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TENSION MECHANICAL PROPERTIES OF RECYCLED GLASS-EPOXY COMPOSITE MATERIAL

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The significance of composite materials and their applications are mainly due to their good properties. This imposes the need for their recycling, thus extending their lifetime. Once used composite material will be disposed as a waste at the end of it service life. After recycling, this kind of waste can be used as raw materials for the production of same material, which raises their applicability. This indicates a great importance of recycling as a method of the renowal of composite materials. This study represents a contribution to the field of mechanical properties of the recycled composite materials. The tension mechanical properties (tensile strength and modulus of elasticity) of once used and disposed glass-epoxy composite material were compared before and after the recycling. The obtained results from mechanical tests confirmed that the applied recycling method was suitable for glass–epoxy composite materials. In respect to the tensile strength and modulus of elasticity it can be further assessed the possibility of use of recycled glass-epoxy composite materials.

KEY WORDS: recycling, glass-epoxy composite materials, tension mechanical properties

INTRODUCTION

Modern constructions require materials with special properties and forms that can respond to difficult working conditions (increased load, pressure, speed, impacts, vibration). These conditions are the field for the applications of composite materials (CMs), and the last thirty years has been a period of their intensive development. The former is not only due to their good mechanical properties and light weight of produced components, but also due to the following factors [1, 2]: easy tailoring of desired properties such as high strength and modulus of elasticity, low density, relatively good impact strength, good dynamic strength and cracks growth resistance, good oxidative and corrosion resistance, and freedom in design and shaping and forming that facilitate easy integration of parts, reducing the consumption of materials and tools, along with the favorable total cost of

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production. The use of CMs is growing every day and for that reason their adequate disposal and subsequent recycling must be carried out after the completion of their service life. Otherwise, these materials will end up on a landfill in the form of waste, which further pollutes and distorts the environment [3].

The industrial CM waste is usually used as a raw material for the same CM production. The quantity of obtained waste is low compared to the production volume. If the CM waste recycling is necessary, additional processing can be required, such as gradual warming up before grinding. The fiber reinforced thermoplastic polymers can be recycled by melting and casting. This is not case with the fiber reinforced thermoset polymers which are dominant in the market. One of the possibilities for their recycling is grinding and the use as fillers in a new material. A second method is the treatment with suitable chemicals which abstract the reinforcing fibers from the thermoset matrix by dissolution of the polymer matrix. Thermal treatment at high temperatures of both components can be a third method for recycling of fibers reinforced thermoset composites, where the fibers are separated from the polymer matrix [4, 5].

The primary method for the recycling of composites is grinding to the desired particle size and further use as filler in a new composite material production. The better strength and thermal properties with ground glass-epoxy composite as filler in the epoxy-resin-based composites can be achieved in comparison with the same epoxy resin composites with common fillers. Also, many pyrolytic methods have been developed for recycling of composites. Combustion of composite materials gives energy and other useful byproducts. The solvent method for glass fibers (GFs) recycling from polymer matrix was also developed [6].

There are many possibilities for application of recycled components from composite materials. Recycled components from composite materials can be used as the reinforcing for lumber (reinforced thermoplastics substituting even wood). Recycled fibers can be used as reinforcing for asphalt (i.e. asphalt for bridges), as interlayer between two pure glass layers in special cast boards and in the process of stirring of volume cast mixtures which provide increased reinforcing due to the remaining recycled fibers [7].

The significance of recycling, based on wide spectrum of applications of recycled components from CMs is undeniable. In this study, glass-epoxy composite material (GECM) reinforced with non-andrecycled glass mats (from the lab-scale performed recycling) was firstly molded by handcrafted mold and mechanical properties were tested. The aim was to investigate the mechanical properties of recycled glass-epoxy composite materials (RGECM), compare their mechanical properties with those of GECM, and to validate the applied recycling method.

EXPERIMENTAL

Molding and Composition of GECM with non-recycled GFs

GECM with non-recycled GFs was molded by handcrafted mold. The mold consisted of two metal plates screwed with screw bolts to ensure adequate pressure force [8]. Once placed in a mold, CM was left 24 h at room temperature to cure and harden. After 24 h

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the mold was opened and hardened CM without any significant defects was taken out of the mold and left to cure completely in air during 7 days at room temperature. The specimens for mechanical testing were cut from the prepared CM.

