ON THE EFFECT OF INTERMEDIATE PRESSING OF PREFORMS ON THE FORMATION OF A DEFECT-FREE STRUCTURE OF FINISHED PRODUCTS FROM CARBON FIBER-FILLED POLYTETRAFLUOROETHYLENE

Assoc. Prof. Voropaev V.V. PhD[1], Assoc. Prof. Skaskevich A.A. PhD[1], Senior lecturer Lesun A.N.[1],
Assoc. Prof. Sarokin V.G.[1], PhD Yankov E.[2]
Yanka Kupala State University of Grodno, Belarus[1]
E-mail: voropaev_vv@grsu.by, askas@grsu.by, lesun_an@grsu.by, sorvg63@mail.ru
University of Ruse 3 – Bulgaria[2]
E-mail: eyankov@uni-ruse.bg

Abstract: *This article describes a method for producing composite materials based on polytetrafluoroethylene with high performance properties. One of the obstacles to achieve this result had been the accumulation of moisture in the semi-finished product, which subsequently led to the appearance of defects in products made of fluorine composites. It is proposed to produce semi-finished preforms under reduced specific pressure, in which the moisture content is easier, cheaper and more efficient to control than with the current technological regulations. It is shown that the use of these semi-finished preforms allows getting almost defect-free products with high performance characteristics.*

Keywords: *INTERMEDIATE PRESSING, POLYTETRAFLUOROETHYLENE, CARBON FIBER, PREFORM, APPARENT DENSITY, MOISTURE, PORES*

1. Introduction

Gas compressors operating without the use of lubricant are applied in all industries where according to the requirements of the technology pure gas without lubricant impurities is required. In the vast majority of cases such compressors have an expensive, complex and material-intensive design, in which the seals occupy only a small part. Despite the relatively small specific gravity of the sealing elements in the cost of compressors, the resource, uninterrupted and safety operation of the whole mechanism largely depend on their properties.

The desire to obtain a sealing material with high strength and tribotechnical characteristics has led to widespread use of composite materials based on polytetrafluoroethylene (PTFE) with carbon fiber fillers in the design of compressor assemblies without lubricants.

2. Prerequisites and means for solving the problem

The foundations of the manufacturing technology of composite materials based on PTFE were developed in the 1960s, and the production of fluorocomposites with carbon fiber fillers has been actively developing since the 1980s. Among the post-Soviet countries the most wide known antifriction material with the commercial name is “Flubon”. Sirenko [1] has defined it as a polymer composite material based on polytetrafluoroethylene, copolymers of ethylene and tetrafluoroethylene and other fluorinated polymers, modified carbon fibers and other fibrous and dispersed fillers [1]. Since practically all currently known composite materials based on polytetrafluoroethylene with carbon fiber fillers fall under this description, regardless of the technology of their production and the exact composition, then in the future for the purposes of this article we will talk about Flubon and its analogues.

According to [2], the production technology of composite materials like “Flubon” consists of the following stages:

1) preparation of a semi-finished composite material, including operations of shredding of a carbon tape to a powder state with regulated apparent density and mixing the obtained product with other components of the composite;

2) disposal of moisture from the semi-finished composite material;

3) pressing of workpieces;

4) heat treatment of workpieces by volumetric heating in an electric furnace.

Changing the parameters of the technological process’ stages we can affect the performance characteristics of PTFE-based composite materials. There are several methods that improve the performance characteristics of materials like "Flubon", which can be used at the stage of preparation of the semi-finished composite material: mechanical activation of a semi-finished product on rubber-processing rollers [3], mixing the ingredients in a bladed mixer with modernized blades (choppers) [4], plasma-chemical modification of the carbon filler in order to form on its surface a layer of fluoropolymer some dozens of nanometers thick [5].

The authors [6] submit that at least two principally different approaches are possible at the heat treatment stage: free sintering, which is traditional, and sintering under conditions of limitation the volume of thermal expansion at the stage of transition of PTFE into a viscous-flow state.

At the same time researchers pay relatively little attention to the development of pressing methods that can effectively influence the performance characteristics of manufactured PTFE-based composite materials, although this operation is one of the most capital-intensive and has a significant impact on the performance characteristics of future products. The authors [7] have proposed a pressing method assuming the combination of this operation with the impact of ultrasonic on the semi-finished composite, however, the obtained values of strength and tribotechnical characteristics are inferior to materials that are already available on the market. Thus, the task to modernize the pressing operation in the manufacturing process of composite materials like “Flubon” remains urgent.

