Multifunctional polymer-based composite materials with weft-knitted carbon fibrous fillers

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Abstract. The production technology of reinforcement filler for new multifunctional polymer based composites with weft-knitted structure had been proposed. In such reinforcement filler high-strength carbon fibers (CFs) from PAN precursors (wefts) were laid in a knitted fabric as straight continuous yarns, so in such case these CFs were not twisted by knitting machine to form the loops. Various kinds of chemical and inorganic fibers can be used as base yarn in this case, in particular glass, aramid, carbon fibers from hydrate cellulose and etc.

Properties of multifunctional polymer-based composite materials with weft-knitted fillers depend upon fiber composition, relative content of weft and base yarns, scheme filler stacking (1D, 2D and 3D composites).

The electrical conductivity of weft-knitted fabrics shows the strong anisotropy along high-strength fibers in comparison with looped rows, depending on the direction of high-strength CFs (weft). Investigation of shielding properties of polymer based composites reinforced by carbon weft-knitted fabrics showed the possibility of using them as shielding materials with the ability to absorb electromagnetic radiation.

The use of composite materials based on carbon fibers in the aircraft construction is a promising and cost-effective direction for the development of the aviation industry. Carbon fiber reinforced plastics make it possible to obtain structural elements of aircraft with specified strength, reliability and safety parameters, reduced fuel consumption and increased flight range.

High-strength and high-modulus carbon fibers from PAN precursors have high physical and mechanical characteristics, but their processing into textile is difficult. This thread is characterized by high brittleness and damage during processing and essential loss of its original properties. Weft-knitted reinforcement fillers to be used in polymer based composites allow realizing the various service properties of carbon fibers and other types of fibers in such composites. Traditionally, composites reinforced by various types of textile materials from aramid, glass and carbon fibers are used for the production of aircraft structures. These fillers are woven fabrics with various structures, which are made on looms.
by weaving of longitudinal (warp) and transverse (weft) threads [1]. The most commonly used fabrics are plain, twill, satin and other simple weaves. The main disadvantage of carbon woven fabrics production is obligatory using of specialized weaving machines, which may require up to 1000 spools of thread to refill.

Unlike woven fabrics, the practice of using of knitted structures as a fibrous filler is not so popular. The most commonly used knitwear is made on a warp knitting machine from low tex threads. In this knitwear, a separate thread is fed to each needle, which also requires a large amount of raw material.

There is a practice of manufacturing for knitted fillers on flat knitting machine [2-4]. So, for example, Md. Abounaim, O. Diestel, G. Homann, Ch. Cherif in their work [5] described the possibilities of production for hybrid fabrics from glass and polypropylene threads. Such textile blanks were used to fix them in 2D thermoplastics. The authors have developed several different weaves, which in their structure have weft threads. However, the processing of high-strength carbon fibers from PAN using the weaves described above is basically impossible, since the roving structure is practically unbendable and does not allow the thread to take the form of a loop. The method of manufacturing of weft knitwear on a Stoll CMS 400 flat knitting machine [6] allows to process high tex thread both for warp thread and for laying as weft yarns. However, this technology also requires a large number of threads, since each weft thread is laid independently, along the wale.

The use of polymer based composite materials with weft-knitted fillers is widened [7-9]. O. Stolyarov, T. Quadflieg, T. Gries proposed the processing of carbon threads by braiding the weft thread with glass thread, using various interweaving and warp knitting machine [10]. As a result, it was found that the type of weaving significantly affects on the elastic and strength properties of knitwear. The tensile strength of "tricot" weaves is greater than the strength of "pillar" weaves, namely such increasing reaches 14 % and more for glass roving and 21% and more for carbon one. A similar enhancing was observed for the Young's modulus:11% and more for composites with glass roving and 25% and more for composites with carbon roving.

The authors of [11] proposed the processing of carbon filaments on a modernized Mayer and Cie circular knitting machine for production of high-strength weft knitwear. During the manufacturing process, the carbon thread is laid between two layers of Dyneema® or polyester. The advantage of this equipment is relatively high productivity. At the same time the knitwear from circular knitting machines is produced only of one given width, in this case 26 inches (66 cm). So, for the manufacture of knitwear of smaller or larger predetermined widths, it is necessary to choose a machine with a smaller or larger cylinder diameter, respectively, which requires the purchase of additional equipment and production facilities. Changing the width of knitting is necessary when working with a thread that has a smooth surface, since when cutting the fabric, the weave structure will be violated and the knit will lose its strength properties.

