Particulate Filled Composite Plastic Materials from Recycled Glass Fibre Reinforced Plastics

Aare ARUNIIT [1]*, Jaan KERS [1], Dmitri GOLJANDIN [1], Mart SAARNA [1], Kaspar TALL [1], Jüri MAJAK [2], Henrik HERRANEN [2]

[1] *Department of Materials Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia*
[2] *Department of Machinery, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia*

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Glass fibre reinforced plastic (GFRP) scrap consisted of acrylic plastic with glass fibre reinforcement in polyester resin matrix was used in our experiments. The multi-functional DS-series disintegrator mills were used for mechanical processing of GFRP scrap. Preceding from the results characterization of the milled powder particles size, shape and other properties the numerical algorithm for modelling of the density of the new filler material was developed. The main goal of the current study is to develop new particulate filled composite plastic material from recycled GFRP scrap. With recovered plastic powder material the higher filler content in polyester resin matrix can be achieved. The new composite is modelled on basis of the properties of new material. Such an approach requires tests of the new material. The considered target characteristics of the new material are the tensile strength, elongation at break and the cost. The multicriteria optimization problem has been formulated and solved by use of physical programming techniques and Pareto optimality concept. The designed new composites were manufactured in different mixing ratios of powder and binder agent. The strength and stiffness properties of new composite material were tested.
Keywords: recycling, glass fibre reinforced plastic scrap, disintegrator milling, plastic powder.

1. INTRODUCTION

Composites are by their very nature mixtures of different materials: polymer, fibrous reinforcement (glass or carbon fibre) and in many cases fillers (these may be cheap mineral powders to extend the resin or have some other function, such as fire retardants) [1].

There are several potential recycling and end-of-life methods for polymeric composites including pyrolysis, hydrolysis, chemical recycling, regrinding, and incineration [2]. For pyrolysis reaction 1 kg composites needs 2.8 MJ energy, but can provide useful energies in the different forms of liquefied natural gas (LPG), fuel oil and composite fillers [3]. Consequently, the energy recovery of composite structures ideally obtainable through the pyrolysis method is 19 MJ/kg [3]. The more complex and contaminated the waste, the more difficult it is to recycle it mechanically [1, 4].

Mechanical recycling techniques have been investigated for both glass fibre and carbon fibre reinforced composites, but the most extensive research has been done on glass fibre recovery. The technique usually used is to initially reduce size of the scrap composite components in some primary crushing process [1]. The theoretical studies on milling by the collision method, which were conducted at Tallinn University of Technology (TUT), were followed by the development of the appropriate devices, called disintegrators, and the different types of disintegrator milling, the DS-series systems [4]. In the mechanical recycling process, all of the constituents of the original composite are reduced in size 50 mm – 100 mm pieces. The main size reduction stage would then be in a hammer mill or other high speed mill where the material is ground into a finer product ranging from typically 10 mm in size down to particles less than 50 μm in size [1].

Typically the finer graded fractions are powders and contain a higher proportion of filler and polymer that the original composite. The coarser fractions tend to be of a fibrous nature where the particles have a high aspect ratio and have higher fibre content [1].

Among the other mechanical direct contact milling methods (ball-milling, attritor milling, hammer milling, etc.) the plastics and composite plastics can be reprocessed by the collision method [5]. The theoretical studies on milling by the collision method, which were conducted at TUT Disintegrator Laboratory, were followed by the development of the disintegrator mills and centrifugal air-separation systems [6, 7].

Fillers are widely used in thermosets, thermoplastics and elastomers [8, 9]. However, in recent years it has become more widely recognized that fillers can enhance the manufacturing and mechanical properties of compounds [10, 11]. Current estimates put the global market for fillers at between 12 and 18 million tonnes annually [12]. For ideal filler, the characteristics should include following: a low cost, the availability, a good wetting and bonding surface a good chemical resistance characteristics [9, 13]. Originally, their main function was seen as reducing the cost of the compound, by filling the thermoplastic or thermosetting resin matrix. One of the targets for particulate fillers is also to decrease the weight of the manufactured composite part.

