Recycling of glass fibers sheets from thermoset reinforced plastic using thermolysis method

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Abstract. This article presents research data on the process of recycling fiberglass reinforcing fillers from polymer composite materials. The analysis of the thermal stability of the polymer matrix is carried out. In this work, the thermolysis of fiberglass reinforced plastic based on E-glass and the epoxy vinyl ester binder was carried out at 400 °C. The influence of thermolysis time on the strength of composite materials based on regenerated reinforcing glass filler was studied. The PCM sample made of the filler obtained by 30-minute treatment at 400 °C and cooled in water withstands the bending load by 1.6 % lower than that of the primary material.

1. Introduction

The issue of recycling products from polymer composite materials (PCM) is agenda for the modern industry. According to various literary sources, the technology for the recycling of reinforcing fillers is limited to laboratory or pilot installations with a volume of up to 1 liter. Recycling processes are individual for each type of composite material.[1]

At the same time, the volume of production of polymer composites is increasing every year and on a global scale is hundreds of thousands of tons[2]. Currently, the world has tested three main methods of PCM utilization: physical, thermal and chemical. A detailed analysis of these methods is presented in the article.[3] Most of the methods presented consider the possibility of processing only homogeneous materials. In this case, the products can be presented in the form of a sandwich panels[4,5], hybrid materials[6], and also have embedded parts, which greatly complicates the process of their recycling.

Pyrolysis is the most common method for recycling of reinforced plastics[7]. Among the physical methods, the most widespread is mechanical. The main advantages of mechanical methods are the comparative simplicity of technological design, and the possibility of application for any PCM and polymers, the simultaneous processing of fibers and polymer binder, as well as the absence of harmful emissions and fumes. The disadvantages of the mechanical method include high energy consumption, the difficulty of regulating the size of the crushed plastics, a decrease in the mechanical properties of the shredded reinforced plastics and limited secondary use of recycled materials [8–12].

Research [13–15] presented chemical methods of PCM recycling based on macromolecular reactions occurring in a polymer binder. The fiber is one of the product of such process.
The extraction of the reinforcing filler from the binder matrix will solve the problem of the recycling, but also lead to obtain significant amounts of recycled materials[12].

2. Materials and methods

2.1 Materials
The fiberglass reinforced plastic (FGRP) is made of linen fabric fiberglass St-62004 (HKK Composite) and the Derakane Momentum 411-350 epoxy vinyl ester non-preaccelerated binder. The FGRP consists of eight layers of fiberglass with reinforcement angles 0.

All of the samples were made by the non-autoclave method (VaRTM) with the use of a SVI-20-43 (MSH Techno) vacuum infusion machine.

2.2 Strength tests
The samples were tested for three-point bending under ASTM D790-10. The sample size was 40x15x2 mm. Supports with a 2 mm radius were used for testing. They were installed at a distance of 32 mm. Loading speed is 1 mm/min.

2.3 Simultaneous thermal analysis
Simultaneous thermal analysis of TG and DSC was carried out using the STA 409 PC Luxx (NetzschGeraetebau GmbH). The sample weight was ~10 mg. A standard corundum holder was used for the samples and measurements were made at a heating rate of 10 K/min.

2.4 Structure investigation.
The sample structure investigation was conducted with the use of a Hitachi S-3400N scanning electron microscope being equipped with an electronic gun with the tungsten cathode. The measurements were taken at an acceleration voltage of 3 kV with the use of the secondary electron (SE) detector. The investigation of the matrix material structures was conducted at macro- and mesolevels during the stratification of the FGRP corrugated element.

3. Experimental part
Temperature boundaries of the FGRP thermolysis research were determined by simultaneous thermal analysis (figure 1).

![Thermogram of the studied binder Derakane Momentum 411-350.](image)

The sample is quite stable before 300 °C. Intensive thermal decomposition processes began at the temperature of 341,4 °C. The combustion process ends at 445 °C, accompanied by a loss of 78 % of
the sample mass. The heating process prolongation leads to the residual carbon burn out, accompanied by a doublet of exothermic peaks at 510.8 °C and 517.8 °C. Complete mass loss of the studied binder sample is observed at 523.5 °C. Thus, the reinforcing filler can be recycled in the temperature range from 350 °C to 550 °C.

Simultaneous thermal analysis of the solidified material were selected and subjected to degradation in the temperature range from 350 to 500°C to determine the optimal temperature of recycling reinforcing filler.

It was found that the intensity of the destruction process was found to be low at 350 °C according to microstructural studies (figure 2). There are areas with slight swelling of the material, while maintaining the fibrillar structure of the sample. The material begins to swell at temperatures of 400, 450 and 500°C. Temperature increases lead to intensifies of the process.

![Figure 2. Structure of samples processed at: 350 °C (x100), b) 400 °C, c) 450 °C, d) 500°C(x50).](image)

Further studies were conducted at the lowest possible temperature of 400 °C. The sample of the composite was subjected to heat treatment in the temperature range from 400 to 600 °C, with a gradual cooling method in a furnace, in air, in water and in the solution of the oiling agent.

4. Results and discussions
As part of this work, the recycling of fiberglass was carried out according to the following technological regime: a sample was placed in a furnace heated to a temperature of 400 °C for a certain time, after which it was removed and cooled. The regenerated fiberglass obtained from FGRP was dried at 120 °C to remove excess moisture until a constant mass was reached. Then new samples were
obtained from the regenerated reinforcing material according to the same technology as in the part 2.1 (figure 3).

![Figure 3. Photos of regenerated fiberglass (a) and FGRP (b) based on it.](image)

Data in figure 4 presented dependence of the recycling process duration at the destruction temperature on the flexural strength of the FGRP base on regenerated fiberglass fillers. Strength properties of this FGRP decreases according to the quadratic law with increasing of exposure time. This fact indicates the deterioration of the physical and mechanical properties of glass fiber.

![Figure 4. The dependence of the FGRP flexural strength on the time of recycling process.](image)

According to the destructive testing, the tensile strength at three-point bending of fiberglass from regenerated reinforcing materials is reduced by 26.8-49.7 % depending on the conditions of the recycling process.

The thickness of fiberglass obtained from regenerated fillers is proportional to the square of the recycling time and decreases with increasing process duration. When the processing time is below 130 minutes, the matrix is not completely removed, according to the figure 5. Subsequently, this leads to an increase in the thickness of the reinforcing filler package.
Figure 5. The dependence of the FGRP thickness on the time of recycling process.

At the same time, the PCM sample made of the filler obtained by 30-minute treatment at 400 °C and quenching in water withstands the bending load by 1.6 % lower than that of the primary material.

5. Conclusion
Thus, this paper presents the possibility of using recycled material so brained in there cycling process as they are in for cingmaterial for the production of FGRP. The technological regimes of FGRP production were determined to obtain products from recycled filler. However, in the future, a deeper study of these processes is required to reduce the temperature of destruction of the polymer matrix and improve the quality of the regenerated glass reinforcing filler.

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