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Statistical methods in the analysis of strength parameters of epoxy-glass composites modified with rubber recyclate

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ABSTRACT

Purpose: The article presents a statistical analysis of strength parameters of newly developed epoxy-glass composite materials modified with the addition of rubber recyclate.

Design/methodology/approach: Three variants of materials with a percentage of recyclate content in the composite matrix of 3%, 5%, 7% and a reference variant without the addition of recyclate were used for the study. The samples were subjected to an impact test on a ZWICK RKP 450IR-GE impact hammer. Resilience measurement values were subjected to statistical analyses at the significance level $\alpha = 95\%$, such as: testing the normality of distributions with the Shapiro-Wilk test, testing differences between pairs with the Student's t-test for dependent groups, and testing ANOVA differences for independent groups.

Findings: The Shapiro-Wilk test confirmed that the resilience variables for all tested samples were in normal distributions; therefore the highest power parametric tests were used to test the differences. Using the Student's t-test, it was confirmed that between pairs of variables in configurations: standard sample with the modified sample, there were significant statistical differences in the distribution of resilience values for all samples. ANOVA confirmed significant changes in impact strength in 10 comparison variants.

Research limitations/implications: The obtained test results showed that in 9 compared cases, there were significant statistical differences, and in one case, there were no significant differences.

Practical implications: The performed statistical analyses confirmed their significant usefulness in the process of qualification of strength parameters for materials with high anisotropy, such as composites.

Originality/value: The manufactured products are innovative in terms of the method of using the addition of rubber recyclate as a filler for epoxy-glass composites. The use of static methods for their study also has practical value. It optimizes the analysis methods of the results of measurements of strength parameters of new composite materials.

Keywords: Statistical analysis, Glass composites, Rubber recyclate, Impact strength, Modification

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ANALYSIS AND MODELLING

1. Introduction

Modifying the properties of epoxy-glass composites through various types of macro and micro-additives is the subject of many scientific studies, as it creates the potential to improve the mechanical and thermal properties of these composites and reduce their production costs [1-5].

The current trend in composite materials research is to search for methods of using waste products for manufacturing new composite materials. Additives of both natural waste [6] and non-degradable waste [3,7,8] are used.

Analyses concerning the influence of rubber recyclate on the properties of epoxy-glass composites mainly concern the strength parameters of the composite, such as tensile strength, impact strength or elastic modulus [5,8,9]. These analyses also concern the addition of rubber as a sandwich layer in composites.

In research on the mechanical properties of composites based on glass mats, much attention is paid to impact strength [5,10]. The paper [11] presents the results of the comparison of, among others, the impact strength of resins used in composites based on a glass mat. The best results were obtained for epoxy resin.

The results of scientific research indicate that adding rubber recyclate to epoxy-glass composites may increase their tensile strength and impact strength but may also reduce their elastic modulus [6,12].

Adding rubber recyclate to the epoxy-glass composite can increase its flexibility and tensile strength, which can be beneficial in applications where the material is exposed to high mechanical stresses. Adding rubber can also reduce the hardness of the composite, which can be beneficial in applications where the material is exposed to wear.

The properties of the epoxy-glass composite with the addition of rubber will depend on how the rubber is added, its type and quantity, and the properties of the polyester-glass composite itself. Different mechanical and strength properties can be obtained depending on how the rubber recyclate is added to the composite and its type and quantity.

Statistical analyses of strength measurements are used to describe and interpret endurance test data [13,14]. They can help identify relationships between different variables (e.g. temperature and strength), determine whether differences between data groups are statistically significant, and predict values for new data [15]. Statistical analysis of strength data can be used to assess the effectiveness of new materials or manufacturing processes; to determine whether products meet certain quality standards or requirements, to compare different strength test methods; or to determine whether differences in strength between batches of products are statistically significant [16].

Many types of statistical studies can be used to analyze the measurement of impact strength [14]. Some of the most commonly used are Student's t-tests – statistical tests used to compare the averages of two groups. They are often used in scientific studies where one wants to check whether a statistically significant difference exists between groups.

The study [16] presents the methodology for determining outliers for strength tests of composites. The MNR (Maximum Normed Residual) method was used in work to indicate the outliers. After the analysis, outliers and the process of dealing with them were indicated.

The study [17] used a two-parameter Weibull distribution to measure the variability of the tensile strength of glass/epoxy and carbon/epoxy laminates subjected to quasi-static tests at a high strain rate.