The problem considered consists of three objectives: the tensile strength and elongation at break subjected to maximization and the cost of the materials subjected to minimization.

The main goal of the current study is to develop new

*Corresponding author. Tel.: + 372-620-3353; fax.: + 372-620-3196.
E-mail address: *Jaan.Kers@ttu.ee* (J. Kers)

composite material with optimal physical and mechanical properties.

2. EXPERIMENTAL

2.1. Materials and methods

The cut-off technological edges of the polymethylmetaacrylate (PMMA) sheet material, then vacuum formed and reinforced with GFRP in the matrix of the polyester resin, were used as technological scrap. The main physical and mechanical properties of milled PMMA+GFRP plastic scrap were as following:

– for the PMMA surface layer: the tensile strength 78 MPa, modulus of elasticity 3.33 GPa, and density 1200 kg/m^3.

– the properties of the GFRP reinforcement (30 wt.% in polyester resin matrix) were: tensile strength 75 MPa, modulus of elasticity 7.70 GPa, and density 1700 kg/m^3.

The composite plastic plates of PMMA+GFP preliminarily cut into pieces with the dimensions of length 100 mm, width 100 mm and thickness 5 mm, were reprocessed by the mechanical method of milling by collision.

The reprocessing technology of the composite plastics in disintegrators consisted of three stages:

– preliminary milling of the composite plastic PMMA+GFP by the DSA-158 disintegrator in the conditions of direct milling (sieving was used to separate the glass fibre from the milled material);

– intermediate milling for the size reduction in the DSA-2 disintegrator in the conditions of multi-stage milling (powder samples for sieve analyses were taken and percentage of the separated glass fibre was determined);

– final milling to remove the glass fibre from the milled material was performed by the DSL-115 disintegrator system applying the direct selective milling conditions

The material preliminarily crushed was suitable for direct milling in the DSA-2 disintegrator. To estimate grindability, the specific energy of treatment was used. The distribution of the particle size was described by the modified Rosin-Rammler distribution function [6].

2.2. Characterization of milled product

The separated PMMA powder was classified by sieving to 5 volume fractions: (0 – 0.16; 0.16 – 0.32; 0.32 –0.63; 0.63 – 1.25; 1.25 – 2.5) and these fractions were analyzed separately. The size and shape of the separated PMMA powder fractions were determined by different methods: the sieving analysis (SA) and image analysis (IA). To evaluate the granularity of coarse powder (having the particle size more than 50 μm), the sieving analysis (SA) was used [5]. The distribution of the particle size is adequately described by the modified Rosin-Rammler function as the applied method [6].

To characterize ellipticity, the aspect ratio *AS* (similar to elongation in literature) was calculated by equation:

$$AS = a/b, \tag{1}$$

where *a* and *b* are the axes of the Legendre ellipse (the ellipse is an ellipse if it has its centre in the object's centroid with the same geometrical moments up to the second order as it is with the original object area).

To characterize the irregularity or the surface smoothness; the value of roundness *RN* was calculated by [14]:

$$RN = P^2/4\pi A. \tag{2}$$

(The roundness of the circle equals to one, if the object shape approaches the line segment, which approaches zero) [14].

The obtained aspect value is an important parameter for calculating the specific surface area of the particles of the tabular shape. Two proportionality constants for the particle shape were used (6 for the spheres and the *AS* value for the tabular-shaped particles) [5]. The specific surface area of the fractions (0 – 0.16; 0.16 – 0.32; 0.32 – 63; 0.63 – 1.25; 1.25 – 2.5) was calculated on the basis of formula [13].

$$SSA = \frac{K}{\rho}\left(\sum \frac{dW}{\overline{X}_m}\right), \tag{3}$$

where *SSA* is the surface area in m^2/g, *K* is the proportionality constant for the particle shape (spheres = 6, blocky and tabular = about 12), *dW* is the mass increment in grams, ρ is the density g/cm^3 and $\overline{X}_m$ is the average particle size of mass.