The complexity of the task is that the semi-finished PTFE-based composite material with carbon fiber fillers is hard to press due to poor adhesion between particles of polymer and filler. Moreover, compressibility worsens with the rise of the filler content in the composition and the size of its particles. In addition, the carbon fiber is a hygroscopic filler and is capable to adsorb up to 7 massive percent of moisture from the air, which must be removed from the semi-finished composite material through a drying operation in the technological process. At the same time, the discrete nature of the technological process often makes senseless the energy-intensive drying operation, since the prepared semi-finished composite material often waits pressing from several hours to several days, accumulating moisture from the air again. As a result, in the future the absorbed water is stored in the volume of a workpiece during pressing operation, creating additional obstacles for obtaining the defect-free composite. Thus, favorable conditions are created for appearance of pores or even cracks in the workpieces at high temperatures of heat treatment due to evaporation of the moisture contained in the workpiece. Naturally, this adversely affects the performance characteristics of the composite material. Billets of products are obtained with low density and insufficient strength characteristics.

Attempts to use non-hygroscopic trademarks of carbon filler also led to poor strength characteristics of products. The reason is that as non-hygroscopic carbon filler graphitized carbon fibers with a high class of heat treatment (1900–2200 Cº) were used. This type of carbon fiber has a dominating fraction size of less than 50 microns after shredding (more than 90 massive percent of filler), therefore filler has not a reinforcing effect.

3. Solution of the examined problem

The possibility to modernize the pressing operation in the technological process of composite materials based on PTFE filled with discrete carbon fibers was studied. During the study a method was developed that involved an operation of preliminary pressing of semi-finished preforms at specific pressure of 5-20 MPa, which later allowed to produce low-porous workpieces with a percentage of fillers of 20–35 massive percent.

The proposed options for the pressing operation are as follows (Fig. 1):

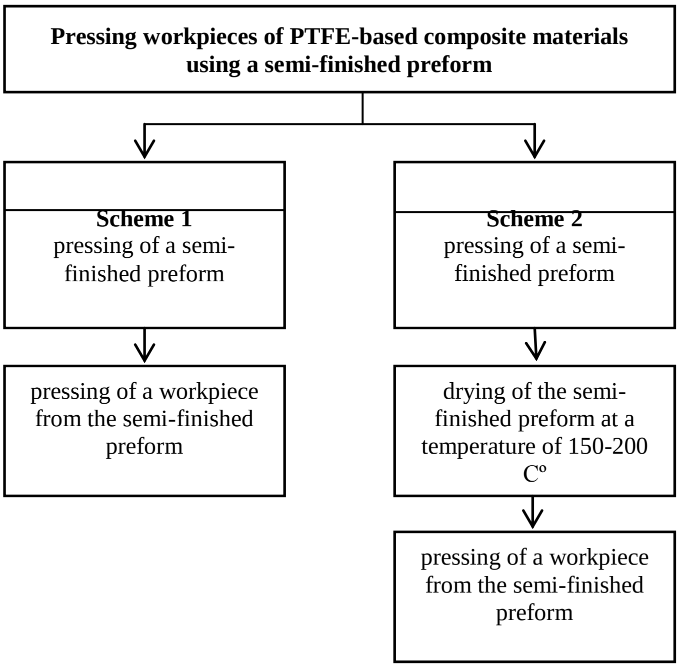


Fig. 1 *– Schemes for pressing workpieces of PTFE-based composite materials using the step of obtaining a semi-finished preform*

The semi-finished product obtained as a result of the intermediate pressing operation is a highly porous semi-finished preform. The semi-finished preform is also much lighter and larger than a workpiece of similar mass obtained by traditional pressing mode (see Fig. 2).

a b

Fig. 2 *– The appearance of the preforms of products from PTFE-based composite materials: a) semi-finished preform; b) finished workpiece*

The high porosity of the semi-finished preform allows the moisture enclosed in the volume of the workpiece to get out in the external environment during due to evaporation when storing. But it is much faster and more reliable to remove moisture from the semi-finished preform by drying the workpiece at a temperature of 150–200 Cº. This is due to the fact that at the drying temperature a guaranteed removal of moisture from the semi-finished preform occurs via intensive vaporization. Unlike this, removal of moisture is difficult at sintering of workpieces, pressed at specific pressure of 60-80 MPa in accordance with the requirements of the existing technical regulations of the manufacturers of composite materials based on PTFE filled with discrete carbon fibers, due to isolation of carbon fibers in polymer matrix.

