Topology and structure analysis of carbon fiber-reinforced polyimide composites

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Abstracts. This paper describes the production of carbon fiber / high-performance polyimide prepregs and the study of prepreg samples quality by scanning electron microscopy, atomic-force electron microscopy and scanning ion-conductance microscopy. The prepreg samples were produced using a laboratory-designed setup by impregnation of carbon fiber with a polyimide solution. The study of the prepreg structure made it possible to establish the connection between polymer matrix composition and quality of carbon fiber impregnation. Thus, the study shows that the polymer matrix composition containing aliphatic fragment and quaternary carbon atom produces the best performance prepreg suitable for FDM 3D printing. **Key words:** carbon fiber, prepreg, composite, polyimide.

1 Introduction

Composites based on continuous fiber-reinforced polymers (CFRPs) (glass, carbon, polymer, etc.) are widely used in in engineering applications [1-4]. Now it is impossible to imagine aerospace technology without their use. CFRPs are demanded in other sectors of the national economy as well – mechanical engineering, shipbuilding, construction, etc. Polymer composites are widely used due to their high strength [5,6], combined with lightness [7]. At the moment, the CFRP composite products preparation methods are consuming and significantly limit the geometry of the resulting product [8] due to necessity of mold usage for producing CFRP parts and high viscosity of polymer solutions and melts that complicates the impregnation of fibers.

A large number of current studies are aimed at creating new high-temperature polymer materials for three-dimensional printing by fused deposition modelling (FDM). This is primarily due to the lack of materials that provide high adhesion to the surface of various unidirectional fibers used for the manufacture of reinforced products using additive technologies. This is primarily due to the lack of materials that provide high adhesion to the surface of various unidirectional fibers used for the additive manufacturing of reinforced products.

Recent studies of 3D printing of thermoplastic composites reinforced with continuous fiber have mainly focused on acrylonitrile butadiene styrene (ABS), polylactic acid (PLA),

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polyamide (PA), and onyx [9-12]. However, the thermal and mechanical properties of these matrices do not meet the high requirements of such mission-critical applications as the aerospace and aviation industries. In this regard, creating 3D printing materials based on high-performance polymers, for example, polyaryletherketone (PAEK) group, is becoming more relevant [13]. Weak interlayer bonding between fibers and polymer matrix is another factor hindering the development of additive manufacturing of reinforced composites by layer-by-layer deposition. The high viscosity of polymer matrix leads to poor impregnation of carbon fiber during printing and, as a consequence, a significant decrease of physical and mechanical characteristics of finished products [14, 15]. The described difficulties are overcome by pre-impregnation of carbon fiber with a polymer solution or melt. The resulting composite filament, called a prepreg, is used for printing by FDM.

Heat-resistant polyimide-based binders with improved rheological characteristics were previously developed, their adhesive properties were studied and a prepregs preparation method was proposed [16]. Polyimides are a class of high thermal resistant compounds [17] and the preparation of prepregs based on them can contribute to the production of polymer composite materials with exceptional operating temperatures. In the present study, we used the most promising binders to obtain test samples of prepregs. The structures of the binders used to study the topology and bulk structure of prepregs are shown in Figure 1.

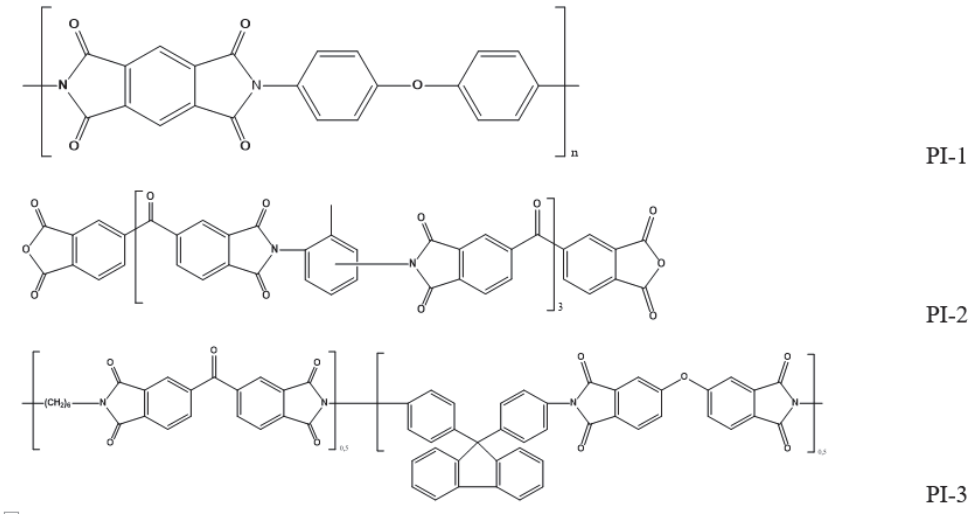

Fig. 1. Structures of selected polyimide binders.

