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Influence of preparing of GFR recyclates on the properties of polyester matrix compsites

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Materials

ABSTRACT

Purpose: The purpose of this project was to estimate the possibility of using polyester-glass fiber recyclate as a reinforced component of polymer matrix in composites. This kind of mechanical recycling can be use as one of the way of polymer composites utilization. Recyclates prepared from GFP - polyester resin reinforced glass filaments.
Design/methodology/approach: Recyclate obtained after grinding was a mixture of cured polyester resin particles and glass fibers. Two different groups of recyclates have been obtaining after separation. First group of recyclate was used to prepare of stratified laminates. Second group of recyclate was used as a filler of polymer matrix.
Findings: The results of the investigation have shown that using of polymer composites wastes as a filler, leads to decreasing of the flexural and impact strength. However obtained material had a bending strength comparable with standard material. The results of mechanical properties have been prove that change of properties depends on the size of fraction recyclate. Fraction containing the particles in fibrous shape better influence on that mechanical properties of laminates. The results of the investigation have shown that using of polymer composites wastes as a filler materials (core), leads to decreasing of the properties in bending and impact tests. It has been shown that content of the recyclate has significant influence on studied mechanical properties.
Practical implications: The results of the investigation have shown that using of polymer composites wastes as a filler, leads to decreasing of the properties in bending and impact tests. Surface treatment of recyclates has been shown that bending strength between matrix and recyclates improve.
Originality/value: The results of the investigations allow to confirm, that the polymer composites waste can be used as a filler polymer matrix in production of new composites, being also one of the way of utilization of composite with thermosetting matrix.
Keywords: Composites; Mechanical properties; Technological design; Thermo-chemical treatment

1. Introduction

Composites with a duroplastic matrix reinforced with fibres are materials which constantly find new applications. This refers both to new types of resins and their modifications, and is also connected with the use of reinforcing fibres of enhanced strength. The new quality fibres allow to not only obtain the designed properties of a composite, but also take into account the process of waste and worn out products utilization [1, 2]. The application of natural fibres, such as flax, hemp, sisal or coconut fibre, instead of the commonly used fibreglass, facilitates the process of utilization by the application of, mainly thermal, recycling. This does not result in the occurrence of large amounts of solid products (slag) in the combustion process, as in the case of composites reinforced with fibreglass [3, 5]. Other methods of recycling, such as chemical recycling, are applied to a limited degree, for most often, the composite matrix are polymers which create a cross-linked non-degraded, durable structure in the process of hardening. Owing to chemical recycling, it is possible to recover the fibrous reinforcement and obtain raw materials or semi-finished products. A number of methods to recycle fibrous polymer composites have been developed, which allow the recovery of fibres by means of a fluidized bed [3], resin decomposition or a low-temperature catalytic pyrolysis. A good example can be the method elaborated at Industrial Chemistry Research Institute Poland [4] which enables the recovery of reinforcing fibres as result of matrix extraction by methylene chloride. Nevertheless, the most popular way to utilize composite waste containing fibreglass is its storage at waste dumps. Such a method of waste disposal is hardly acceptable from the environmental point of view. Another solution proposed is material (mechanical) recycling, which consists in grinding the composite waste material to a form that would allow the introduction of the processed waste into new products and, at the same time, it would enable taking the advantage of the properties of the reinforcing fibres contained in the waste [4,6,7,8].

The broken-up waste can be successfully used as, for example, a filling material for a polymer matrix, replacing a part of fibrous or powder filler and improving the mechanical characteristics or other properties (eg., resistance to wear) of the matrix applied. Waste materials processed in this way are used experimentally in the furniture industry (for the manufacture of composite boards) and as an additive to asphalt, concrete, polyester moulding compounds, polymer-concretes and in many other products, where an addition of recyclate does not lower the functional properties. This type of recycling requires, however, an appropriate preparation of the recyclate connected with the size and shape of fraction. It also requires the application of surfacing in order to improve adhesion with polymer.

2. Experimental part

2.1. Waste preparation process

For the investigations, waste materials were used, formed during the production of composite constructions manufactured by specialized firms. The waste used in the investigations contained both post-production waste and defective and damaged products. The matrix of the composite waste was polyester resin, and the reinforcement was a fibreglass mat or fabric. The device used for the breaking up was a mill. The size reduction method applied ensured a longitudinal shape of the recyclate particles containing non-damaged fibres with an uncovered surface [5].

The recyclate was characterized by high diversity both in the shape and size of grains [9]. In that fraction, single fibres and grain of a different size and shape were present. The so prepared recyclate (marked as the non-segregated fraction > 1,6 mm) was subjected to a sieve analysis with fraction separation. Thus, when taking into account the shape and type of particles occurring in particular recyclate fractions, it may be generally affirmed that the particles of a size below 0,315 mm constitute the “powder fraction” and of those of a larger size – “fibrous fraction”. In order to determine the influence of the recyclate’s shape and size on the mechanical properties, sandwich laminates were produced, where the external layer consisted of glass fabric and the core contained from 25 to 55 wt. % of recyclate.