The reinforcing for CM preparation were 20 mm long "E"-glass-fibers based on low-alkali (wt<1%) silicate glass with surface density 550 g/m^2 and volume fraction 60%. E-glass-fibers have good mechanical, hydro-thermal and electrical properties (Tables 1 and 2).

Table 1. Composition of „E"-glass

Structural component	Fraction (wt%)
SiO_2	52 – 56
Al_2O_3	12 – 16
B_2O_3	5 – 10
Na_2O and K_2O	0 – 2
MgO	0 – 5
CaO	16 – 25
TiO_2	0 – 1.5
Fe_2O_3	0 – 0.8
Fe	0 – 1

Table 2. Physical properties of "E"-glass

Property	Value
Specific weight, g/m^3	2.6
Tensile strength, MPa	2400
Modulus of elasticity, GPa	73
Elongation at break, %	3.3
Thermal elongation, 10^{-6} K^{-1}	5
Thermal conductivity, W/mK	1
Dielectric constant, ξ	6.7
Electrical resistivity, Ωcm	10^{14}
Moisture absorption, at 20°C $\rightarrow$ 65% wt	0.1

The polymer matrix used in this study was epoxy resin. The properties of used epoxy resin are given in Table 3.

The CM with non-recycled GFs (Tables 1 and 2) and epoxy resin polymer matrix (Table 3) was prepared by previously described method. The GFs as structural components in a form of glass mat were obtained by cutting into 2 cm long continual fibers (Figure 1). The polymer matrix was synthesized from 2,2-bis(4-hydroxyphenyl)propane, bisphenol A and epichlorohydrin. 3-Aminomethyl-3,5,5-trimethylcyclohexylamine (modified cycloaliphatic amine) was used as hardener in the epoxy resin system. The molded GECM contained 47 wt% of GFs regularly dispersed (in the form of a glass mat) in the epoxy matrix.

Table 3. Properties of epoxy resin

Property	**Unit**	**Reference**	**Analysis results**
Appearance		Yellow viscous liquid	Yellow viscous liquid
Epoxy number	n/100 g	0.51 – 0.54	0.52
Epoxy equivalent		196 – 185	192
Density	g/cm^3		1.26
Viscosity at 25°C	mPa·s	10000 – 15000	13700
Color (Gardner color scale)		3	Less than 3
Non-volatile components content	% min	99	99.5
Organic chlorine content	% max	0.3	0.17

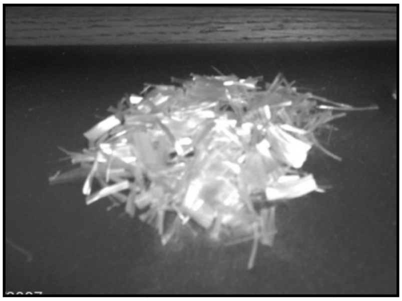

Figure 1. Appearance of cut glass fibers

Recycling of GECM

The obtained and tested CMs were recycled and this resulted in the recycled GFs. Once obtained recycled GFs were used for GECM preparation with recycled GFs.

In order to obtain GFs from CM, epoxy resin must be completely removed with a suitable reagent. The 50-g CM samples were immersed firstly in concentrated sulfuric acid (98 wt%), where small amount of epoxy resin was removed. To remove the remained epoxy resin, the samples were further kept in 200 cm^3 solution of nitric acid (68.5 wt%) at 90°C during 5 h. After that, the epoxy resin was completely removed and recycled GFs (RGFs) were obtained. The RGFs were separated from nitric acid by filtration, rinsed with distilled water and neutralized with ammonium hydroxide solution (25 wt%) and again with distilled water till pH 7 was attained. The neutralized and rinsed RGFs were dried in an oven for 24 h at 110°C, cooled, and made ready for the preparation of RGECM. The loss of GFs during the recycling process was 5.8 wt%, which is negligible amount since the process consists of several phases. Figure 2 compares the appearances of non-recycled and recycled GFs.