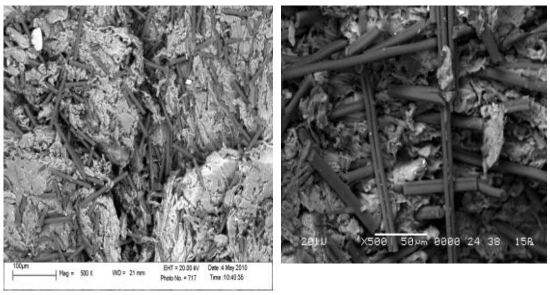
The moisture absorption measurements of the semi-finished preforms show that the semi-finished preform absorbs more than 99% all possible moisture from the air during the first 5 hours after drying. At the same time, the increase in the specific pressure of pressing semi-finished products from 5 to 20 MPa slows down the rate of moisture absorption after drying by only 0.2%, and the absolute humidity of the semi-finished preform 24 hours after drying in both cases was 1.79%, which corresponds to the initial level. Such results mean that it is necessary to perform the operation of finishing pressing the preform at specific pressure of 60-80 MPa immediately after drying of the semi-finished preforms, or repeat drying when the semi-finished preforms wait finishing pressing more than 1-2 hours.

To make possible longer breaks in the technological process, the following operation was proposed. After drying, the semi-finished preforms were dipped in industrial oil to obtain a moisture-proof film that prevents re-absorption of moisture. It has been proven that treating the semi-finished preforms with industrial oil after drying reduces moisture absorption, since their absolute humidity 24 hours after drying was only 0.3%. Moreover, it turned out that at the same absolute humidity the oil consumption for semi-finished preforms obtained at specific pressure of 20 MPa is two times lower than for semi-finished preforms obtained at specific pressure of 5 MPa. It follows from this that it is desirable to obtain semi-finished preforms at a lower pressure without using an operation of treatment in industrial oil, and at a higher pressure – using such an operation, since this will lead to a reduction in energy costs in the first case and oil costs decrease – in the second case.

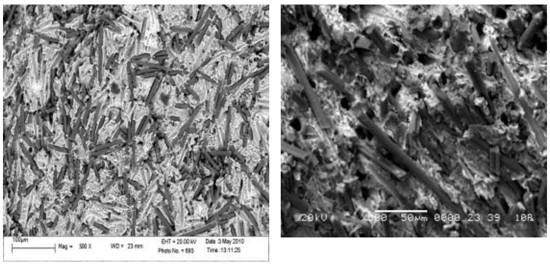
Thus, the introduction of an intermediate pressing of semi-finished preforms followed by drying and processing in industrial oil can significantly increase the interoperational storage period in the technological process and reduce the negative effect of absorbed moisture on the performance characteristics of PTFE-based composite materials.

4. Results and discussion

The effect of intermediate pressing on the internal structure of preforms and finished PTFE-based composite materials was evaluated by SEM images of the surface of fragments, which had been obtained through chipping of samples after liquid nitrogen exposure (Fig. 3):



workpiece before sintering (scale x500)



Workpiece obtained without intermediate pressing operation

Workpiece obtained from the semi-finished preforms workpiece after sintering (scale x500)

Fig. 3 *– Surface morphology of samples' fragments of PTFE-based composite materials with various pressing methods*

Analyzing the results of scanning electron microscopy we can conclude that, when using intermediate pressing, the number of regions with an uneven distribution of filler particles in the polymer matrix is significantly reduced. We can also observe an increase of the contact area between the polymer and individual filler particles. Thus, the introduction of intermediate pressing operation into the technological process of obtaining PTFE-based composite materials leads to the formation of a more homogeneous structure in comparison with existing technical regulations of the manufacturers of composite materials based on PTFE filled with discrete carbon fibers.

The influence of intermediate pressing on obtaining the defect-free PTFE-based composite materials also was determined by the apparent density according to existing standards.

Fig. 4 presents a comparison of the apparent density of the semi-finished preforms for PTFE-based composite materials with different contents of carbon fiber filler and different pressing schemes.

As can be seen from Fig. 4, the apparent density of workpieces of PTFE-based composite materials obtained by the traditional method is less and decreases faster as the filler content increases in comparison with the proposed workpieces' pressing schemes. Despite the continued decrease in density with increasing filler content, schemes of pressing using the semi-finished preform allow material characteristics to be more predictable, without drastic changes in apparent density with the increase of filler content from 20 to 30% of the mass.