2.2. Preparation of recyclate surface

In order to increase adhesion of recyclate particles to the matrix material, the recyclates were subjected to thermal and chemical treatment. Such procedures mots often consist of physical or chemical activation processes. In the case of physical activation, the most common methods applied are: ionization, plasma or radiation processing, UV irradiation, or corona discharge methods [1]. In the case of chemical treatment, the methods usually used are: surface treatment with silanes or acrylate compounds, glycolysis, or activation in methylene chloride. Due to the technical capacity of the factories dealing with the manufacturing of composite products, it was decided that heat treatment (soaking) would be applied for the investigations as well as surface treatment in a methylene chloride solution. The soaking process was conducted for 3 hours at temperatures of 60°C, 100°C and 120°C. Verification of the surface treatment influence on the properties of the composite was made on the basis of bend and impact tests. The examinations were carried out for composite samples with a polyester matrix containing 35% of recyclate of the fraction size above 1,6 mm (non-segregated recyclate). Also, examinations of the surface structure of a composite fracture containing the recyclate were made, which allowed a qualitative evaluation of the recyclate/matrix bonding strength.

Table 1.
Mechanical properties of laminates containing recyclates

Flexural strength, MPa				
Recyclate	Grain size of recyclate, mm			
value wt., %	>1,6	1,6-1	1-0,315	0,315-0,063
25	247	199	165	210
35	242	178	163	203
45	232	179	139	205
55	191	128	81	167
Impact strength, J/mm^2				
Recyclate	Grain size of recyclate, mm			
value wt., %	>1,6	1,6-1	1-0,315	0,315-0,063
25	106	100	65	94
35	92	76	56	77
45	88	75	58	73
55	81	47	54	68

3. Analysis of the results

When analyzing the dependence of bending and impact strength on the size of the broken-up waste particles (Table 1), one can notice that with a decreasing particle size, the mechanical properties lower, reaching their minimum values for a fraction which consists mostly of resin particles or grainy composite particles. This is connected with the form of the recyclate which, with the decreasing grain size, changes its form from fibrous to granular (fraction 1-0,3 mm). The occurrence of a greater amount of granular precipitations of recyclate contributes to noticeable lowering of bending and impact strength. The non-segregated fractions and those of the size from 1,6 to 1,0 mm, consisting mainly of fibreglass and agglomerates of composite particles, fulfil not only the role of filling, but also maintain their reinforcing properties. The differences between strength values for those fractions are minimal, which allows the supposition that additional separation of broken-up recyclates is not necessary, and, at the same time, this may facilitate the recycling process itself. A fraction of recyclate grain size below 0,315, i.e. the "powder fraction", has a positive influence on the properties. It contributes to a distinct growth of both impact and bending strength. When compared to a fraction containing recyclate precipitations of a size between 1 and 0,315 mm, there is almost a 25% growth in the strength. The reason for this is the form of fine recyclate containing tiny single glass fibres and small resin particles. The fibres occurring in that fraction are not damaged; they have an uncovered surface, owing to which they are well joined with the matrix material and strengthen it considerably. This results in enhanced strength of the laminate core, whereas the fine resin particles contained in the fraction may fulfil the role of a filler increasing the interlayer shear strength.

An increase in the mass fraction of a recyclate in the core contributes to a decrease of the mechanical properties. The examined properties are not only influenced by the type and size of the recyclate applied, but also by the form of the lining used. The use of two layers of fabric as the lining is a better solution, since laminates in general reach a higher level of strength properties, e.g. bend or impact strength, compared to laminates with glass mat fabric.

On the basis of the examinations carried out it may be concluded that mechanical properties of laminates with a filler in the form of polyester-glass recyclate depend not only on the recyclate fraction size, but most of all on the form of recyclate. The presence of precipitations in a fibrous form (composite agglomerates in "fibrous" fractions >1,6 mm, 1 - 0.3 mm or short single fibres in a "powder" fraction) in particular fractions, provides for comparable mechanical properties of laminates. Strength properties are inversely proportional to the recyclate's mass fraction. The highest values of strength properties were obtained for laminates with a 25 wt.-% addition of polyester-glass recyclate for all fractions. The lowest properties are characteristic of laminates with the greatest amount of waste material, namely 55% wt-%. Intermediate values were reached by laminates with a 35 and 45 wt.-% of recyclate addition, the results for which were comparable (Table 1).