Analysis of variance (ANOVA) – is a type of statistical analysis used to compare the averages of several groups. ANOVA is often used in scientific studies to see if there is a statistically significant difference between groups [18].

In this work, research was carried out to determine the effect of the addition of a waste product in the form of rubber recyclate as a factor modifying the mechanical properties of the epoxy-glass composite on the impact strength and the nature of material damage. The aim was to isolate several variants of research materials A composite with the best mechanical properties in terms of impact strength and damage kinetics. Experimental studies and statistical analysis of the results of these tests were used as a verification method.

Statistical studies enabled an accurate assessment of the repeatability of the obtained results and thus greater certainty as to the impact strength value of the manufactured material in the case of using the developed manufacturing technology by the manufacturer on an industrial scale.

2. Materials and methods

Composite materials were produced by manual lamination with double-sided pressure. Glass emulsion mat 1002/300/125 with a density of 450 g/m^2, epoxy resin Epidian $^@$ 6 with hardener, as well as rubber recyclate from recycled car tires, were used. The EM 1002 mat is an emulsion mat made of chopped glass fibres made of E-glass with a content of less than 1% alkali. Laminates manufactured using this mat are characterized by good mechanical properties and very good resistance to weather conditions over a long time [19].

Epoxy resin Epidian$^@$6 with Z-1 hardener was used as the matrix of the composites. This resin is used to make composites containing organic or inorganic fillers.

Table 1 presents the physicochemical parameters of epoxy resin used in materials.

Table 1.
Characteristics of Epidian epoxy resin® 6 [20]

Parameter, unit	Value
Epoxy number, Mol/100 g	0.510-0.540
Density at 25°C, g/cm^3	1.17
Viscosity at 25°C, mPa*s	1000-1500
Gelation time 100 g at 20°C, min	20
Curing time at 20°C, days	7

As an additive modifying the properties of composites, a fraction of rubber recyclate from the recycling process of car tires with a grain size of up to 1.2 mm, obtained using a laboratory screen shaker, LAB-11-200 from EKOLAB, was used. Four variants of research materials were produced from these components: K0 – pure epoxy-glass composite without the addition of recyclate, K3 – composite containing a 3% addition of rubber recyclate to the composite matrix, and variants K5 and K7 containing respectively 5% and 7% rubber recyclate additive to the composite matrix. Figure 1 shows the process of manufacturing the K5 composite by manual lamination.

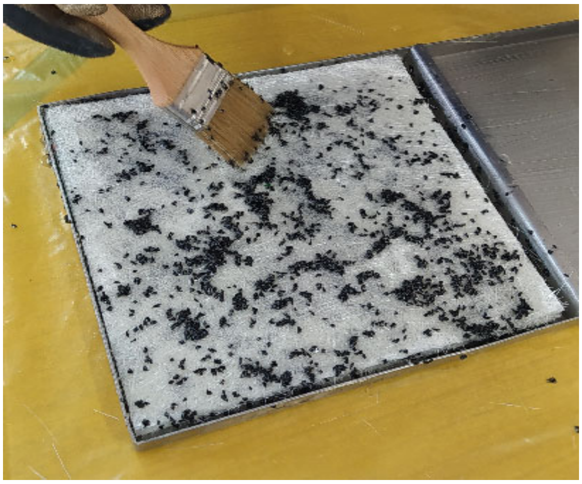

Fig. 1. Production of K3 composite by manual lamination

From the manufactured composite materials, test samples were cut using the water cutting method by PN-EN ISO 179-1:2010, which were subjected to impact tests carried out on a Charpy RKP450 pendulum hammer with TestXpert II software.

Figure 2 shows samples K3 and a view of the measuring station.

a) b)

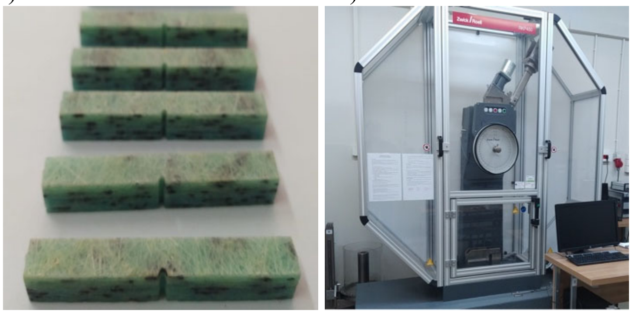

Fig. 2. a) K3 composite samples prepared for testing, b) Charpy-type pendulum hammer

The impact test of epoxy-glass composites presented in the article with the addition of a modifier in the form of a rubber recyclate consisted of subjecting a material sample to a specific shock load and assessing its behaviour during and after the load set. The impact test aimed to assess the material's resistance to fracture or fracture during sudden shock load. Thanks to the use of additional equipment during the test, it was possible to determine not only the impact strength but also the changes in bending force and the registration of deflection over time.

