



Polyimide Composite Materials Containing Modified Nanostructured Boron Carbide

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ABSTRACT

This article describes the study of producing composites based on polyimide matrices containing nanostructured boron carbide as reinforcement particles. To improve the adhesion between ceramic particles and matrix material the boron carbide was pre-modified. The composites were produced using high temperature *in situ* polymerization method, with aromatic tetracarboxylic dianhydrides and aromatic diamines used as monomers. In particular, 4,4'-isopropylidene diphthalic anhydride, 4,4'-(p-phenylenedioxi)bis[phthalic anhydride], 4,4'-oxydianiline, 4-[4-(4-aminophenoxy)phenoxy]aniline were used as monomers, while the filler content was 20 to 60 wt. %. Mechanical properties, imidization degree and thermal resistance of the composites produced were studied as well.


Keywords: Polyimide composite, Dianhydride aromatic acids, Boron carbide, Nanofiller, Polyimide, Adhesion.

INTRODUCTION

Polymers are known to be prone to substantial destruction during operation in high radiation environment. These structural changes can be prevented by reinforcing a polymer with radiation-absorbing fillers. The variety of polymer and reinforcement materials allows to adjust the

strength, stiffness, operating temperature range, radiation protection and other properties in a focused way by selecting ingredients and changing component ratio and composite micro and nanostructures. Polyimides have the highest thermal resistance and ionizing radiation resistance among polymer matrices, so using these polymers it the most promising in terms of producing radiation protection composites.



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Aromatic polymers are known to show generally higher radiation resistance than aliphatic ones, which is due to the energy dissipation caused by aromatic ring's resonance structures¹⁻⁵. Thus, the subjects of interest are aromatic polymer materials of high radiation resistance, such as epoxy resins⁶⁻⁸, polyimides^{9,10}, phenol resins^{11,12}, polystyrene^{13,14}, polyethers¹⁵ and composites based on this materials.

It is polyheteroarylenes, with the chains formed by continuously interlacing aromatic cycles and heterocycles, that are featured by the highest heat and thermal resistance (Figure 1).

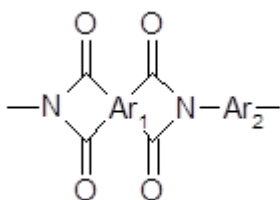


Fig. 1. Polyimide unit structure

In recent decades numerous studies were aimed at modifying molecular interactions in the polyimides to improve their processability using conventional technologies, such as melt casting or solvent casting, while retaining a polymer's thermal-oxidative resistance.

High thermal resistance (chemical resistance during heating, Td) of polyimides is due to their structure stabilization and bond strengthening caused by conjugation effect, since a cycle's heteroatom has a lone electron pair (in case of nitrogen) and there are high electronegativity atoms (in case of carboxyl group oxygen), while imide cycle is stabilized due to C-N bond conjugation.

Radiation resistance of polyimides is due to the high bond strength within imide cycle and polyimide exposure accompanied by competing processes, such as macrochain breakdown and molecular cross-linking.

In addition to their exceptionally high radiation resistance, polyimides have a number of valuable and unique physical, mechanical, electrical and chemical properties. They can be used

over a long period of time at 200 °C, while their short-term use is possible even at 480 °C. In fact, polyimides have excellent physical and mechanical properties within wide temperature range. These characteristics enable polyimide domination in numerous fields of application.

Polyimides provide basis for the whole conventional line up of polymer materials, such as coupling and filled compositions, including those containing continuous high-strength and high-modulus fibers and their textile forms; glass, carbon and organic fiber-reinforced plastics; bonding agents, sealants and films).

Using nanosized powder particles of radiation-absorbing materials (BN, B₄C, Pb and W) leads to 1.5-time increase in neutron absorptivity and 30-40% increase in gamma-ray scattering factor.

Composition materials were shown to have not only radiation resistance, but also higher mechanical strength and higher thermal resistance, comparing with an unfilled polymer¹⁶.