When analyzing the influence of recyclate surface preparation on the properties of composites containing recyclates, one may conclude that the adhesion of recyclate to the matrix is best enhanced by treatment in a methylene chloride solution. The examination results are presented in Table 2. In comparison to the recyclate that did not undergo any treatment, the impact and bend strength were enhanced by ca. 30%. The surface treatment consisting in recyclate soaking slightly increases the composite strength when compared to the strength of a composite containing non-modified recyclate. After heat treatment of the recyclate surface, improvement of adhesion of recyclate grains to the matrix can be observed. The structure of fractures showed that as a result of soaking, infiltration of recyclates by polyester resin occurred; large numbers of recyclate clusters not infiltrated with the matrix were not observed.

Table 2.
Mechanical properties of composites containing recyclate

Flexural strength, MPa				
Chemical	Thermal treatment preparations			
preparation	20°C	60° C/3h	100°C/3h	120°C/1h
57	34	42	43	36
Impact strength, J/mm^2				
1,98	1,18	1,42	1,71	1,51

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A corroboration were the impact tests' results, where changes of force and deformation during impact bending were recorded (Fig.2). On the basis of the obtained diagrams, it is possible to determine the value of energy needed to initiate a fracture (elastic strain energy) and energy connected with fracture propagation (plastic energy).

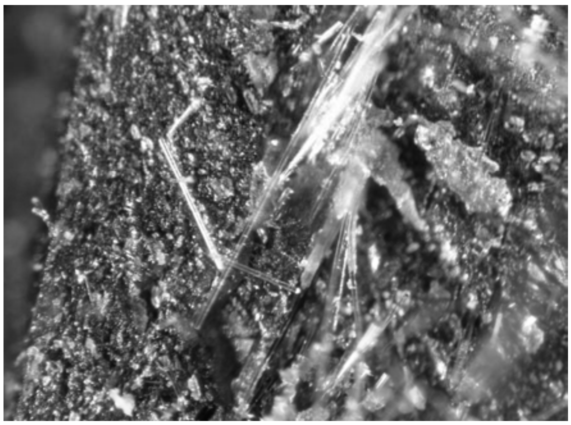

Fig.1. Surface structure of composites containing recyclate. Good bonding between recyclate and polymer matrix (mag. 32x)

The determined values of elastic strain energy indicate that in the case of materials activated in methylene chloride, the value of energy is the highest and amounts to ca. 2 J/mm^2.

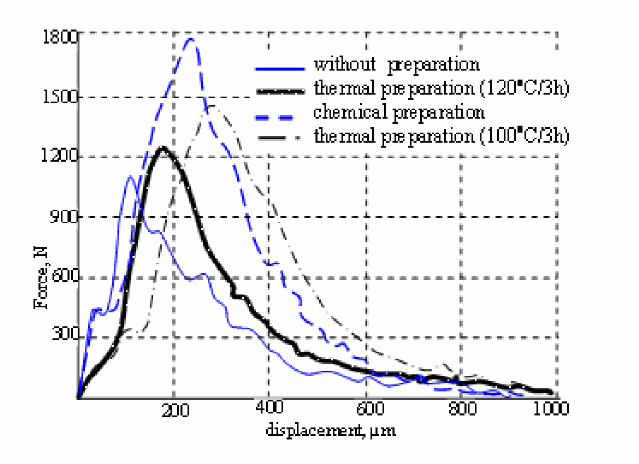

Fig. 2. Change of force in impact test of composite with recyclate

The lowest energy value was recorded for composites with not soaked (processed) recyclates. As far as recyclates subjected to heat treatment before introduction are concerned, the highest value of elastic strain energy was found for the treatment at 60°C. At a higher temperature of treatment (120°C), there was no increase in elastic strain energy noticed, but the energy necessary for (plastic) gap development increased, the reason for which may be the growth of the recyclate grain surface due to oxidation and styrene evaporation.

4. Conclusions

The applied method of composite waste size reduction has yielded satisfactory results in terms of the obtained recyclate quality, without damaging the fibres. It caused fibres' separation or the creation of recyclate conglomerates in a fibrous form. The sieve analysis allowed the isolation of fibrous fraction (>0,3mm) and powder fraction (< 0,3mm). Observations of particular screenings have shown that the recyclate consisted of fiberglass, resin particles and agglomerates of composite particles in various proportions, depending on the fraction. Promissing results were obtained for laminates with a core containing an addition of non-segregated recyclate. The obtaining of laminates with a recyclate addition, characterized by satisfactory strength properties, does not have to be connected with its separation into fractions, which considerably shortens the time of composite waste preparation.

An important element that enhances the quality of laminates is the pretreatment process. The application of simple methods of chemical or thermal activation of the recyclate grain surface may improve the strength of the matrix/recyclate connection. The chosen methods of surface treatment that may be applied at a semi-industrial scale do not require any extra capital investment. A manufacturer can make use of appropriately prepared waste materials, e.g. ones of a small fraction to strengthen adhesives intended for connecting the constructional elements. The implemented broken-up waste materials work not only as fillers, but also as laminate strengtheners.

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