Influence of modes of washing-out of the polyvinyl acetate-based substrate on the properties of carbon fiber reinforced plastics obtained by TFP

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Abstract. The article shows the advantage of using water-soluble polyvinyl acetate-based non-woven fabric as a substrate in the manufacture of TFP preforms of products made from polymer composite materials, including gas turbine engine blades. As compared with the applied woven materials, elastomers and films, water-soluble non-woven fabric is easily removed from the surface of the semi-finished product without disturbing its structure and without causing damage to the fibers. It has been established that high-quality washing-out of the substrate does not affect the properties of carbon fiber-reinforced plastics.

1. Introduction
Currently, carbon fiber-reinforced plastics based on volume-reinforced preforms created by TFP (Tailored fiber placement) technology [1-4] are more and more common in the manufacture of products from polymer composite materials (PCM), as they can withstand multiaxial loads, unlike traditional textile materials.
The TFP process is about the directional laying of the roving on the base layer (substrate) using a piercing zigzag stitch consisting of a system of upper and lower threads (Fig. 1) [5]. The three-dimensional structure of the semi-finished products is created by introducing a third direction of reinforcement: each subsequent layer of fibers is attached to each other with piercing threads (polyamide, aramid, etc.) in the process of creating the preform.

Figure 1. Layout view of the TFP preform [5]
As a rule, the base carrier layer is an auxiliary material to be removed from the finished composite part at the stage of production of dry preforms or at the impregnation stage. At present, flexible elastomer sheets (in particular, rubber sheets) [6], woven reinforcing materials (carbon and glass fabrics), and separation thermoplastic films [7-10] are used as such a base for roving. The use of reinforcing fabric as the main layer leads to loss of bearing capacity and deterioration of the mechanical properties of the finished product. This is due to the partial destruction of the reinforcing fibers in connection with the penetration of the needle into the tissue structure [11]. Moreover, when separating any sewn base, there is a major risk of damage and configuration changes of the fibrous semi-finished product.

Earlier [12, 13], we used a water-soluble polyvinyl acetate-based non-woven fabric as a substrate in the manufacture of preforms. However, we did not study the effect of the substrate on the properties of carbon fiber-reinforced plastics in detail. Despite the advantages of water-soluble non-woven fabric, there are no indications of its widespread use for the manufacture of preforms in the literature. Thus, this study is a development of the previous studies [12, 13], and is devoted to the influence of technological modes of washing-out of water-soluble non-woven fabric on the microstructure, weight and strength properties of samples of sewed carbon fiber-reinforced plastics.

2. Materials and methods

Preform samples were obtained on a JCW 0100-500 numerically controlled embroidery machine (ZSK Stickmaschinen GmbH, Germany).

Preforms of planar sample of sewed carbon fiber-reinforced plastics with dimensions of 40x20x4 mm with reinforcement scheme [0°, +45°, 90°, -45°] N and model samples of gas turbine engine (GTE) compressor blades were made on the basis of HTS 45 carbon fiber (TohoTenax®, Japan) and Rusar-S piercing fixing thread (Thermotex LLC, Mytishchi, Russia). A water-soluble polyvinyl acetate-based non-woven fabric (Aurora, China), 40 μm in thickness, was used as a support layer (substrate). Planar samples consisting of 8 layers were sewn onto a substrate in one technological operation. The preform samples of the GTE compressor blades had identical characteristics (size, weight, laying, sewing parameters), and their component blocks were cut separately from the common substrate with the same outsize to ensure the same substrate material content in all tested samples. Each preform of the experimental blades consisted of 12 separate blocks sewn onto the substrate. These blocks were subsequently laid out on top of each other to obtain the final design of the semi-finished product. After manufacturing the preforms, their weight together with the substrate was determined. Next, the preforms were put in the water for a period of 1 to 15 minutes in the temperature range from 20 to 100 °C to remove the substrate. The washing-out quality of the substrate was evaluated visually. Then the preforms were dried and their weight was re-determined.

After drying, the preforms were used to produce samples of planar carbon fiber-reinforced plastics and GTE blades using vacuum molding technique.

Araldite LY-556 epoxy resin (Huntsman, Switzerland) was used as a binder. Isomethyltetrahydrophthalic anhydride (i-MTHFA) (90 mph) (Triune Chemicals Materials (TCM), China) served as a hardener, and 2-methylimidazole (0.2 mph) was an accelerator (Modifikator LLC, Tomsk, Russia).

The preforms were impregnated at a room temperature of 23 °C and a discharge of about -1 atm for 30 minutes. After impregnation, the samples were hardened for 4 hours at 110 °C without removing the discharge.

The samples with a length of 40 mm, a width of 20 mm and a thickness of 4 mm were cut from the hardened planar samples and GTE blades. For each type of material, the number of samples was at least 5.

The interlaminar shear strength τM in the reinforcement plane was determined using the short-beam method [14] on a Zwick Z100 universal testing machine (Zwick Roell, Switzerland). The loading speed was 10 mm/min, the distance L between the supports was 20 mm. The ultimate shear stress was determined by the formula:

\[
\tau_M = \frac{3}{4} \times \frac{F_{\text{max}}}{bh^2}
\]
where $F_{\text{max}}$ – load corresponding to destruction of the sample, $b$ – sample width, $h$ – sample thickness.