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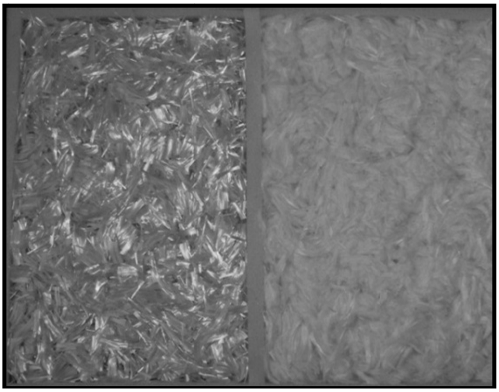

Figure 2. Appearance of non-recycled (left) and recycled (right) GFs

Molding and Components of RGECM with recycled GFs

After recycling and obtaining RGFs, the CM was molded with RGFs by the same method as in the preparation of GECM with non-recycled GFs. The structural components of RGECM with RGFs were the glass mat (reinforcing) obtained from RGFs and epoxy resin as the matrix. The standard specimens for mechanical testing were cut from the prepared RGECM.

Tensile testing

Five specimens for mechanical testing of GECM (N-1, N-2, N-3, N-4, N-5) and RGECM (R-1, R-2, R-3, R-4, R-5) were prepared The specimen dimensions were 250x25x2.5 mm. Before testing, the specimen's thickness and width were precisely measured (±1%). Further machine processing of specimens was performed with a diamond tool tip moving at a speed that reduces generation of heat in the specimen. Cutting was carried with a not ched cutter thickness of 1 m/min on the machine ALG-100. Testing was performed according to the standard test method ASTM D3039 [9].

The testing was carried out on the tensile tester SCHENCK TREBEL RM 100 with the use of hydraulic jaws, and the deformations (ε_l) in the longitudinal direction were continuously recorded.

The incorporated load was registered by the measuring cell (capacity of 100 kN). The elongation was measured by using dual extensimeter Hottinger DD1. There were two parallelly connected extensimeter related to the measure elongationon on the both sides of the specimen, and the parallel connection to the extensimeter facilitated the averaging of the measured values. The measuring range of the extensimeter was ± 2.50 mm, and it worked on the principle of measuring tape with accuracy of 0.05.

The cross-sectional dimension, the values of tensile strength, and the modulus of elasticity of the samples were calculated by using th eequations (1-3) [10].
The cross-section of the specimens was calculated with the following equation:

$$A_0 = b \cdot d \qquad [1]$$

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Tensile strength was calculated with equation (2) as follows:

$$R_{m,1} \frac{P_{\max}}{b \cdot d} \qquad [2]$$

where: $R_{m,1}$- tensile strength in longitudinal direction, MPa; P_{max}- maximal force at break, N; A_0 - cross-section of specimen, mm^2; b - specimen wideness, mm; d - specimen, thickness, mm

The modulus of elasticity (E_{long}) was calculated from equation (3) where ratio $\Delta P/\Delta\varepsilon_1$ was determined by linear regression method from the straight part of registered curve stress - strain:

$$E_{uzd} = \frac{\Delta\sigma}{\Delta\varepsilon} = \frac{\Delta P}{\Delta\varepsilon_1} \cdot \frac{1}{b \cdot d} \qquad [3]$$

RESULTS AND DISSCUSION

The tensile test in longitudinal direction was performed on five specimens of each prepared CM (GECM and RGECM), and the tensile strength and modulus of elasticity in longitudinal direction were obtained. It may be noted that the test was successful because in the all tested specimens the fracture occurred in the middle of the specimen (the measurement part). The calculated values of the tensile strength in longitudinal direction and the corresponding modulus of elasticity are given in Table 4. Figure 3 shows the percentage deviation of the tensile strength and modulus of elasticity of the RGECM specimens from the corresponding mean values of the GECM specimens.