2 Materials and methods

2.1 Materials

Commercially available monomers of carboxylic acids dianhydrides were used for the synthesis of the sizing composition and polyimide binders. Pyromellitic dianhydride (PMDA), benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (BTDA), 4,4′-oxydiphthalic anhydride, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6-FDA) were preliminarily dried in vacuum for 8 hours at temperatures of 215°C, 220°C, 225°C, and 150°C, respectively. Commercially available 4,4′-oxydianiline (ODA) and 3,5-diaminobenzoic acid were used as received. The solvents were dried by distillation over desiccants.

4,4′-(9-Fluorenylidene) dianiline was prepared by the condensation of aniline and 9-fluorenone as described [18].

Carbon fiber 1.5K (made in Taiwan) was used to make prepregs based on polyimide sizing agents. To improve the quality of impregnation and increase the adhesion between the carbon fibers and polyimide binders, the fiber was resized before impregnation. Instead of a deleted factory sizing composition, pre-designed polyimide-compatible sizing was applied. A solution of polyamide acid oligomers (PAA-sizing) based on 6-FDA and ODA was used as sizing agent. The preparation of the sizing solution and the carbon fiber resizing process were carried out as described [16].

Polyimide binder 1 (PI-1) was synthesized as follows. A 250 mL round-bottomed three-necked flask equipped with an overhead stirrer was charged with ODA (9.57 g, 47.8 mmol) and DMF (85 mL), then cooled with an ice bath under argon atmosphere and stirred for about 20 min up to ODA dissolution. PMDA (10.47 g, 47.8 mmol) was added to cooled reaction mixture. The reaction was stirred for 20 h. The resulting solution was stored in the refrigerator.

Polyimide binder 2 (PI-2) was synthesized as described [19].

Polyimide binder 3 (PI-3) was synthesized by one-pot high-temperature synthesis on the basis of 3,5-diaminobenzoic acid, 4,4′-(9-fluorenylidene) dianiline, and 4,4′-oxydiphthalic anhydride similarly as described [18, 20].

2.2 Measurements

The analysis of the macroscopic state of the prepregs surface and prepregs cross-sections was conducted by scanning electron microscopy (SEM) using a small-sized scanning electron microscope Hitachi SU1510.

Atomic-force microscopy (AFM) was used to study the topology of the prepreg surface. The study was performed using a Nanoscope 3a multimode microscope (Veeco, USA) in the tapping mode (HA_NC cantilevers (NT-MDT, Russia)). Prepreg samples were fixed to a magnetic disk using a double-sided adhesive tape. Random areas ranging in size from 1 to 3 microns (for individual samples – up to 12 microns) on the surface were studied. The number of pixels in the images is 512×512.

Prepreg surface topography was evaluated using an ICAPPIC scanning ion-conductance microscope (SICM ICAPPIC). SICM ICAPPIC is developed on the basis of an inverted optical microscope Eclipse Ti-2 (Nikon, Japan), located on the STable anti-vibration table (Supertech instruments, Hungary). The microscope includes several functional parts: Mechanical Stand scanning platform (ICAPPIC, UK), Universal Controller feedback system (ICAPPIC, UK), Piezo control system positioning system (ICAPPIC, UK) and Axon Digidata 1550B signal input and output interface (Axon Instruments, USA) and Multiclamp 700B. Laser puller P-2000 (Sutter Instruments, USA) for the manufacture of nanocapillaries as probes.

3 Carbon fiber prepreg samples preparation

For carbon fiber resizing and prepregs production by impregnation with a polymer binder solution, a laboratory setup was constructed. It consists of a factory sizing removing furnace (1), impregnation unit (2), pressing rollers (3), drying oven (4), and winding unit (5). A model of the laboratory installation used for carbon fiber impregnation and photos of its main components are shown in Figure 2. To form a circular cross-section of prepregs, a 0.4 mm diameter die was installed at the entrance to the drying oven.