EXPERIMENTAL

Materials and reagents

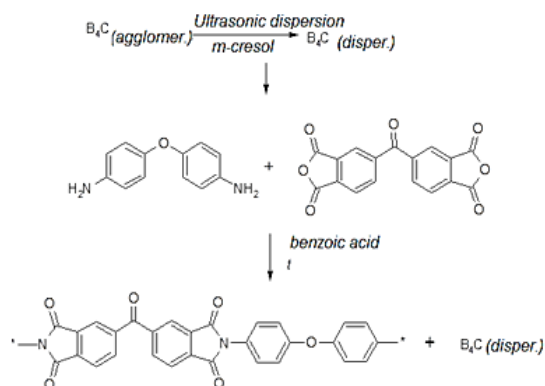
Dianhydrides (4,4'-isopropylidene diphthalic anhydride), 4,4'-(p-phenylenedioxi)bis[phthalic anhydride] and diamines (4,4'-oxydianiline, 4-[4-(4-aminophenoxy)phenoxy]aniline) were synthesized by the authors using developed techniques. m-cresol and benzoic acid were purchased from the Vekton LLC, while boron carbide was purchased from the ImKhim LLC Service.

Composite manufacturing

Nanocomposites were produced using *in-situ* polymerization method over the filler, i.e. nanostructured boron carbide. 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 4,42-oxydianiline were selected as monomers for developing primary technique.

65 ml of m-cresol and 2.00 g of nanostructured B₄C (calculated as 20 wt.% of the final polyimide) were fed into 250-ml three-necked

flask equipped with a sonicator, reflux condenser and inert gas inlet tube. The reaction mass was subjected to ultrasonic treatment, with treatment duration and acoustic wave frequency values shown in Table 2, followed by mixing with standard mechanical mixer. 3.28 g (16.4 mmol) of 4,4'-oxydianiline was added to the mixture and mixed till completely dissolved (about 10 min.), followed by single addition of 5.30-g (16.4 mmol) of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 3.00 g (24.6 mmol) of benzoic acid.



The reaction mass is then mixed at room temperature for 10 min. heated to 80 °C and mixed again for several h, followed by heating to 180 °C and mixing over the duration specified in Table 3. Once the dwelling was over, the reaction mass was cooled down to room temperature and poured into the glass equipped with magnetic mixer, which contained 250 ml ethyl alcohol. The deposit produced was filtered out and flushed with 50 ml ethyl alcohol filter, followed by drying in the drying chamber at 150 °C and 15 mm Hg.

The dispersion quality was determined by means of sample microphotograph, which was obtained using scanning electron microscopy and Hitachi SU-1510 VP-SEM, with its voltage of 7 kV and its working distance of 5.5 mm.

Imidization degree was determined to assess the imidization efficiency for Fourier-transform infrared spectra of the polyimide nanocomposites produced. Characteristic signals of polyimide, polyamidoacid and monomer absorption are shown in Table 1¹. Imidization degree could be determined by comparing the adsorption band intensity of the sample film (I) and

completely imidized reference film (I_0) (Kapton[®], manufacturer: DuPont). To make up the film thickness difference, a normalizing factor, i.e. adsorption band intensities, which remain unchanged during imidization (e.g. 1500-cm⁻¹ aromatic adsorption bands ($I_{(rel)} / I_{0(rel)}$)), was used. Imidization degree (%) was determined using the following equation:

$$P = \frac{I_{(imid)} / I_{(rel)}}{I_{0(imid)} / I_{0(rel)}} \times 100$$

Adsorption spectra were recorded using Fourier-transform infrared spectrometer Bruker VERTEX 70 with extended IR range of 8000 to 50 cm⁻¹ and FT-Raman module RAMII, Bruker Optics.

RESULTS AND DISCUSSIONS

Determination of optimal modification mode for nanostructured boron carbide

To produce the composites of high filler content (over 30 wt.%) without significant loss of mechanical properties and loss-of-filler composite cracking, the surface of nanostructured boron carbide needs to be modified.