Table 4. Results from tensile testings

Specimen	Type of GFs	Specimen wide b, mm	Specimen thickness d, mm	Cross section A_0, mm^2	Max force at break P_{max}, N	Tensile strength R_{m1}, MPa	Modulus of elasticity E_1, GPa
N-1	Non-recycled	14.9	2.6	38.7	8500	219.64	3.17
N-2		15.0	2.6	39.0	8640	221.54	4.81
N-3		14.8	2.7	39.9	9600	240.60	2.88
N-4		15.0	2.5	37.5	9260	246.93	3.52
N-5		14.9	2.7	40.2	8970	223.13	4.14
R-1	Recycled	14.8	1.8	26.6	5700	214.29	2.84
R-2		15.0	2.0	30.0	5950	198.33	3.05
R-3		14.8	2.2	32.6	5850	179.45	3.76
R-4		14.9	2.1	31.3	5990	191.37	2.92
R-5		14.8	1.9	28.1	5660	201.42	3.48

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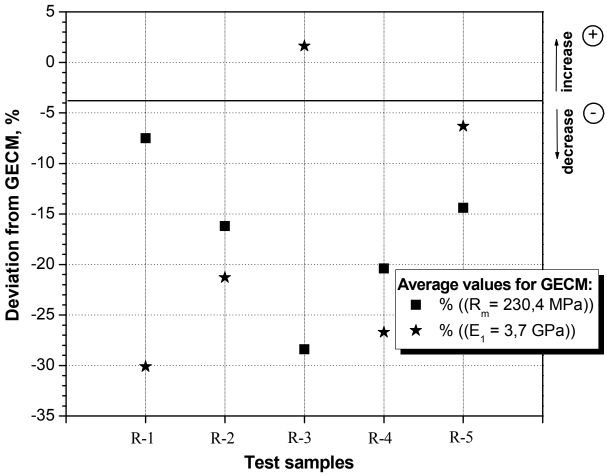

Figure 3. Deviation of tension test results

The relative uniformity of the obtained values of maximum force at break P_{max} for both GECM and RGECM can be noted. However, the values of P_{max} are smaller for the RGECM samples than for the samples from GECM.

Based on the results for the five tested specimens for each material the calculated mean tensile strength of the two materials were 230.37 MPa for GECM and 196.97 MPa for RGECM, and the mean values of the modulus of elasticity 3.70 GPa for GECM and 3.21 GPa for RGECM, respectively. Also, it was observed that the values for the tensile strength and the modulus of elasticity for RGECM are lower compared to GECM. The deviations from the mean value of measured (calculated) values both for the tensile strength and modulus of elasticity are relatively small in this type of testing. The minimum of tensile strength deviation for GECM was 3.14% for sample N-5 and the maximum 7.2% for sample N. The minimum of tensile strength deviation for RGECM was 0.7% for sample R-2 and maximum 8.9% for sample R-3 for RGECM.

The explanation for the slightly higher dispersion of the results for the modulus of elasticity of both materials can be the fact that it was relatively difficult to accurately determine the elasticity modulus because of the relatively small initial curvature in the stress-strain curves ($\sigma - \varepsilon$). In regard of the tensile strength, it is well known that due to different orientation of fibers in the glass mat as the reinforce, all the GFs are not under the same stress. Different stresses can occur with short fibers, due to the different orientation of individual fibers, which cannot coincide in each sample, and therefore leads to the different maximum force at break.

Figure 4 shows a schematic representation of a short fiber that is inserted into the matrix exposed to the longitudinal tensile stress σ_a. It can be seen that there are areas close to the ends of fiber that are not exposed to the entire load, and the mean stress in the fibers of limited length is slightly smaller than that which would have an infinitely long fiber exposed to the same external load.

