POLYMER BASED COMPOSITE MATERIALS REINFORCED BY HIGH-STRENGTH CARBON FIBERS WEFT KNITTED FABRICS

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Abstract

The new weft knitted fabrics containing high-strength carbon fibers from PAN precursors for the reinforcing of polymer based composite materials (PCM) are proposed. The higher level of mechanical properties of PCM reinforced by the proposed carbon fiber filler is achieved by increasing the relative content of high-strength and high-modulus carbon fibers in weft knitted fabrics by the using of warp threads with the lowest linear density. The tensile strength of PCM reinforced by the proposed weft knitted fabrics containing up to 95% of high-strength carbon fibers Toho Tenax HTA 40 E13 3K (800 tex) with a polyamide thread (5x2 tex) was 1.1 GPa at a composite density of 1,6 g/cm^3.

Keywords: polymer composite materials, carbon fibers, knitted structures, combined weft knitted fabrics, strength.

Introduction

Construction and functional polymer composite materials (PCM) reinforced by the various types of textile materials (fabrics, tapes, weft fabrics) made from aramid, glass, and carbon fibers are widely used. Plain or twill weave fabrics and unidirectional tapes produced from high-strength and high-modulus carbon fibers traditionally used as reinforcing fillers for construction PCM. High-strength and high-modulus carbon fibers from PAN precursors are characterized by the high level of physical and mechanical properties, but their textile processing is very complicated, because such kind of thread consists of a large number of highly brittle elementary fibers, susceptible to damage during the processing. Furthermore, such high-strength and high modulus fibers and threads lose their primary properties during textile processing. Therefore, the development of new types of reinforcing fillers is promising for better implementation of the properties of carbon fibers in fillers and improving the properties of polymer composites reinforced by such fillers.

However, the problem of the use of reinforcing fibrous fillers for structural PCMs, in particular a knitted and weft knitted structures, taking into account changes in their properties during the production of composites has not been sufficiently studied. New production technologies for reinforcing fillers based on various types of carbon fibers ensure the wide possibilities for creating of carbon and hybrid fibrous fillers for PCMs and developing the products based on them with specified characteristics. The specific properties of carbon fibers (CF) and fillers from these fibers for composite materials (CM) allow to solve a number of complex materials science problems such as the creation of structural CMs and multifunctional products with given service parameters. CMs reinforced by the complex weft knitted fillers can simultaneously be structural (high-modulus, high-strength), conductive, radio-absorbing, corrosion-resistant, etc. The potential of the carbon fibers in composite materials is far from exhausted. The development of polymer based composite materials reinforced by the high-strength and high-modulus carbon fibers for aircraft structures is an urgent scientific and practical problem. So, for the best implementation of the properties of both carbon fibers and the improvement of the properties of the plastics reinforced by carbon fibers, the development of new types of fibrous reinforcing filler from high-strength and high-modulus carbon fibers from PAN precursors is very promising.

The physical, mechanical, and fatigue characteristics of polymer-based composites reinforced by carbon fiber are higher than corresponding values for the polymer-based composites reinforced by the glass fibers, allowing their use in critical aircraft structures. Using carbon fibers for the reinforcement of plastics also significantly reduces weight of details in comparison with glass fibers and metal alloys, in particular aluminum spars in helicopter propeller blades. However, the use of carbon fibers is limited by the high cost of threads and the lack of their production in Ukraine. At the same time, the use of carbon fibers in industrial production is increasing and requires the study for the methods of manufacturing both carbon fibers and fibrous fillers for PCMs and the possibility of improving their characteristics. Due to the high brittleness of carbon fibers from PAN precursors and the ability to be damaged during textile processing, there is a need to develop new technologies for the production of fibrous fillers for various structures. The use of the knitted technology of weft knitting (rib with weft), developed in the IPMS NASU, allows the creation of a unidirectional structure from straight high-strength and high-modulus carbon threads and optimization of the structure of carbon fiber filler to improve the physical and mechanical properties under the mechanical loads. The surface specific gravity of the fibrous knitted filler in unidirectional PCM can be adjusted smoothly and in a wide range, using threads and bundles of different linear densities and changing the step of their distribution in the weft knitted fabric by using knitting equipment of different classes (gates).