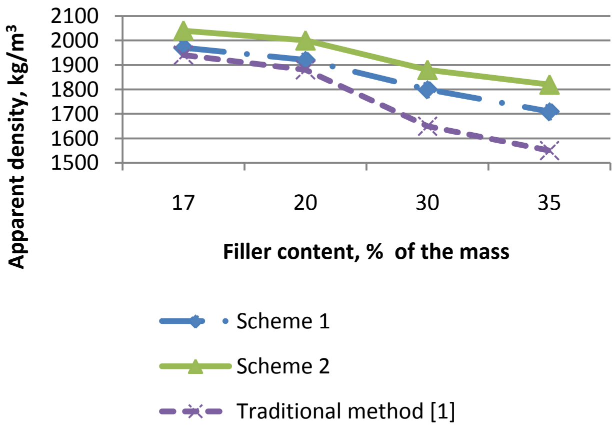


Fig. 4 *- Dependence of the apparent density of workpieces of PTFE-based composite materials on the pressing method and the filler content*

We've also considered the effect of the proposed pressing schemes on the apparent density of PTFE-based composite materials after heat treatment. Fig. 5 shows that the apparent density of the finished PTFE-based composite materials is less than the apparent density of the workpieces they were made from. However, the number of pores in products obtained using the intermediate pressing operation is still less than when using pressing technology in accordance with the requirements of the existing technical regulations. Moreover, with an increase in the filler content in the composite over 20% of the mass. the operation has an even greater positive effect on the creation of a defect-free internal structure of products than with a small amount of filler.

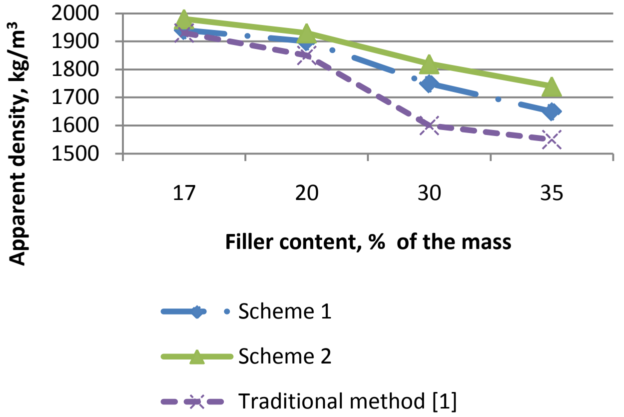


Fig. 5 *- Dependence of the apparent density of finished PTFE-based composite materials on the pressing method and filler content*

It is also curious to note that the dependence of the apparent density of workpieces of PTFE-based composite materials on the pressing method and the filler content (Fig. 4) is practically equal the graphs presented in Fig. 5.

5. Cunclusion

Summarizing, we can conclude that pressing workpieces of PTFE-based composite materials using a semi-finished preform (Fig. 1) allow us to obtain products with a higher apparent density in comparison with the traditional method of pressing. This indicates a decrease in the number of pores and, as a consequence, defectiveness in products made of composite materials based on PTFE when using the intermediate pressing operation.

The developed pressing methods lead to the increase of the contact area between the polymer and individual filler particles and thereby enable the use of coarse fraction carbon fiber as a filler. Consequently it becomes possible to realize a high tensile strength innate to carbon fiber. At the same time, preliminary tests show that the tensile strength of the PTFE-based composite materials filled with discrete carbon fibers demonstrates the potential to achieve the tensile strength of the matrix material even with a filler content of 30% by weight, which is impossible under existing technical regulations. The compressive strength at 10% deformation of such materials reaches values from 45 to 50 MPa. The wear rate of PTFE-based composite materials obtained by pressing through the use of a semi-finished preform is also relatively low and ranges from 1.0 to 2.5 × 10^{-7} mm^3 / N×m.

In addition, the proposed pressing scheme (scheme 2 in Fig. 1) is energy-saving, since drying is not required during the heat treatment of preforms, and the exposure time of the semi-finished preform at a temperature of 150-200 Cº is significantly less than the duration of the drying stage in the traditional scheme of sintering workpieces.

Pressing schemes (Fig. 1) are easy to implement and do not require special equipment or expensive additional tooling. Their implementation the by enterprises engaged in the manufacturing of PTFE-based composite materials can be carried out without significant costs and give tangible competitive advantages to both the enterprises themselves and their consumers as well.

6. References

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