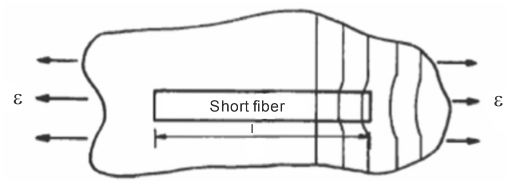

Figure 4. Schematic representation of deformations around short fiber inserted in the matrix exposed to the axial tension

Also, if we compare the deviations of the composites with non-recycled GFs and RGFs (Figure 3), it can be observed that the tensile properties of the composite material obtained by using RGFs as reinforcement are worse, the tensile strength is by 14.5%, and the modulus of elasticity by 13.2% lower compared to the values of the materials formed with non-recycled GFs. The differences in the values of the tensile properties of the two composites tested were expected. An explanation follows from the fact that recycled fiber surface layer was damaged during the recycling process (cooking, exposure to acids, etc.), thus good bonding of GFs with the matrix (epoxy resin) is disturbed as compared to the non-recycled fibers good interaction with the polymer matrix. By applying the same type of loading, the breaking of the fiber-matrix bonds in the composite with RGFs occur easier and at lower loadings than in the CM with non-recycled GFs, because of the poorer fiber-matrix adhesion. A confirmation of the conclusions is certainly the SEM images shown in Figures 5 and 6, where above phenomena are observed at higher magnifications.

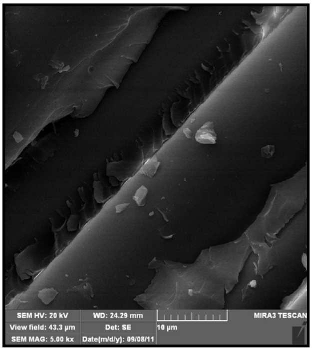

Figure 5 The breaking of the fiber-matrix bonds

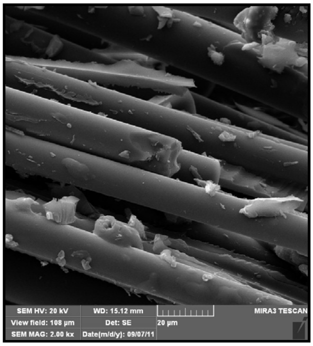

Figure 6 Poorer fiber-matrix adhesion

CONLUSIONS

The aim of this study was to examine and compare the properties of the composites prepared with RGFs and non-recycled GFs, as well as to present the possibility for recycling of CMs.

The obtained values of tensile properties of the composites with RGFs are acceptable and satisfactory, although they are lower than the corresponding values of the composite with non-recycled GFs (tensile strength values were 14.5% and module of elasticity by 13.2% lower than the corresponding values CM with non-recycled GFs). It can be concluded that the RGECM retains its tensile properties with minimal fluctuation compared to GECM, and as such it can be used for different purposes.

Also, on the basis of the obtained results it can be concluded that the method of recycling GECM based on the exposure to nitric acid can be applied to recycle small amounts of the material, and further research should be directed toward the improvement of the applied method to solve the problem of recycling of the compounds from the decomposed epoxy resin from composite material obtained by boiling in nitric acid. The method should be developed in the direction of the application of several different acids to shorten the time of exposure of the composites to acid attack and increase the efficiency of the recycling process at lower temperatures [11,12]. The recycling of composite materials and recycling in general can significantly save the energy and the raw materials, and certainly pollution would be drastically lowered.

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МЕХАНИЧКА СВОЈСТАВА РЕЦИКЛИРАНОГ СТАКЛО-ЕПОКСИ КОМПОЗИТНОГ МАТЕРИЈАЛА

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Примена композитних материјала, захваљујући својим добрим својствима, сваким даном постаје све већа што намеће питање могућности њиховог рециклирања и тиме продужења њиховог животног века. Након једанпут коришћеног композитног материјала у одређене сврхе врши се њихово одлагање у виду отпада. Овакав отпад углавном представља сировину за производњу исте врсте композита поступком рециклаже, што повећава њихову примену. Имајући ту чињеницу у виду, овај рад представља допринос у подручју истраживања механичких својстава рециклираних композитних материјала. У раду су приказана затезна механичка својства стакло-епокси композитниог материјала који је био у експлоатацији, поступак његове рециклаже, као и затезна механичка свостива стакло-епокси рециклираног композитног материјала. Поређењем резултата се дошло до података о исправности поступка рециклаже стакло-епокси композитног материјала као и процене о даљој могућности примене, узимајући у обзир добијене вредности за затезну чврстоћу и модул еластичности.

Кључне речи: рециклажа, стакло-епокси композитни материјали, механичка својства

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