To increase the strength of polymer composites reinforced by the complex carbon fiber filler, it is necessary to study ways for the increasing of the relative content of high-strength carbon fibers in the filler.

During structural PCMs production it is necessary to ensure not only a given orientation of the fibers and also their fixation in a corresponding position by manufacturing preforms (fixed packages of layers of carbon fabrics).

It is advisable to vacuum the filler blank before impregnation with a binder to create conditions for filling with a binder not only the space between individual threads but also the gaps between the elementary fibers of the carbon threads of the reinforcing filler with simultaneous removal of air located in the pores between the elementary fibers.

Hot pressing and vacuum molding can be used for the production of PCMs reinforced by the carbon fiber filler of weft knitted structure.

Thematic literature analysis

Unlike woven fabrics, the problem of using knitted structures as a reinforcing fibrous filler has not been sufficiently studied. Warp-knitted fabrics made of low-tex threads are more often used. In such knitwear, a separate thread is fed to each needle, so such process requires a significant amount of raw materials (thread spools).

The practice of manufacturing knitted fillers for PCM on flat knitting equipment is known and described [1–3]. In [4] the possibilities of manufacturing hybrid fabrics from glass and polypropylene threads for producing a 2D polymer composite with a thermoplastic matrix is presented. The authors developed several different weaves that have weft threads in their structure. However, the processing of high-strength carbon fibers from PAN using the above-described weaves is not good since the roving structure is practically not subject to bending and does not allow the thread to take the shape of a loop. The method of weft knitwear production using a flat knitting machine of the Stoll CMS 400 class 5 [5] allows the processing of high-tex threads for warp threads and laying the weft thread. However, in such fabric production, each weft thread is laid independently along the loop columns, and the number of filling threads must correspond to the number of weft threads. The use of knitted fillers for composite materials containing carbon threads in their structure has recently become increasingly widespread [6–8]. Using various weaves and warp knitting equipment allows to process carbon threads by "braiding" the weft thread [9]. As a result, it was found that the type of weave has a significant effect on the elastic and tear properties of such knitted fabrics. The strength limit of tricot weave fabrics is higher than corresponding values for the chain weave fabrics, in particular, it is of 14% higher for glass roving and of 21% higher for carbon roving. A similar gradation was observed for the Young's modulus: the increasing of 11% and 25% were obtained for glass and carbon, respectively. The processing of carbon threads on a modernized circular knitting machine from Mayer and Cie (www.mayercie.com) for producing high-strength weft knitwear is proposed in [10]. During the loop formation process, a carbon thread is laid between two layers of Dyneema or polyester. The main advantage of this equipment is the high productivity. However, it should be noted that knitwear from circular knitting machines is characterized by the only specified width, in this case 26 inches (66 cm). If we need knitwear of a smaller or larger width, it is necessary to select a machine with a smaller or larger cylinder diameter, respectively. It requires the purchase of additional equipment and production space. Changing the knitting width is necessary during the processing of a thread with a smooth surface since the structure of the fabric is damaged during cutting, and the knitwear loses its strength properties. Changing the required specified width is easily adjusted on flat-knitting machines. In [11], the production of weft knitwear on flat-knitting machines is described. A single satin weave is used as the main weave. However, using these fabrics as a fibrous reinforcing filler for structural polymer composites does not provide the necessary strength characteristics since the weave is single, so the front and back sides can withstand different loads.

Materials and Methods

The "rib with weft" method of weft knitting enables the processing of fragile threads or large-diameter threads that cannot be formed into a loop in conventional knitwear. In this paper, we propose the production of a double-weft weave on flat knitting machines, allowing an equal load to be taken from both the front and back sides. Together with the possibility of textile processing of high-strength carbon, glass, aramid, etc. threads, the developed technology for weft knitted fabrics production requires from 1 to 4 spools of thread regardless of the width of the fabric.

