Sustainable Ways and Methods of Recycling Epoxy Fiberglass Waste

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Abstract. This article presents two technological ways of recycling the wastes of the production and application of products made of highly oriented fiberglass bound by the epoxy matrix. The first technology is aimed at shredding the epoxy-based products obtained by pultrusion to create fine and ultrafine powders (up to 2-10 microns) used as fillers in various composites. The second technology offers a way to obtain coarse powders with a particle size of up to 100 microns, used in the composition of heat-insulating materials and fire-retardant intumescent coatings. Proposed is the mechanical grinding of fiberglass to a finely dispersed state with subsequent heating to a temperature of 400 °C in the presence of a foaming coke and liquid glass. This technology allows the full utilization of waste from the production and application of epoxy fiberglass, such as windmill blades and parts of molded products, leading to the creation of an environmentally friendly fire-resistant and heat-insulating material in the form of plates, blocks and other products with operation temperature up to 400°C, as well as fire retardant coatings for building materials and structures. By varying the content of the foaming agent and soluble glass in the composition of the intumescent mixture, one can regulate the average density, thermal conductivity and strength of the material within significant limits, achieving characteristics that exceed those of traditional heat-insulating materials. The proposed material based on recycled epoxy fiberglass is inflammable and resistant to unfavorable environmental impacts; it has high biostability and provides heat and mass transfer during the operation in buildings and structures.

1. Introduction
The concept of sustainable development (CSD), the best available technologies (BAT), circular economy, the Fourth industrial revolution - these are the main directions of the ecological, economic and social development of mankind, in its desire to prevent (or at least slow down) the global destruction of nature and humanity. In the UN formulation, the meaning of CSD is as follows: “We do not inherit the Earth from our ancestors; we borrow it from our children". One of the most concerning environmental threats is the contamination of land and the oceans with polymer materials [1]. For a long time now, plastics have surpassed all other artificial materials in the total amount of production and consumption, although there is no reliable information on the total volumes of plastics produced since their development and their location after the end of the service life. Some estimations [2] say
that by the year 2015 around 8.3 billion tons of polymeric materials were produced all over the world and about 6.3 billion tons of plastic waste were formed, 9% of which were recycled, 12% burned, and 79% deposited in different ways. And if this tendency of plastic waste generation and management remains, then by 2050 about 12 billion tons of plastic waste will be disposed of in landfills or end up in the natural environment. On the other hand, "the existence of our technically advanced civilization is no longer possible without the use of plastics. In 2018, about 360 million tons of them were produced, from clothes to cars, from a bath to an airplane, from food packaging to toys and a bulletproof vest - today no industry is unthinkable without the unique properties of plastics" [1].

New high-tech, more efficient polymeric materials with properties unseen before are being intensively developed and introduced. At the same time, the composition of polymeric materials becomes more complicated, providing a variety of properties preset by consumers. This increases the technical complexity of utilization of industrial waste and polymer products that have finished their service life. Whereas the secondary processing of thermoplastic polymer materials into products of the "second grade" can be economically feasible even considering their expectedly lower physical and technical characteristics (due to aging during their primary operation and destruction during recycling), thermoset waste materials have certain limitations - it is impossible to remelt and recycle them into other products.

However, the founder and President of the Davos World Economic Forum, Klaus Schwab, author of a guidebook for meeting the "imminent" future "Fourth Industrial Revolution", puts high hopes in a new class of recyclable thermoset polymers called polyhexohydrotriacins. Their application, in his opinion, is an important step towards the creation of a circular economy (economy of a closed cycle), which is self-healing in nature [3]. At the same time, it is hard to believe that one new class of polymers will be able to provide the whole variety of technical properties that composite materials have, considering the wide range of the existing thermosetting binders, and, in particular, the outstanding characteristics of high-strength fiber-reinforced composites based on epoxy oligomers [4].