To study the microstructure of GTE blades based on tfp preforms with a substrate in the product and without a substrate (after it was washed out), we used a SkyScan 1172 tomograph (Bruker, Germany).

3. Results and their discussion

The influence of modes of washing out of the substrate from the fibrous structure of tfp preforms of GTE blades on their weight and quality are presented in Table 1.

**Table 1.** The influence of modes of washing out of the substrate on the properties of preforms obtained by stripping a carbon tow.

| Parameter                          | 1   | 2   | 3   | 4   | 5   |
|------------------------------------|-----|-----|-----|-----|-----|
|                                    | $T = 20\ ^\circ\text{C}$ | $T = 40\ ^\circ\text{C}$ | $T = 60\ ^\circ\text{C}$ | $T = 80\ ^\circ\text{C}$ | $T = 100\ ^\circ\text{C}$ |
|                                    | $\tau = 15\ \text{min}$ | $\tau = 10\ \text{min}$ | $\tau = 5\ \text{min}$ | $\tau = 3\ \text{min}$ | $\tau = 1\ \text{min}$ |
| Substrate dissolution time, s      | 43  | 36  | 21  | 10  | 4   |
| Substrate dissolution quality      | +   | +   | +   | +   | -   |
| Washing-out quality                | -   | +   | +   | +   | -   |
| Preform weight without a substrate, g | 33±0.1 | 33±0.1 | 33±0.1 | 33±0.1 | 33±0.1 |
| Preform weight after washing-out and drying, g | 33.65 | 33.15 | 33.13 | 33.10 | 33.67 |

Note: «+» - good-quality performance of operation, «-» – low-quality.

As the Table shows, the substrate dissolution time decline substantially with increasing temperature. Moreover, in almost all cases, we can obtain high-quality washing-out of the base layer. In this case, there is no change in the fibrous structure of the obtained preform, which remains flexible, indicating the absence of traces of polyvinyl acetate. It should be noted the substrate is not washed out in a qualitative manner at room temperature and short exposure times at 100 $^\circ\text{C}$. The preform remains rigid, i.e. dissolved polyvinyl acetate was not completely removed. Additional washing with running water also did not completely remove the polymer. Thus, based on results of testing of tfp preforms of the compressor blades, we can say that modes 2, 3, and 4 are suitable for washing-out of the water-soluble substrate with a water temperature range of $40 \div 80\ ^\circ\text{C}$ and an exposure time of $3 \div 10\ \text{min}$.

Mode 4 was chosen as the optimal mode of operation for washing-out of non-woven fabric from the blade preforms (or preforms of similar sizes), since less time is spent on washing-out, which is a significant advantage in the series production, ensuring considerable time saving.

Figure 2 shows the microstructure of the material of the GTE blades with the substrate washed out from the preform and without washing-out of the substrate, obtained on an X-ray tomograph. As Fig.2b) shows, those blades that are made on the basis of preforms without washing-out of the substrates demonstrate an increased content of the matrix between the layers, caused by the presence of the substrate, which is expressed by the increased distance between the reinforcing layers. Apparently, this kind of layer may be considered as a defect. In the case of materials with the washed out substrates, no layers enriched in the matrix are observed.
Figure 2. Tomogram of material of GTE blades based on tfp preforms without a substrate (a) and with a substrate (b)

Table 2 shows what influence the presence of the substrate in the structure of the material has on the strength characteristics of planar samples and samples of GTE blades, the preforms of which consist of several blocks of sewn semi-finished products, stacked on top of each other to form the desired thickness of the product.

When the substrate was washed out, the shear strength was 10–15% higher in the case of planar samples and 25–30% higher in the case of compressor blades.

| Parameter               | Planar samples | Compressor blades |
|-------------------------|----------------|-------------------|
| Production of a preform | without washing-out of the substrate | with washing-out of the substrate |
| Internal delaminations  | None           | None              | Present           | None           |
| Interlaminar shear strength $\tau_M$ in the reinforcement plane, MPa | 105            | 118               | 110               | 142            |

In the production of prefabricated preform structures in one technological operation, the substrate was below the preform, and was incommensurably small compared with the thickness of the entire preform. The presence of a substrate in the composition of planar semi-finished products had no effect on carbon fiber-reinforced plastics, since it completely dissolved in the PCM during polymerization. Therefore, it is not necessary to wash the substrate out of such preforms. In the production of compressor blade preforms consisting of separate sewn parts and subsequently stacked on top of each other, the number of non-woven fabric layers corresponded to the number of blocks, which led to an increase in the weight of the semi-finished product and the final product, as well as to internal delamination and reduction in the shear strength of the finished products. Therefore, washing out of the substrate is needed in the production of complex composite preforms.

4. Conclusion
It has been established that despite the fact that the polyvinyl acetate-based substrate dissolves in the volume of carbon fiber-reinforced plastics during their shaping in the mounting and does not have any function in the future, it increases the weight of the preforms and the weight of finished products. In
addition, the substrate presence in the composite preform leads to such structural defects of the finished products as delamination, which reduces the interlayer strength in the reinforcement plane. Thus, it is recommended to remove non-woven fabric (wash out) from the preforms.

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