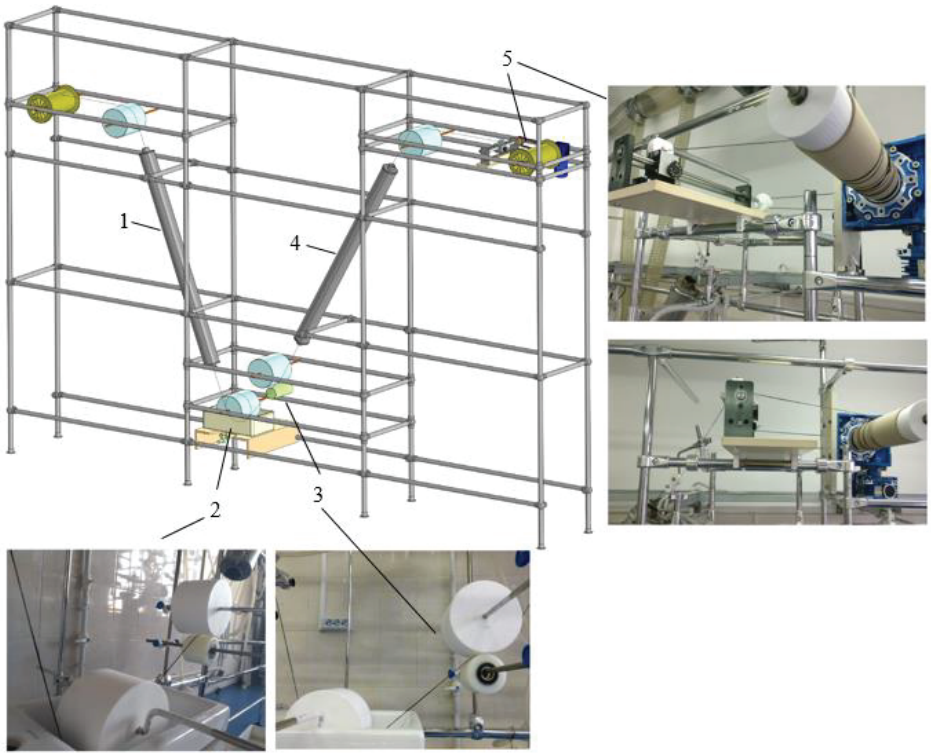

Fig. 2. Model and main components of the impregnation setup.

Solutions of polymer binders in DMF were prepared for the manufacture of prepregs. The solution was placed in an impregnation bath through which the fiber was stretched. When receiving prepregs, the sizing removing furnace (1) was not used. The parameters of the impregnation process are given in Table 1.

Table 1. Parameters of the process of prepreg obtaining by impregnation from a solution.

Parameter	Value
Sizing content [wt%]	20
Fiber drawing speed [m/h]	10
Drying oven temperature [°C]	
zone 1	250
zone 2	310
zone 3	370

4 Study of the fiber prepregs topology and prepregs cross-section

The quality of prepregs was evaluated in several ways. The uniformity of fiber impregnation with a polymer binder solution was studied using scanning electron microscopy (SEM). During the study, the surface of the prepreg and fibre cross-section were examined. Micrographs of the surface and sections of prepreg samples based on PI-1, PI-2 and PI-3 binders are shown in Figure 3.