During the bench tests, impact values were recorded for a set of samples for four types of material. In addition, thanks to the existing instrumentation and software, the results of the analysis of changes in the value of bending force, as well as the deflection of samples in small time intervals, were recorded. Based on the obtained results, force-displacement graphs were obtained, which were used to illustrate the energy expenditure necessary to destroy the sample in the elastic deformation area.

The obtained results were used to perform further comparative analysis of the materials held in terms of the above-mentioned parameters and allowed to determine the influence of rubber recyclate on these parameters. In addition, the results allowed us to select the most advantageous variants of the tested composite materials.

3. Results

3.1. General remarks

Figure 3 shows the impact test results for four variants of samples made of sandwich composites produced by manual lamination with double-sided pressure.

Figures 4a and 4b show a diagram of the deflection-force dependence for two selected samples, K0 and K7, subjected to dynamic testing on a Charpy hammer.

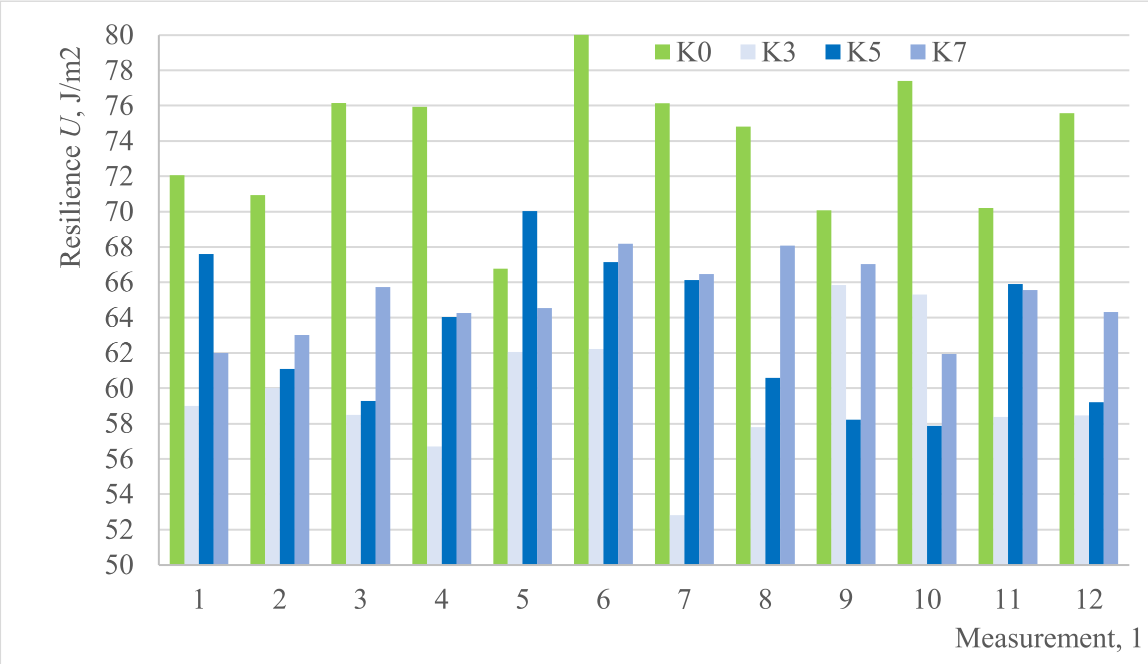

Fig. 3. Impact test measurement results for composite materials K0, K3, K5 and K7

These graphs illustrate the registration of the elastic state (*Ue*) – marked with coloured fields under the graph and the development of destruction (*Up*). For the K0 sample – without the addition of rubber recyclate – the maximum force F_{MAX} of 2983 N resulted in a deflection of 1.52 mm. For the K7 sample, the maximum force of 3205 N resulted in a deflection of 1.27 mm. After exceeding the maximum force, processes related to the development of material destruction occur, resulting in maximum deflections: for samples K0 with a value of 5.2 and sample K7 with a value of 4.75 mm.