Such weft knitted fabrics can be used as unidirectional fillers where more than 85% of the fibers are located in one direction. PAN carbon fibers are used as a weft thread, and high-strength glass or chemical fibers are used as a base. Due to such distribution of the fibers, the composite polymer material is characterized by the anisotropy of physical and mechanical properties in the direction of preferred loads.

The main principle of rib with weft knitwear manufacturing is to lay the basis of straight weft threads in each loop row (Figure 1). In such knitwear, one of the threads forms the basis of the main weave, and the other thread is laid between the needle beds in a straight loop, without knitting. Also, in knitwear, the weft thread is laid from one thread feed system, which allows the weft thread to be fixed clearly in the structure of the knitwear. Such fixation is more reliable and will enable the obtaining of fabric with high-performance indicators [12]. Unlike weaving, the production of weft knitted fabrics does not require complex equipment, such as looms, and in the case of carbon fabric production - precision machines with the mandatory use of multi-seat spoolers.

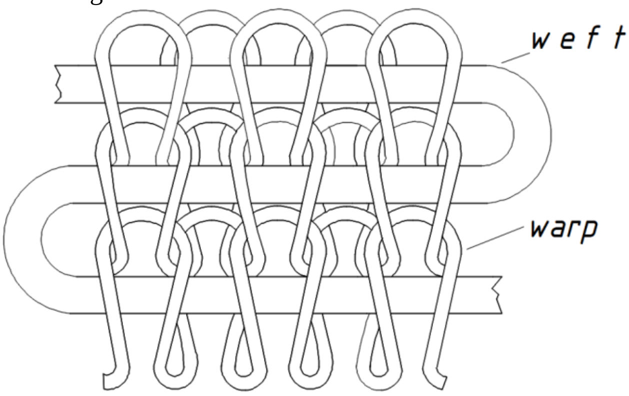


***Figure 1** – The scheme of interweaving «rib with weft»*

The weft knitting method, "rib with weft," allows produce carbon fabric using one bobbin of weft thread and one bobbin of warp thread. Thus, this method enables the production of carbon-knitted fabric by combining high-strength threads into unidirectional (by weft) loops of warp. For the production of weft knitted fabrics for current research a flat knitting machine with two-bed tongue needles of the PVRK-6, 6E type was used after the modernization of the feeding mechanism and tension of the weft thread. This type of equipment allows the processing of threads with a large number of elementary fibers or threads of large diameter that cannot be formed into a loop. This method can be used to obtain a combined filler and hybrid composites based on it, where the various threads are combined, for example, carbon and aramid, carbon and carbon, glass and aramid, and others.

During the selection of the type of knitted weaves for high-strength and high-modulus carbon threads from PAN precursors, the possibility of introducing them into the knitted fabric with a straight thread was taken into account, i.e., without knitting them with the needles of a knitting machine, giving them the shape of loops. It should be noted that the surface density of the fibrous knitted filler in unidirectional PCMs can be adjusted in a wide range, using threads and bundles of different linear densities and changing the step of their distribution in the knitted fabric by using knitting equipment of various classes.

The choice of fiber material was determined by a set of physical, mechanical, and technological parameters and economic factors (fibers availability). From the technological point of view combined weft knitted fabrics are obtained by interweaving fibers of different natures and creating a knitted (loop) structure, which makes it possible to obtain materials with a wide range of service properties.

The investigated weft knitted fabrics were prepared from the following starting materials:

1 Carbon thread from PAN precursors 200 tex (Toho Tenax HTS40 E13 3K);

2 Carbon thread from GC fibers 100 tex;

3 High-strength light-heat-stabilized polyamide thread 10 (5x2) tex.

The properties of the starting fibers are presented in table 1.

