addition to a composite material decreases the weight fraction of the polyimide binder in the sample.

It should be noted that the carbon-reinforced plastics based on polyimide binders in all the three cases showed higher strength and heat resistance than the glass-reinforced plastics. After keeping in air at 350°C for 100 h, IDA-based composites preserve approximately 40% of the initial G' and 20% of the initial strength. The thermal aging experiments show that, on the whole, the carbon-reinforced plastics based on polyimide binders are more resistant to thermal aging than the glass-reinforced plastics.

This difference may be due to different adhesion of polyimide binder melts to carbon and glass fabrics [10]. The TGA curves of carbon and glass fabrics used for preparing composites are shown in Fig. 1. In the temperature range 150–400°C, the weight of the glass fabric decreased by 1.2%, whereas the weight of the carbon fabric remained unchanged. This may be due to removal of the lubricant from the glass fabric surface. The lubricant decreases the adhesion of polyimide binders to glass fabric and initiates thermal degradation.

The carbon- and glass-reinforced plastics after thermal aging were subjected to strength tests at room temperature by the three-point bending method. The results (Fig. 2) clearly demonstrate the main trends in variation of mechanical characteristics of the composites with increasing heating time. It can be seen that samples

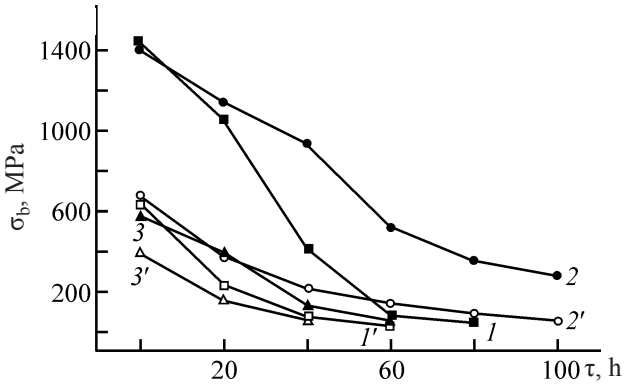


Fig. 2. Bending strength σ_b of carbon- and glass-reinforced plastics as a function of the annealing time τ: (*1*) ELUR-0.08P–IPO, (*1'*) T15(P)–IPO, (*2*) ELUR-0.08P–IDA, (*2'*) T15(P)–IDA, (*3*) ELUR-0.08P–(ITA–carbon pitch), and (*3'*) T15(P)–(IDA–carbon pitch).

of carbon- and glass-reinforced plastics based on IDA binder preserved their integrity, and their σ_b was 20% of the initial level.

CONCLUSIONS

(1) The possibility of preparing reinforced plastics based on infusible polyimide binders IDA and ITA by impregnation of prepregs with prepolymer melts was demonstrated.

(2) Carbon- and glass-reinforced plastics based on IDA binder showed higher resistance to thermal aging in air at 350°C, compared to similar composites based on IPO and ITA–carbon pitch binders. After keeping for 100 h in air, carbon-reinforced plastics based on IDA binder preserve about 40% of the initial elastic modulus and about 20% of the strength.

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