Table 2 summarises the values of the maximum force F_{MAX}, deflection *f*, work *W* and resilience *U* for all tested sample variants from four types of material.

Table 2.
Results of the impact test of the tested materials

Composite / Parameter	F_{MAX}, N	f, mm	W, J	U, kJ/m^2
K0	2983	1.52	5.06	74
K3	2651	1.44	5.59	60
K5	2542	1.46	5.31	63
K7	3205	1.27	5.81	66

3.2. A statistical analysis of the obtained measurement results

Testing the normality of distributions Shapiro-Wilk test for small samples.

The Shapiro-Wilko test is considered the best test to check the normality of the distribution of a random variable. The main advantage of this test is its high power, i.e. for a fixed α, the probability of rejecting the H0 hypothesis, if it is false, it is higher than in other such tests. Assumed α = 95%. The null and alternative hypotheses were as follows:

- H_0: The distribution of the examined feature is normal,
- H_1: The distribution of the examined feature is not normal.

Table 3 presents the obtained values of the Shapiro-Wilk test statistics for composite materials subjected to resilience tests.

Table 3.
Values of the Shapiro-Wilk test statistics for the tested composite materials

Type of material	Value *p*
K0	0.730
K3	0.695
K5	0.239
K7	0.634

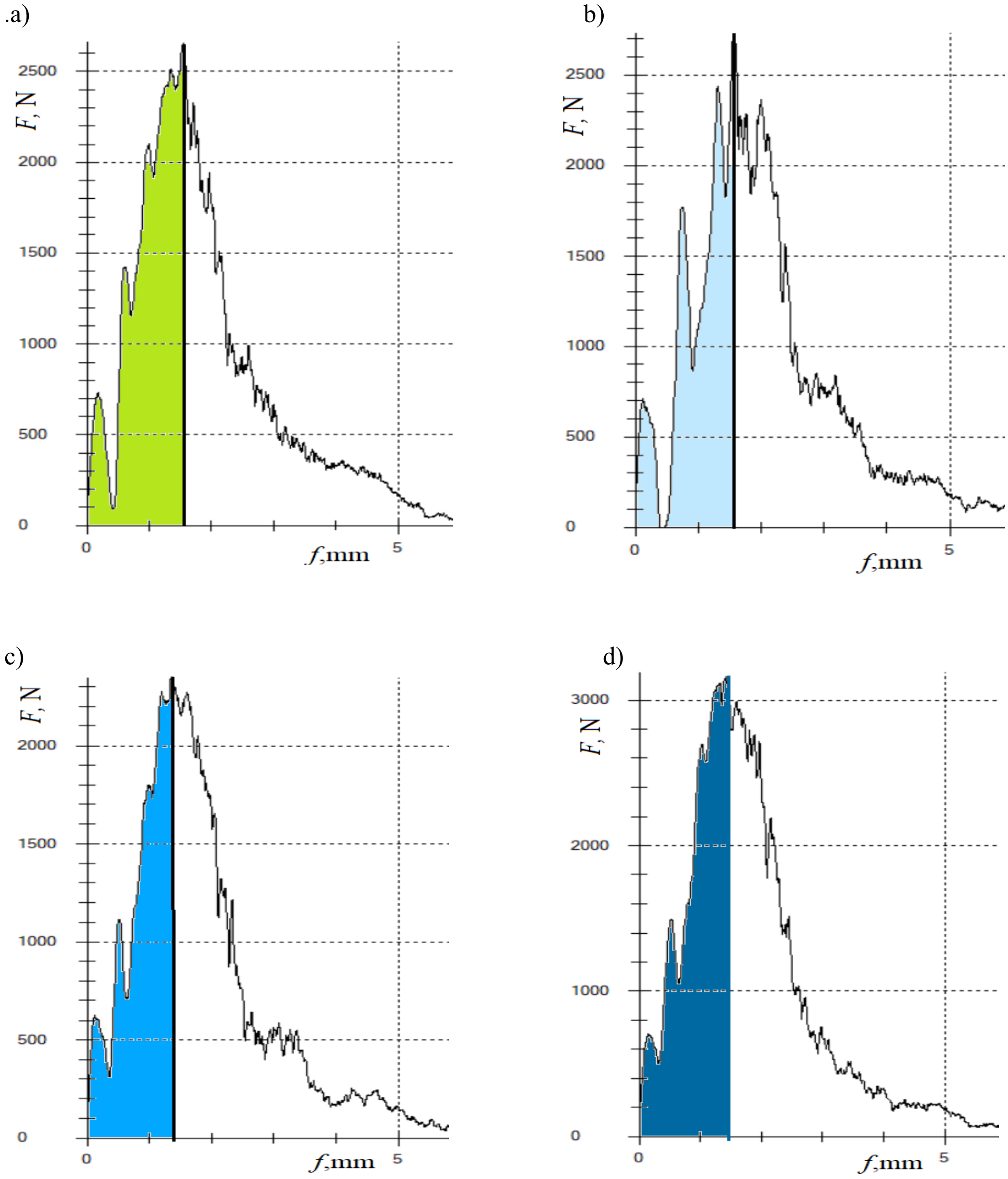

Fig.4. Force-bending diagram *F(f)* (a) for sample K0 (b) for sample K3 (c) for sample K5 (d) for sample K7

All obtained p-probability values were greater than 0.05; therefore there was no reason to reject the null hypothesis. Impact variables for all tested samples were normally distributed. Therefore, parametric tests were used to test the differences.

<u>Testing differences between pairs of materials</u>

The resilience variables for all tested samples were normally distributed; therefore, the Student's t-test for related samples was used to test the differences. Sample K0 without recyclate was taken as a standard sample. The following hypotheses were assumed:

a) Null hypothesis H_0 of no differences between population means: H_0: $\mu 1 = \mu 2$,
b) Alternative hypothesis about differences between populations means H_1: $\mu 1 \neq \mu 2$.

Table 4 presents the obtained statistical data values of the Student's t-test.

All *p*-probability scores obtained were less than 0.05; therefore, there was no basis for accepting the null hypothesis.