Table 1

Properties of carbon filaments

<table>
<tr><th></th><th>Linear density, Tex</th><th>Tensile strength, MPa,</th><th>Tensile Modulus, GPa</th><th>Elongation at break, %</th><th>Number of filaments</th></tr>
<tr><td>Carbon thread from PAN precursors</td><td>200</td><td>4400</td><td>240</td><td>1,8</td><td>3000</td></tr>
<tr><td>Carbon thread from GC fibers</td><td>100</td><td>1200-1500</td><td>60</td><td>1,9</td><td>3000</td></tr>
<tr><td rowspan="2">High-strength light-heat-stabilized polyamide thread</td><td rowspan="2">5</td><td>Specific tensile load, cN/ Tex</td><td rowspan="2">-</td><td rowspan="2">23</td><td rowspan="2">140</td></tr>
<tr><td>85,8</td></tr>
</table>

For high-modulus carbon threads, we used the simplest forms of weaving - stockinette weave and rib 1+1. When choosing the rib weave of carbon fabric, two needle beds and two rows of base loops are used and a straight weft thread of high-strength carbon fiber from PAN precursors is laid between them. During carbon knitwear production high-strength and high-modulus (brittle) carbon thread from PAN precursor is a weft thread, and low-modulus carbon fiber is used as a base, for example, fibers based on hydrated cellulose (GC), or chemical fibers (polyamide, aramid).

The structure of weft knitted fabrics and carbon carbon composite materials CCCM reinforced by them were studied by optical microscopy.

The pre-treated layers were impregnated three times with a hot-curing epoxy binder to produce the samples. The binder used was ED-20 epoxy resin, I-MTHF anhydride hardener, and UP606/1 accelerator. The system had low viscosity and a long shelf life. The pre-impregnated carbon knitted fabric preform polymerization was carried out by vacuum molding.

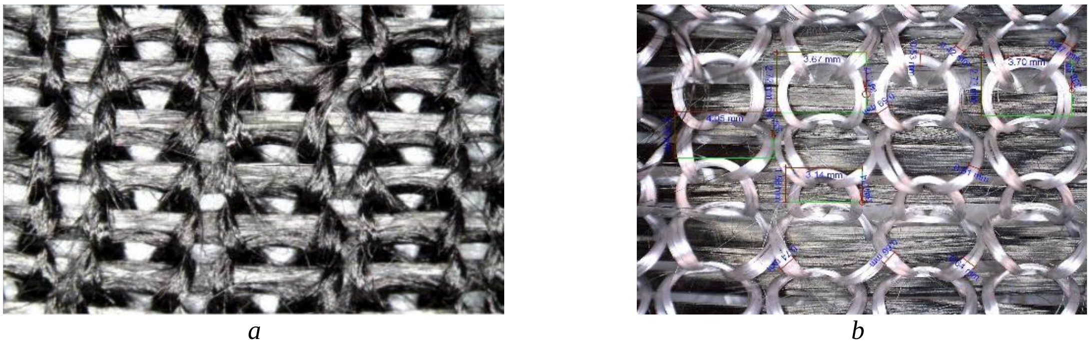
The mechanical properties of polymer based composite materials reinforced by weft knitted structures of different compositions, taking into account the arrangement of high-strength carbon fibers (1D (0-0) and 2D (0-90), were determined using standard methods. The samples produced from the obtained PCMs are shown in Figure 2.

a *b*

***Figure 2** – Sample of PCM reinforced with fibrous weft knitted filler for determining of tensile strength*

Results and Discussion

Samples of weft-knit fabrics were produced using high-strength carbon threads Toho Tenax HTA 40 E13 3K (200 Tex) as weft threads, and carbon threads from GC fibers (100 Tex) and high-strength light- and thermo-stabilized polyamide threads (5x2 Tex) as warp threads (Figure 3).



a *b*

***Figure 3** – Combined fibrous filler: a - Toho Tenax HTA 40 E13 3K (200 tex) - carbon thread from GC fibers 100 Tex; b- Toho Tenax HTA 40 E13 3K (800 tex) - polyamide thread (5x2 tex)*

The results of mechanical testing of polymer composite materials (PCM) reinforced by the combined weft knitted fabrics Toho Tenax HTA 40 E13 3K (200 Tex)—carbon thread from GC fibers (100 Tex), where the content of high-strength carbon fibers was about ≈50%, showed that the values of tensile strength limit were between 408 MPa and 447 MPa. Such materials are promising for developing functional PCMs, such as conductive, shielding, etc., but the strength indicators for structural applications need to be increased.