Highly oriented epoxy composites of cold and hot curing - glass, basalt and carbon fiber reinforced plastics (FRP) - are used both for the manufacturing of highly stressed structures, such as blades of wind turbines, and pultruded molded products (e.g., pipes, channel bars, I-beams, rebars, etc.), intended for the assembly of spatial building structures and reinforcement of cement concrete. In the course of their production, technological waste is generated in the form of substandard products. Besides, during dismantling of composite structures at the end of their life cycle, scrap is collected that needs to be disposed.

Thermosetting plastics are infusible and insoluble (except for the destruction in strong oxidants - concentrated sulfuric or nitric acids, etc.). Therefore, it is expedient to either incinerate their waste, obtaining heat and slags, which also require disposal, or grind them using the resulting powders as fillers in various composites based on polymer or inorganic matrices (binders). Other technologies such as solvolysis, high voltage pulse fragmentation, pyrolysis and fluidized bed method are also being developed, which provide the industry with additional options for handling composite materials when they reach end-of-use [5].

Undoubtedly, the approach involving the application of the ground polymer waste as a filler for composite materials of construction purposes is the most preferable from an environmental point of view, given the large capacity and long service life of building structures.

The first stage of various technologies for the recycling of the epoxy fiberglass is grinding of the industrial composite waste and products that reached the end of their service life. Considering the high strength and hardness of epoxy fiberglass, the process of grinding is energy-intensive and multi-stage: from breaking down the composite material to continuously reducing the particle size through shredding, crushing, milling, or other similar mechanical process. The resulting scrap pieces can then be segregated, by using sieves and cyclones, into powdered products (rich in resin) and fibrous products (rich in fibers) [6, 7].
2. Materials and methods
This article suggests two technologies for grinding of products made of highly oriented fiberglass plastics. The first technology allows the production of fine and ultrafine powders (up to 2-10 microns) from the profile molded fiberglass epoxy-based products, obtained by pultrusion, which will later be used as fillers in various composites. The second technology is designed for the production of coarse powders (up to 0.1 mm) used in thermal insulation materials and fire-retardant intumescent coatings.

The raw material for the first technology was manufactured by Tetneft-Presscomposite Ltd and consisted of pipes and I-beams obtained by pultrusion. The dimensions of the samples were 250x250x300 mm and the wall thickness reached 20 mm. Equipment and technology for crushing of these waste products were developed by UltraMol Ltd.

The technological difficulties of crushing and fine grinding of raw materials (scraps) were determined by the following factors: large initial dimensions, complex shape and large wall thickness, high hardness and abrasiveness of the crushed material due to the properties of glass fiber filler, the content of which reached 80%.

Stages of processing:
1. Shredding up to 20 mm fraction. A two-shaft shredder with trapezoidal bits on the shafts and a pressure plate was used. The rotation speed of the shafts (100 rpm) and the simultaneous action of the pressure plate ensured the gradual separation of material pieces.
2. Crushing to fractions of 2-3 mm was carried out on a rotary single-shaft knife crusher with a 5 mm mesh and a rotor speed of 800 rpm.
3. The stage of grinding to a fraction of less than 20 microns was carried out by the representatives of UltraMol Ltd on a hammer-impact rotor-vortex mill MMU-460, designed for fine and ultrafine grinding of brittle materials (Figure 1). The material was exposed to consecutive processing in two stages: the first is coarse grinding with hammer-blades; the second is grinding by creating turbulent flows of a dust-gas mixture in the tail of the hammer-blades. This mill shows the highest efficiency in the size range of 20-60 micrometers, while the input particle size can be up to 5-10 mm. The mill is equipped with a built-in aerodynamic classifier, which ensures the specified particle size at the exit from the grinder.