Significant statistical differences occurred between pairs of impact strength variables for all tested samples.

Table 4.
Paired-sample Student's t-test test statistic values for the test samples

A pair of variables	Value *p*
K0 & K3	0.000
K0 & K5	0.000
K0 & K7	0.000

<u>ANOVA difference testing</u>

As shown in the previous chapter, there were significant statistical differences between all samples in the following configurations: the standard sample and the sample with the addition of rubber recyclate, i.e. there was a significant change in impact strength. However, it was decided to check whether significant statistical differences between the tested samples correspond to the tested types of materials treated as independent samples. Resilience variables for all tested samples were normally distributed, and ANOVA was used to test differences. The independent-samples ANOVA test extends the Student's t-test for more than two samples. Definition of hypotheses:

The null and alternative hypothesis of no differences between the population means was adopted:

- H_0: μ1 = μ2 = μ3 = μ4,
- H_1: ~ (μ1 = μ2 = μ3 = μ4).

The Brown-Forsythe test was used to check the equality of variances. Because it is less sensitive than Levene's test to failure to meet the assumption of normal distribution. The resulting value of $p = 0.066$ was greater than the composite minimum significance threshold of $PV = 0.05$, so the assumption of the equality of variances was met. Therefore, ANOVA tests were performed to assess the significance of the average resilience variation.

The value of the calculated test probability $p = 0.00$ allowed for rejecting the null hypothesis assuming no differentiation of average values. It follows that not all sample groups came from one population, which was the basis for further "a posterior" (post-doc) comparisons.

In total, 12 comparisons were made for all material configurations. Results obtained (Tabs 5 and 6) from both the NIR test and the chi-square median test (Fig. 5) showed that:

- there were nine comparisons corresponding to the types of material between which there were significant statistical differences,
- there was one comparison for which there were no significant statistical differences between the tested materials, i.e. 5 (7% random) and 3 (5% random). The calculated value of p = 0.088 was higher than the assumed minimum significance threshold of $PV = 0.05$).