Organosilicon compounds containing alkoxy-silyl groups are the most commonly used modifying agents capable of forming stable bonds with inorganic particles. During the interaction between organosilicon compounds and the surface of boron oxide, which can be found on the surface of nanostructured boron carbide, a chemical bonding between an organosilicon fragment and a particle's surface hydroxyl groups occurs, eventually leading to the hydrophobization of filler's particle surface, which allows to form stable bond with a polymer, while reactive amino group appears on particle surfaces, thus allowing to achieve additional covalent bonding.

In this case (3-aminopropyl) triethoxysilane (trade name: silane coupling agent KH-550), which is widely used for composite production, was used as a modifying agent. This cross-linking agent is very sensitive to moisture, so using it for filler surface modification requires dried solvents.

The method of infrared spectroscopy by cross-linking agent's residual signals following complete filler drying was used for assessing the efficiency of modifying nanostructured boron carbide surface. Modification origin is determined by 3200-

2400 cm^{-1} bands that refer to NH_2 group of the cross-linking agent and by up-to-1610 cm^{-1} signal that refers to CH_2 groups of (3-aminopropyl) triethoxysilane.

Table 1: Characteristic adsorption frequencies used for determining imidization degree [1]

Compound	Adsorption band, cm^{-1}	Origin
Aromatic imides	1780	C=O asymmetric stretching
	1720	C=O symmetric stretching
	1380	C-N stretching
	725	C=O bend
Amidoacids	2900-3200	COOH and NH_2
	1710	C=O (COOH)
	1660 (amide 1) 1550 (amide 2)	C=O (CONH)
Anhydrides	1820	C-NH
	1780	C=O
	1780	C=O
	720	C=O
Amines	~3200 (two bands)	NH_2 symmetric structure NH_2 asymmetric structure

10 g of nanostructured nonmodified boron carbide powder and 100 ml of dry solvent were fed into 250-ml four-neck flask equipped with a sonicator, reflux condenser, inert gas inlet tube and thermocouple (Table 4). The powder was dispersed in the solvent by using 20 kHz ultrasound for 15 min. followed by replacing sonicator waveguide with mechanical mixer and adding (3-aminopropyl) triethoxysilane (Table 4). The reaction mass was then mixed and heated simultaneously (Table 5). Once the dwelling was over, the reaction mass was cooled down to room temperature and poured into the glass, followed by centrifuging and filtering out modified nanostructured boron carbide powder, which was then dried in the drying cabinet at 80 °N for 6 hours.

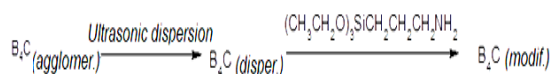
Nanostructured boron carbide surface modification

10 g of nanostructured nonmodified boron carbide powder and 100 ml of toluene were fed into 250 ml four-neck flask equipped with a sonicator, reflux condenser, inert gas inlet tube and thermocouple. The powder was dispersed in the solvent by using 20 kHz ultrasound for 15 minutes, followed by replacing sonicator waveguide with mechanical mixer and adding 20 g of (3-aminopropyl) triethoxysilane. The reaction mass was then mixed and heated to 90 °C simultaneously,

followed by 2 h dwelling at this temperature. Once the dwelling was over, the reaction mass was cooled down to room temperature and poured into the glass, followed by centrifuging and filtering out modified nanostructured boron carbide powder, which was then dried in the drying cabinet at 80 °N for 6 hours.

Filler surface modification

The evenness of filler distribution inside



composite material was assessed using scanning electron microscopy and Hitachi SU-1510 VP-SEM, with its voltage of 7 kV and its working distance of 5.5 mm. Fig. 2 and 3 show composite microphotographs featured by visible distribution of particular elements. Modifying the filler with (3-aminopropyl) triethoxysilane allows to trace its distribution by that of the silicon. Fig. 4 shows IR-spectrum of a composite material based on nanostructured boron carbide and polyimide (BPDA/ODA/20 B_4C), which was produced using Fourier-transform infrared spectrometer Bruker VERTEX 70 with extended IR range of 8000 to 50 cm^{-1} and FT-Raman module RAMII, Bruker Optics.