3. Results and discussion
In the course of the experiments on grinding of fiberglass waste produced by Tatneft-Presscomposite Ltd, the fundamental possibility of these materials destruction to fractions less than 10 microns was acknowledged. Besides, the preliminary grinding modes were determined, as well as the main technological equipment and the features of its operation for the processing of high-strength polymer composites waste (Table 1).
Table 1. Characteristics of the process of fine grinding on the MMU-460 installation

| No | Material                  | Resulting fraction | Grinding temperature | Rotor speed, chopper / separator | Productivity |
|----|---------------------------|--------------------|----------------------|---------------------------------|--------------|
| 1  | Pultruded products waste | 10-50 micron       | 97-108°C             | 5800/3000 rpm                   | 41 kg/h      |
| 2  | Pultruded products waste | 2-10 micron        | 130-137°C            | 5800/5000 rpm                   | 35 kg/h      |
| 3  | Pipe waste                | 10-50 micron       | 105-110°C            | 5800/3000 rpm                   | 37 kg/h      |
| 4  | Pipe waste                | 2-10 micron        | 133-150°C            | 5800/5000 rpm                   | 27 kg/h      |

Analysis of the results of fiberglass waste fine grinding revealed the following features that should be considered while improving equipment and carrying out the economic assessment of the technology:
- high heating of products (up to 150°C);
- high abrasive wear of the stator and rotor-swirler;
- increase in abrasive wear of the working bodies of the mill when the particle size is less than 60 microns;
- the high volatility of obtained powders makes the sanitary requirements for the personnel working conditions more stringent;
- the density of the crushed material affects the productivity of grinding;
- to obtain ultrafine fiberglass powders, it is necessary to use special materials for lining of the grinding zone.

Although the technical efficiency of powders as modifying fillers of composite materials increases with an increase in their dispersion level [8, 9], high energy consumption of grinding process limits this desire and forces one to seek equally effective use of coarsely ground materials.

In European practice, one of the potential applications of mechanically recycled FRP involves partial replacement of coarse aggregates in concrete and mortars with waste products [10]. However, the few investigations performed on this topic suggested that recycled FRP fillers did not notably affect the durability of cementitious materials, but significantly reduced their mechanical properties [11].

A technology presented in this article describes the way to use coarsely dispersed waste materials as fillers for compositions of fire-resistant coatings and thermal insulation materials of building structures, in which the epoxy fiberglass powder is pyrolyzed to form coke. This application allows the recycling of windmill blades, which has been widely discussed in recent years due to the ever-growing number of elements that have reached their end-of-use and due to the tightening of legislation limiting their disposal in the landfill [12]. Currently, around 2.5 million tons of composite materials are used in the wind sector worldwide [13], and approximately 40-60 thousand tons of them will be out of service by the year 2023 (about 14 thousand pieces), according to the data presented by WindEurope organization [14].

Despite the fact that the processing of composite parts of wind turbines is a significant issue, it is important to understand that the amount of waste generated by this industry does not exceed 10% of the total number of thermosetting plastics requiring processing [5]. Therefore, it is necessary to develop versatile technologies that will allow the recycling of other products of the composite sector [15]. In this regard, this study also considers the possibility of using waste from the production of polymer-composite profiles obtained by pultrusion, such as glass and basalt-fiber reinforced rebars based on an epoxy binder (liquid dian resin hardener - iso-methyltetrahydrophthalic anhydride) to develop a heat-insulating and fire-retardant material.

The experiments were carried out on rods with a diameter of 8-12 mm, which were ground as follows: the cut off rods with a length of 15-20 mm were crushed in a jaw crusher with a working gap of 1 mm, then the resulting crumb was processed in a disc grinder with a gap of 0.1 mm between the discs. Photographs of crushing products of the first and second stages are shown in Figure 2.
Figure 2. Appearance of crushed samples of fiberglass rebar: a) after crushing in a jaw crusher, b) after grinding in a disk grinder

Researches are known [16, 17], where a fire-retardant epoxy-based coating was produced with ammonium polyphosphate in the content that worked as a foaming additive, which swelled due to gas formation in case of a sharp increase in the ambient temperature (e.g. during fire), and an epoxy polymer in a pyroplastic state that created a layer of protective foam material with a porous structure made of coke on the surface of building material.