Table 5.
p-probability values of post-hoc tests (NIR)

Type of material	K0	K3	K5	K7
K0		0.000	0.000	0.000
K3	0.000		0.029	0.000
K5	0.000	0.029		0.088
K7	0.000	0.000	0.088	

Table 6.
Location measures (resilience)

Type of material	K0	K3	K5	K7
mean	73.88	59.86	63.09	65.60
standard deviation	3.88	3.67	4.19	1.83
coefficient of variation	5.25	6.13	6.65	2.78
mean + standard deviation	77.77	63.53	67.29	67.43
mean - standard deviation	70.00	56.19	58.90	63.78
first quartile (Q_1)	66.77	52.81	57.88	61.94
third quartile (Q_3)	76.13	62.10	66.38	66.87
quartile deviation	4.68	4.64	4.25	2.46
interquartile range	9.36	9.28	8.50	4.93

4. Discussion

The presented results of composites tests showed that the addition of rubber recyclate, and in particular the percentage amount of recyclate added in relation to the mass of the composite, has a significant impact on the impact strength of the new material and the course of the process of destruction of composite samples during the impact test.

The Shapiro-Wilk test confirmed that the impact variables for all tested samples were in normal distributions; therefore the most powerful parametric tests were used to test the differences. Using the Student's t-test, it was confirmed that between pairs of variables in configurations: standard sample with a modified sample, there are significant statistical differences in the distribution of impact values for all tested samples. The ANOVA tests confirmed significant changes in impact strength in 10 comparison variants.

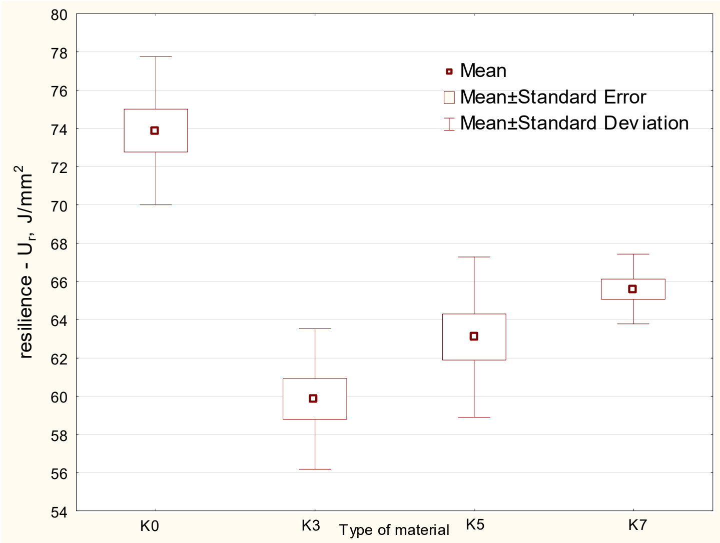

Fig. 5. Box plots for tested materials (Mean, Mean±Standard Error, Mean±Standard Deviation)

The addition of rubber recyclate and the method of its distribution had a decisive impact on the impact properties of the manufactured test material. Of the tested materials, the most favourable impact parameters in terms of maximum impact strength were shown by samples from K7 material. In terms of damage kinetics parameters, the most favourable parameters were shown by samples made of K7 material.

The obtained results of statistical tests showed that there were significant statistical differences in the comparable case comparisons. The performed statistical analyses confirmed their significant usefulness in qualification strength parameters for materials with high anisotropy, such as composites.

5. Conclusions

The addition of rubber to a glass composite can affect its mechanical properties in different ways, depending on the amount and type of rubber and how it is introduced into the composite.

Due to the properties of sandwich composites, it is possible to model and design materials, adapting them to specific applications and manufacturers' requirements. The conducted research has shown that using recycled materials significantly impacts pro-ecological activities and allows the creation of favourable functional and economic parameters.

Keep in mind that the addition of rubber to glass composite can lead to deterioration of other properties such as tensile strength or hardness, so it is important to choose the right amount and placement of rubber to achieve the desired properties.

Statistical analysis of strength data is important because it allows for a better understanding and interpretation of the data, which in turn can help you make more informed decisions about the design and manufacture of high-strength products.

References

[1] A. Wilczyński, Polymer fiber composites, WNT, Warszawa, 1996 (in Polish).

[2] M. Bocian, K. Jamroziak, Ballistic shields made of composite materials on a polymer matrix Technical Transactions. Mechanics 103/6-M (2006) 53-56 (in Polish).

[3] E. Kowalska, M. Żubrowska, M. Borensztejn, Heterophasic thermoplastic polymer compositions modified with rubber waste, Polimery 48/9 (2003) 633-640 (in Polish).