Table 2: Temperature impact on the efficiency of modifying nanostructured boron carbide surface

No	Solvent	Dwelling temperature, °C	Dwelling duration, h	Functional group share of the product, rel. units %
1	Toluene	90	1	98
			2	100
			3	100
		95	1	98
			2	100
			2	100
			2	100
2	o-Xylene	90	1	98
			2	100
			2	100
			2	100
			2	100

As the series of temperature adjustment experiment showed, 2 h toluene or o-Xylene treatment was enough for surface modification.

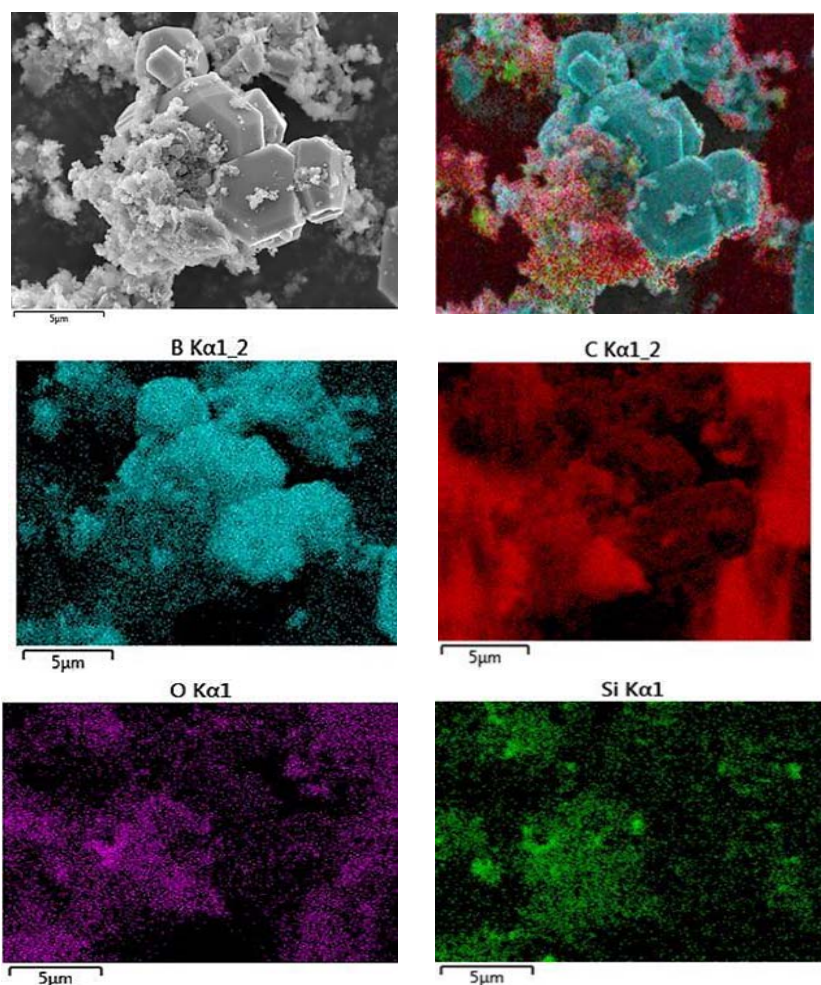


Fig. 2. Filler distribution inside composite material

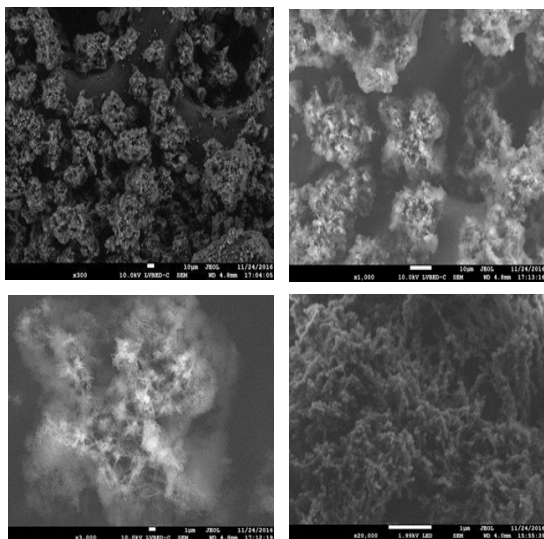


Fig. 3. Microphotograph of a composite material based on nanostructured boron carbide and polyimide