By analogy with this technology, in order to create a porous heat-insulating and fire-protective material, it was proposed to mix fiberglass waste crushed to 100 microns with ammonium polyphosphate in a ratio of 85 and 15%, respectively, and subject it to sharp heating. Ammonium polyphosphate (NH₄PO₃)n is the main functional component of fire retardant paints and varnishes [18]. To establish the swelling temperature during the structural formation of the thermal insulation material, a thermogravimetric analysis of the mixture, including epoxy fiberglass powder and ammonium polyphosphate, was carried out (Figure 3).

Figure 3. The composition of fiberglass powder with ammonium polyphosphate: a) thermogravimetric curves of the composition; b) macrostructure of the composition obtained at a temperature of 360 °C at a 250-fold magnification

TGA and DTA curves show that the coke formation of the epoxy polymer begins at a temperature of 220 °C, and the thermal decomposition of ammonium polyphosphate is most intense at 360 °C (Figure 2a). However, the porosity and strength of the coke foam in the fired material are not sufficient to create a stable structure of the heat-insulating material (Figure 2b).

Therefore, in order to maintain the porosity and increase the strength of the heat-insulating material, soluble sodium glass was additionally introduced into the composition. It is known [18, 19] that fire retardant coatings on its basis, exposed to sharp heating, form a strong porous structure on the surface of a building structure, thus protecting it from fire.
The experiments showed that in the process of sharp heating, the composition with the addition of soluble glass increased in volume by a factor of 4 (Figure 4), leading to the creation of a solid porous material with an average density of 360 kg/m$^3$, thermal conductivity of 0.094 W/(m·K) and compressive strength of 3.2 MPa.

![Figure 4](image-url)

**Figure 4.** Sample of a composition based on finely ground composite rebars with ammonium polyphosphate and sodium glass: a) before heating, b) after swelling at a temperature of 360 °C

The relatively high strength of the porous composite was due to the dispersed reinforcement of its structure with the glass fiber of the pyrolyzed waste (Figure 5).

![Figure 5](image-url)

**Figure 5.** Macrostructure of the composition fired at a temperature of 360°C: a) general view of the fiberglass in the structure of the composition working as micro-reinforcement at 500-fold magnification, b) a fragment at 1000-fold magnification

X-ray microanalysis of the contact zone between the coke and glass fiber (Figure 6) showed the presence of the following elements: oxygen, phosphorus, aluminum, silicon, calcium, sulfur. Noted was the presence of carbon in the composition of the interfacial layer, which was formed due to the burnout of the epoxy resin. The presence of phosphorus is explained by the introduction of an expanding additive in the form of ammonium polyphosphate, and the presence of silicon is caused by the addition of liquid glass. The spectrum also contains aluminum atoms due to their diffusion from the mold that was used when heating the sample.
Figure 6. X-ray microanalysis of the contact zone between coke and glass fibre

4. Conclusions

Thus, the suggested technologies for grinding the production and application wastes of highly oriented fiberglass epoxy-based products make it possible to obtain both fine and ultrafine powders (up to 2-10 microns), used as fillers in various composites, and coarse powders with a particle size of up to 100 microns, used as a component of heat-insulating and fire-retardant intumescent coatings.

The proposed technology allows the full utilization of waste from the production and application of epoxy-based highly oriented plastics, including windmill blades, polymer-composite rebar and other epoxy fiberglass products, leading to the creation of an environmentally friendly fire-resistant and heat-insulating material in the form of plates, blocks and other products with operation temperature up to 400°C, that can also be used as coatings for the fire protection of structures made of steel, wood and plastics. The mechanical grinding of fiberglass plastics to a finely dispersed state, followed by heating to a temperature of 400 °C in the presence of a foaming agent and liquid glass, allows the production of heat-insulating compositions with an average density of 360 kg/m³, thermal conductivity of 0,094 W/(m·K) and compressive strength 3.2 MPa.

The proposed intumescent material is inflammable and resistant to unfavorable environmental impacts; it has high biostability and provides heat and mass transfer during the operation in buildings and structures. The developed waste-free technology meets the BAT criteria and the principles of a circular economy.

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