Changing of required knitting width is easily adjustable on flat knitting machines or fully fashioned machine. In their work, a group of authors [12] described the production of weft carbon knitwear on flat knitting machines. Plain knitted fabric was used as the main weave.

However, the use of these fabrics as fibrous filler will not provide the necessary strength properties, since the weave is single and the front and back sides of knitwear can take a different load.

In IPMS of NAS of Ukraine, a weft-knitted fabrics to be produced on flat knitting machine has been developed, which allows to accept an equivalent load from both the front and the back sides. Along with the possibility of textile processing of high-strength carbon, glass, aramid and other threads, the developed technology for the production of weft knitted fabrics requires from 1 to 4 bobbins of threads for any width of the fabric.
These knitted fabrics can be used as unidirectional fillers, in which more than 85% of the fibers are located in one direction. PAN carbon fibers are used as weft threads, and high-strength glass or chemical fibers are used as warp. Due to this distribution of fibers, the composite polymer material is characterized by anisotropy of physical and mechanical properties in the direction of loads.

The principle of manufacturing of weft-knitted fabric (rib with a weft) is laying of straight weft threads in each row of stitches (Fig. 1).

In such knitwear, one of the threads is the thread of the main weaving, and the other thread is laid between the needle beds straightly, without knitting (Fig. 2). Also in the knitwear, the weft thread is laid out from 1 thread feed system, which makes it possible to clearly fix the weft thread in the structure of the knitwear. This fixation is more reliable and allows to get a fabric with high performance properties.

For the production of these fabrics upgraded flat knitting machine was used. This type of equipment allows to process fragile threads (with a large number of elementary fibers) or threads of large diameter that cannot be formed into a loop. By using of this method, it is possible to obtain a combined filler and hybrid composites reinforced by it, in which various filaments can be combined, for example, carbon and glass, carbon and aramid, carbon and carbon, glass and aramid and others (Fig. 3.4). The service properties of weft knitted fabrics are presented in Table 1.
Table 1. Characteristics of carbon weft knitted fabrics

| Fabrics        | Fiber content, % | Density of knitting (10 cm) | Thickness, mm | Density, g/sm³ | Tensile strength, GPa | Elongation in the direction of weft, % |
|----------------|------------------|-----------------------------|---------------|---------------|----------------------|----------------------------------------|
|                | Number of columns | Number of rows              |               |               |                      |                                        |
| warp Ural 100 (100 tex) | 30±2             | 54                          | 23            | 1,2-1,3       | 638                  | 21-23                                  | 3-3,6                                  |
| weft Tenax (830 tex)    | 70±2             |                             |               |               |                      |                                        |                                        |

The properties of multifunctional polymer composite materials reinforced by weft-knitted fabrics depend on the composition, content of weft and warp fibers (Table 2). So, for structural composites it is possible to use weft-knitted fabrics with a high-strength carbon fiber content of up to 95% and reinforcement scheme where the most part of the high-strength fibers are located in the direction of mechanical load.

Table 2. Properties of unidirectional carbon plastic

| №  | Carbon fiber content, % | Density, g/cm3 | Breaking force, N | Tensile strength, MPa |
|----|-------------------------|---------------|-------------------|-----------------------|
| 1  | 75                      | 1,39 – 1,45   | 54800-74380       | 767-987               |
| 2  | 95                      | 1,40 – 1,51   | 88300 - 99000     | 1014-1157             |

Carbon fibers are characterized by not only the complex of high physical and mechanical properties and low specific gravity, but also by increased values of electrical and thermal conductivity, which make it possible to create functional materials on their basis. The development of polymer based composites for structural purposes with predetermined functional properties requires ensuring the necessary level of materials functional properties without reducing their physical, mechanical and operational characteristics. For modern technical purposes the relevant functional properties are electrical conductivity, shielding and absorption of electromagnetic radiation in the microwave range. The electrical resistivity of the polymer based composite materials and the electrical conductivity of the knitted fibrous fillers are presented in Table 3 and Table 4.