[4] N. Abramczyk, S. Drewing, K. Panasiuk, D. Żuk, Application of Statistical Methods to Accurately Assess the Effect of Gamma Aluminum Oxide Nanopowder on the Hardness of Composite Materials with Polyester-Glass Recyclate, Materials 15/17 (2022) 5957. DOI: https://doi.org/10.3390/ma15175957

[5] M. Kozioł, An effect of polymer matrix on mechanical performance of laminates reinforced with glass fibre, Kompozyty 10/4 (2010) 317-321 (in Polish).

[6] A.A. Nayeeif, Z.K. Hamdan, Z.W. Metteb, F.A. Abdulla, N.A. Jebur, Natural filler based composite

materials, Archives of Materials Science and Engineering 116/1 (2022) 5-13.
DOI: https://doi.org/10.5604/01.3001.0016.0972

[7] M. Chojnacka, Application of block copolymers and recycled rubber materials for modyfying of asphalts, Elastomery 16/3 (2012) 24-29 (in Polish).

[8] M. Al-Shablle, M. Al-Waily, E. Njim, Analytical evaluation of the influence of adding rubber layers on free vibration of sandwich structure with presence of nano-reinforced composite skins, Archives of Materials Science and Engineering 116/2 (2022) 57-70. DOI: https://doi.org/10.5604/01.3001.0016.1190

[9] S. Białasz, Practical use of rubber recyclates as a way to protect the environment, Ecological Engineering 19/5 (2018) 63-74 (in Polish).
DOI: https://doi.org/10.12912/23920629/94958

[10] M.M. Singh, H. Kumar, G.H. Kumar, P. Sivaiah, K.V. Nagesha, K.M. Ajay, G. Vijaya, Determination of strength parameters of glass fibers reinforced composites for engineering applications, Silicon 12/1 (2020) 1-11. DOI: https://doi.org/10.1007/s12633-019-0078-3

[11] M. Sienkiewicz, Polyurethane-rubber composites obtained with the use of rubber recyclates as a way to manage post-consumer car tires, PhD Thesis, Gdansk University of Technology, Gdańsk, 2010 (in Polish).

[12] M. Sienkiewicz, M. Wawrowska, K. Wiecierzycka, H. Janik, Methods of chemical modification of the surface of rubber granulate and rubber goods which are improving their adhesion to polyurethane, Elastomery 19/3 (2015) 26-34 (in Polish).

[13] O. Shechtman, Z. Gutierrez, E. Kokendofer, Analysis of the statistical methods used to detect submaximal effort with the five-rung grip strength test, Journal of Hand Therapy 118/1 (2005) 10-18.
DOI: https://doi.org/10.1197/j.jht.2004.10.004

[14] M. Shah, P. Mondal, A. K. Nayak, A. Bordoloi, Advanced titania composites for efficient CO_2 reforming with methane: Statistical method vs. experiment, Journal of CO_2 Utilization 39 (2020) 101160.
DOI: https://doi.org/10.1016/j.jcou.2020.101160

[15] C. Watała, How to effectively use statistical methods in planning and conducting a scientific experiment?, StatSoft, Warszawa. 2005 (in Polish). Available from: https://media.statsoft.pl/_old_dnn/downloads/jak_skutecznie_wykorzystywac_metody_statystyczne.pdf

[16] R. Jaśkiewicz, A. Stepniowska, Methodology of outliers determination for composite materials strength tests, Transactions of the Institute of Aviation 3/244 (2016) 77-82 (in Polish).
DOI: https://doi.org/10.5604/05096669.1222748

[17] K. Naresh, K. Shankar, R. Velmurugan, N. Gupta, Statistical analysis of the tensile strength of GFRP, CFRP and hybrid composites, Thin-Walled Structures 126 (2018) 150-161.
DOI: https://doi.org/10.1016/j.tws.2016.12.021

[18] T.K. Kim, Understanding one-way ANOVA using conceptual figures, Korean Journal of Anesthesiology 70/1 (2017) 22-26.
DOI: https://doi.org/10.4097/kjae.2017.70.1.22

[19] Mata emulsyjna EM 1002/450/125 KROSGLASS (in Polish). Available from: http://www.krisko.lublin.pl/chemia/zywice-poliestrowe-polimal/maty-tkaniny-rowingi/maty-szklane/mata-krosglass-450-1-rolka-50-5kg.html (access in 10.01.2022)

[20] Epidian® 6 (v-1 kg) (in Polish). Available from: https://www.zywicasklep.pl/epidian-reg-6-v-1-kg (access in 10.01.2022)