It should be noted that during the production of the samples for mechanical tests, the layers of weft knitted fabric were impregnated with an epoxy resin (hot curing) and placed in a mold. Despite the simplicity of laying the blanks in the mold, stable polymer matrix content in the plastic and its uniform distribution was not achieved due to the manual application of the resin with a spatula. Deviations in the polymer matrix content in the carbon plastic from the optimal level for PCMs based on the epoxy resin (35%) and the high residual porosity of the sample material led to a reduction in the mechanical properties of the resulting composites.

Preliminary vacuum impregnation was used for further production of PCM samples based on carbon-containing weft knitted fabrics. It was found that, due to the features of the carbon knitted filler's volumetric structure, for high-quality impregnation of blanks, reduction of the package volume, removal of air contained between elementary fibers, and preservation of the arrangement of the blank layers before formation, it is necessary to carry out preliminary vacuumization of the assembled package in a vacuum cabinet.

It is possible to increase the level of mechanical properties of PCM reinforced by carbon fiber filler by increasing the relative content of high-modulus carbon fiber from PAN precursor (Toho Tenax), namely by increasing the number of weft threads (tex) and using warp threads with the lowest linear density. The linear specific gravity of carbon weft threads and polyamide warp thread was calculated reach the values of relative content of high-strength carbon fibers of 75% and 95% in the knitted fabric. Increasing the relative content of high-modulus carbon fiber from PAN precursors in the fabric is achieved by increasing the number of weft threads using 2 or 3 bobbins with such carbon fiber. At the same time, thin (5x2 tex) warp threads were used while maintaining the technological and structural strength of such a carbon weft knitted fabric. The warp threads in the manufacture of filler fabrics of structural polymer composites do not carry a load, and their function is to preserve the integrity of the fabric during the production of fabric filler and its introduction into the composite.

The values of tensile strength limit for investigated materials are presented in Table 2.

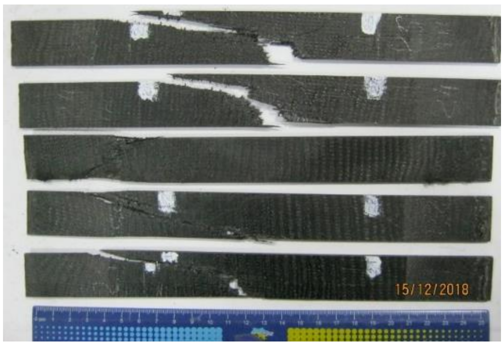
Table 2

Properties of unidirectional carbon plastics reinforced with carbon weft knitted fabric

	Carbon fiber content, %	Specific gravity, g/cm^3	Tensile force at break, N	Tensile strength limit, MPa
11	75	1,39 – 1,45	54800-74380	767-987
12	95	1,40 – 1,51	88300 - 99000	1014-1157

It is necessary to pay attention to the change in the mechanisms of fracture of PCM samples depending on the reinforcement scheme. Higher values of the tensile strength for unidirectional PCM samples is corresponding to gradual (long-term) fracture. Such mechanisms of fracture for PCM reinforced by fibrous fillers with weft knitted structure can have advantages in determining the operational characteristics, such as material fatigue strength (Fig. 3).

a



. b

Figure 3 *– PCM reinforced by the unidirectional carbon weft knitted filler:*
a – before testing; b – after testing

Conclusions

A new weft knitted fabric filler (rib + weft) for reinforcing of polymer based composite materials is proposed for the creation of a unidirectional structure of straight high-strength carbon threads from PAN precursors.

The use of weft knitted fabrics (rib + weft) containing up to 95% of high-strength and high-modulus carbon threads allows to improve the physical and mechanical properties of PCMs reinforced by them and to produce the new structural PCMs. The tensile strength limit of PCMs reinforced by weft knitted filler from carbon fiber Weaves Toho Tenax HTA 40 E13 3K (800 tex) - polyamide thread (5x2 tex) was equal 1.1 GPa.

For PCMs with proposed weft knitted carbon fillers, the higher level of mechanical properties was achieved for materials with a specific gravity of 1.5-1.7 g / cm^3.

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