Table 3. Electrical resistivity of polymer based composite materials

| Material                     | Longitudinal electrical resistivity \( \rho_x \) | Transverse electrical resistivity \( \rho_y \) |
|------------------------------|-----------------------------------------------|---------------------------------------------|
|                              | Value, \( 10^{-6} \) Ω·m                         | Value, \( 10^{-6} \) Ω·m                    | Variation, % | Variation, % |                                |
| ToxoTenax - Ural 100 [0/0]   | 535,0                                         | 71,2                                        | 27,6         | 9,2          |                                |
| ToxoTenax - Ural 1000 [0/0/90/90] | 199,4                                        | 99,8                                        | 35,2         | 11,2         |                                |

Table 4. Mean value of round electrical conductivity of carbon weft-knitted fabric

| Material                     | Electrical conductivity, ohm-meter (Ω·m) |
|------------------------------|------------------------------------------|
| Toho Tenax (400 tex) - Ural 100 tex | 1,76·10⁻³                                 |
| Toho Tenax (2 x 400 tex) - Ural 100 tex | 1,08·10⁻³                                 |
The development of combined carbon fiber-glass fibers fabrics makes it possible to use them as a heating element for the voltage of 24V-36V, for example, for anti-icing systems. The introduction of metal filaments into the composition of the filler essentially increases the electrical conductivity of the composites (Fig. 5,6). The electrical conductivity of knitted fabrics, depending on the direction of high-strength carbon fibers (weft), shows the anisotropy of electrical conductivity along high-strength fibers in comparison with a row direction.

![Fig. 5. Weft-knitted fabrics with copper wires](image)

![Fig. 6. Rib 1 + 1 with copper wires](image)

The increasing using of polymer based composite materials in aerospace engineering and other fields requires enhancing reliability of structures, so the problem of monitoring the state of structures (SHM technology - structural health monitoring) becomes very actual. One of the most promising is the using of fiber optic sensors as part of monitoring system. The production technology of such materials is based on the introduction of fiber optic components into the composite structure at the manufacturing stage. It is a complicated technological process, which includes the direct introduction of various elements and sensor control systems into the filler. One of the solutions of the problem of introduction of optical fiber and its uniform arrangement in the composite may be the development of a new type of filler with the infiltrating of optical fiber with a weft thread with a certain step (Fig. 7)

![Fig. 7. Carbon weft knitwear with optical cable](image)

![Fig. 8. Carbon knitwear with optical cable in the plastic](image)

The development of polymer based composite materials with a certain level of absorption of microwave electromagnetic waves which contain carbon and glass fibers makes it possible to use the electrically conductive properties of carbon fibers and the dielectric properties of glass fibers. Such a textile filler has a certain structure that can shield and/or absorb the energy of electromagnetic waves in a given frequency range.
The results of determining the shielding properties of polymer composites reinforced by carbon weft-knitted fabrics showed the possibility of their using as shielding materials with the ability to absorb electromagnetic radiation (Table 5).

**Table 5.** Electro-physical properties of knitted fabrics

| Knitted fabric                  | Volume resistivity, Ohm | Surface resistivity, Ohm • cm | Shielding from electromagnetic radiation in the range of 5,6-8,0 GHz |
|---------------------------------|-------------------------|--------------------------------|---------------------------------------------------------------|
|                                 | lengthwise | crosswise | lengthwise | crosswise | reflection, % | absorption, % | passing % | screening coefficient |
| Carbon + Polyamide              | 26,2        | 6,41      | 5,76       | 1,41      | 63            | 37             | -         | 1,0 |
| Carbon                          | 1,81        | 2,67      | 0,63       | 0,93      | 79            | 21             | -         | 1,0 |
| Weft-knitted carbon fabric      | 2,19        | 1,88      | 0,78       | 0,67      | 68            | 32             | -         | 1,0 |
|                                 | 1,99        | 1,66      | 0,44       | 0,36      | 74            | 26             | -         | 1,0 |
|                                 | 4,70        | 1,48      | 1,41       | 0,44      | 66            | 34             | -         | 1,0 |
| Carbon + Organic                | 14,65       | 7,36      | 3,15       | 1,58      | 64            | 30             | 6         | 0,94 |
| Carbon knitwear from “Ural” threads | 4,19        | 2,53      | 0,82       | 0,49      | 80            | 20             | -         | 1,0 |

Another advantage of weft-knitted fabrics over woven fabrics is their high elasticity and extensibility. Such canvases can wrap objects of various shapes with virtually no wrinkling (Fig. 10-11).
Thus, the development of new types of filler makes it possible to create the polymer based composites reinforced by carbon fibers with wide possibilities of functional properties and the following advantages in comparison with classical materials:

1. production of polymer based composite materials with a fibrous filler with high physical and mechanical properties;
2. the possibility of production of combined knitted fabrics for functional composites from various types of raw materials without the problem of equipment refueling;
3. the production of knitted fabrics with adjustable structure and electrical conductivity for using as a heating element;
4. the production of a textile filler which is able to shield and / or absorb the energy of electromagnetic waves in a given frequency range.

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