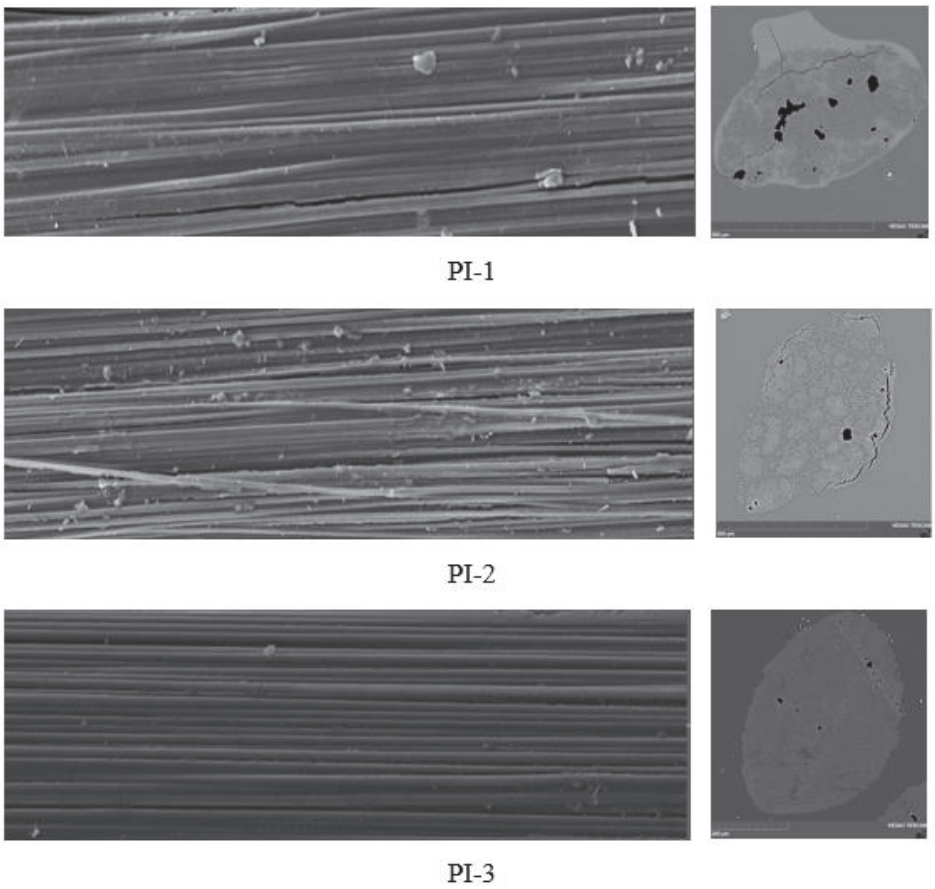

Fig. 3. SEM images of the surface and cross-section of prepreg samples.

Analysis of microphotographs shows that all samples have different impregnation degrees and different surface morphology. The PI-3 prepreg sample is the most uniform impregnated. It shows the smallest port number, and also has the evenest surface, while the quality of other prepregs can be assessed significantly lower. The PI-1 sample has rather large pores, and the PI-2 sample is insufficiently impregnated. Because of this, inhomogeneities of the surface and the distribution of filaments in the volume of the prepreg arise.

The topology of the surface of the samples was also studied using atomic force microscopy (AFM) (Figure 4). Similar to the results demonstrated by SEM-micrographs, AFM images demonstrate different morphology of prepreg samples based on different polyimides. Thus, the images and profilograms of the PI-1 and PI-2 samples show that the surface of the samples has a significant roughness: the height difference is up to 300 nm. Large "mounds" of the binder can be seen on the PI-2 sample. Apparently, due to poor impregnation by the sample of the PI-2 solution, the polymer accumulated on the fiber surface. The PI-3 sample demonstrates a relatively flat surface with low roughness and height differences of not greater than 5 nm.

Root mean square roughness (Rq) was calculated using the formula 1. The obtained values were 91.86 nm, 121.7 nm and 1.04 nm for samples PI-1, PI-2 and PI-3, respectively. As expected, the samples PI-1 and PI-2 show close Rq values, two orders of magnitude higher than the value calculated for the PI-3 prepreg.