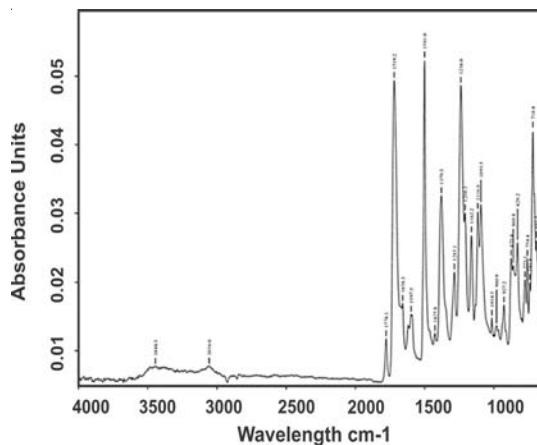
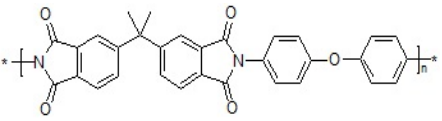
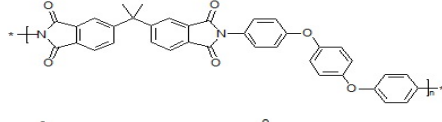
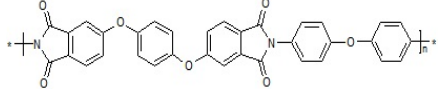
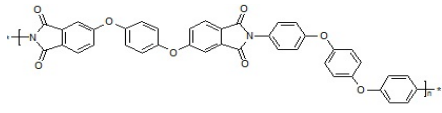


Fig. 4. Adsorption spectrum of a composite material based on nanostructured boron carbide and polyimide (BPDA/ODA/20B₄C), which was produced using Fourier-transform infrared spectrometer Bruker VERTEX 70 with extended IR range of 8000 to 50 cm⁻¹ and FT-Raman module RAMII, Bruker Optics

Table 3: 5- и 10-% weight loss temperature, °C

Sample	Polyimide matrix	Filler content	Argon			Air	
			5%	10%	5%	10%	
	IDPA/ODA		527.47	537.53	483.38	518.00	
	IDPA/ODA+20%B4C		521.82	532.49	453.00	489.10	
	IDPA/ODA+40%B4C		515.28	541.01	422.75	468.21	
	IDPA/ODA+60%B4C		496.88	525.23	436.84	488.68	
	IDPA/BABP		526.47	531.77	522.07	532.67	
	IDPA/BABP+20%B4C		516.15	528.42	438.26	465.13	
	IDPA/BABP+40%B4C		509.39	536.62	408.10	456.04	
	IDPA/BABP+60%B4C		485.62	528.11	384.76	450.26	
	HCDA/ODA		560.47	579.02	548.52	571.18	
	HCDA/ODA+20%B4C		558.91	574.23	501.57	528.41	
	HCDA/ODA+40%B4C		536.77	566.01	488.21	526.98	
	HCDA/ODA+60%B4C		551.94	597.69	464.74	520.29	
	HCDA/BABP		531.67	555.37	506.39	547.33	
	HCDA/BABP +20%B4C		491.55	555.31	491.48	539.91	
	HCDA/BABP +40%B4C		536.61	568.01	435.82	488.24	
	HCDA/BABP +60%B4C		561.24	596.77	433.47	485.06	

CONCLUSION

During the study the authors produced a number of composites based on polyimide matrices containing nanostructured boron carbide as reinforcement particles. The composite materials produced showed high thermal resistance and even filler distribution inside polymer matrix. The

composites of high filler content (over 30 wt.%) also showed high thermal resistance due to modification of boron carbide with 3-aminopropyl-triethoxysilane.

The technique developed is suitable for polyimide matrices and various nanostructured boron carbide ingredients inside a composite an ensures even filler distribution and the highest imidization degree.

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