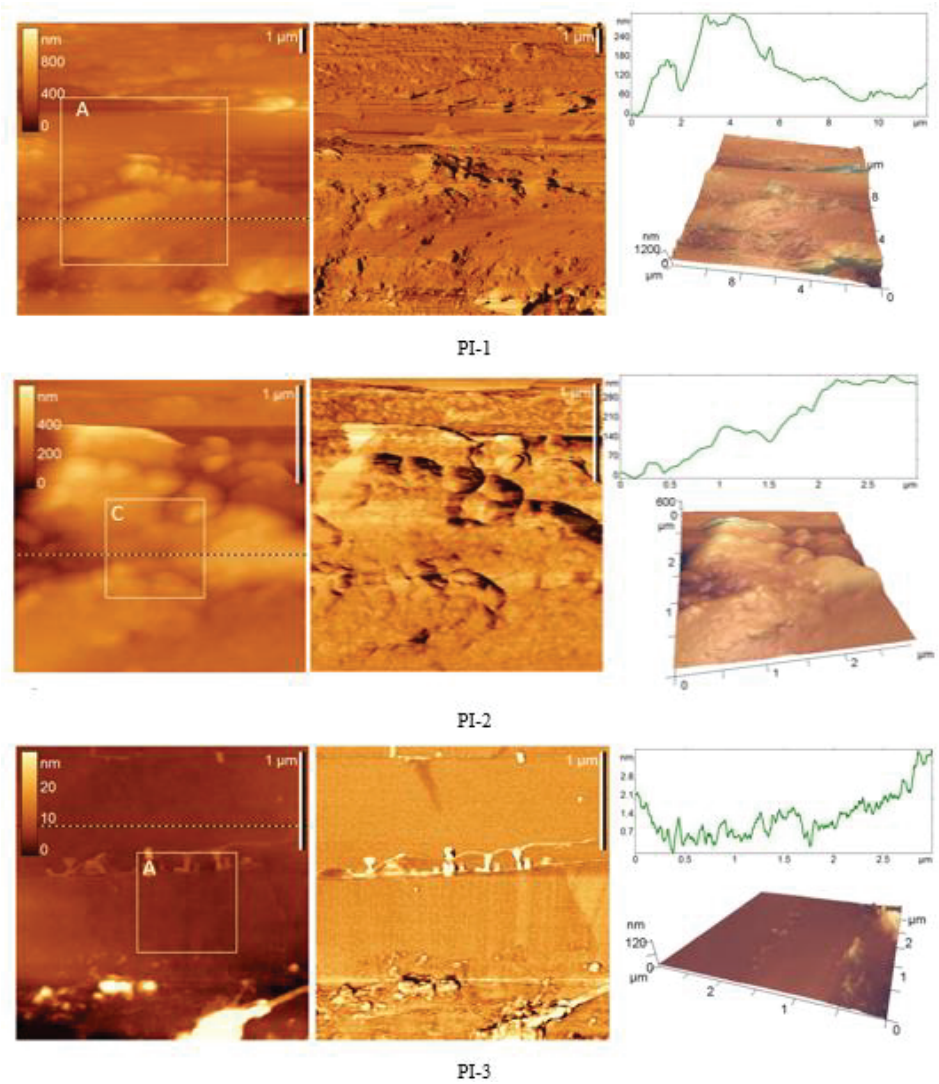

Fig. 4. AFM-photos of the prepreg surface.

$$R_q = \sqrt{\frac{1}{N}\sum_{j=1}^{N} r_j^2}\,, \tag{1}$$

where r_j – deviation from the midline vertically, N – number of points (pixels).

The roughness of the prepreg samples was also studied using the scanning ion-conductance microscopy (SICM). The micrographs obtained during the study are shown in Figure 5. The presented profilograms correlate with the data of scanning electron and atomic force microscopy.

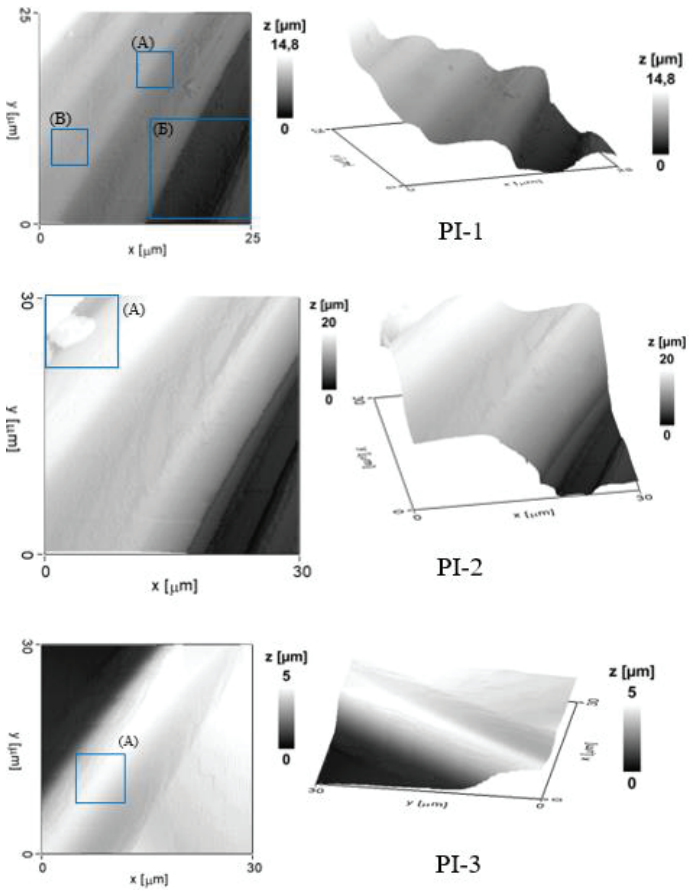

Fig. 5. SICM photos of the prepreg surface.

5 Conclusion

Summarizing the results of the described studies, we can state that the PI-3 prepreg has optimal impregnation and a smooth surface among the studied samples. The presence of irregularities on the surface of the PI-1 and PI-2 prepregs can lead to disruption of the printing process, and the voids formed as a result of uneven impregnation will certainly affect the physical and mechanical properties of the final products. Thus, the polyiimide binder PI-3 based on 9,9-bis-(4'-aminophenyl) fluorene with a carded carbon atom seems to be optimal for creating heat-resistant prepregs based on carbon fiber.

Acknowledgement

The scientific equipment provided by shared research facilities «Scientific Research Analytical Center» of National Research Center «Kurchatov Institute» – IREA" was used.

The research work was provided with support of National Research Center «Kurchatov Institute».

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