2.3. Preparation of composite materials

The mixtures of composite material were made in different compositions of fine (0 mm – 0.16 mm) and coarse filler (1.25 mm – 2.5 mm) materials and polyester matrix resin. To assure homogeneous mixtures and to avoid air entrapment the vacuum mixing technology was used. The vacuum mixed composite was casted into one-sided silicone moulds and de-moulded after 12 hours curing. Firstly, to study the effect how post-cure temperature is influencing the mechanical properties of composite plastics the batch of specimens was manufactured with 50 wt.% of resin content and ratio of fine (0 mm – 0.16 mm) and coarse filler (1.25 mm – 2.5 mm) fractions was 1/1. Then, first group of the specimens were post-cured at room temperature 20 °C and second group was post-cured in the oven at 50 °C for 12 hours. Secondly, the composite materials were manufactured with different resin/filler ratio. Thirdly the ratio of fine (0 mm – 0.16 mm) and coarse filler (1.25 mm – 2.5 mm) fractions was changed. These tests were intended to study the influence of the resin/filler ration to the mechanical properties of the composite material. After post-curing the top surface and edges of specimens were grinded and polished.

2.4. Mechanical testing of new composites

The mechanical properties of experimentally manufactured new composite materials were tested. Mechanical properties of the polymeric materials are mainly defined by tensile strength of the material. The tensile strength of the composite materials mainly depends on the adhesion strength between the matrix and reinforcement material.

Tensile test of composite plastic materials was performed according to standard EN ISO 527-1:2000. The

mechanical properties, such as tensile strength, elongation, modulus of elasticity were determined. Specimens for tensile test were prepared according EN ISO 527-2:2000 to type 1B. The cross-sections of the specimens were measured with calibrated calliper gauge with measurement accuracy 0.01 mm. The axial extensometer with the gauge length of 50 mm (travel +50 % to –10 %), was used to measure axial strain in the specimen. The applied testing system was the servo hydraulic testing machine Instron 8800. The tensile tests were performed with loading rate 2 mm/min, tolerance ±20 %. From manufactured compositions of the new composites the 5 specimens of each batch were selected and tested to get average values of the mechanical properties.

2.5. Modelling of new composite

In the following the new composite is modelled on basis of manufactured new composite materials. The considered target characteristics of the material are the tensile strength and elongation at break. Another important factor is cost of the new material. The combination of fractions of the PMMA powder, the mixing ratio of fractions and the mixing ratio of resin and powder are considered as design variables. The relation between the objectives and design variables is modelled on the basis of the experimental data. The response surface has been composed by use of artificial neural networks [15]. Real-coded genetic algorithm in combination with gradient method is utilized for finding global extreme values of the objective functions [16 – 20]. One simplified approach is to use the combination of fractions of the PMMA powder, the mixing ratios of fractions obtained in [5] and consider the mixing ratio of resin and powder as design variable. Five fractions (size in mm 0 – 0.16; 0.16 – 0.315; 0.315 – 0.63; 0.63 – 1.25; 1.25 – 2.5) of the recycled PMMA powder were used to prepare the mixtures of the filler materials. In [5] two key factors, density of the filler material and the specific surface area, are considered in modelling of new composite. The first factor – density of the filler material should be maximized and the second factor – specific surface area should be minimized in order to reduce the amount of the resin used i. e. the price of the new composite.

However, the maximal density and minimal specific surface area of the filler material are concurrent objectives and the results of the optimization problem posed in [5] are given as Pareto frontier. These points of the Pareto frontier correspond in general to different values of the optimality criteria considered in the current study (the tensile strength and elongation at break). Moreover, maximal density of the dry powder may be not in unique accordance with that in mixture of new material (powder amount in new material depends on specific surface area, roundness, aspect ratio, etc).

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Tensile test

To study the effect how post-cure temperature influences the mechanical properties of composite plastics the batch of specimens was manufactured with 50 wt.% of resin content and ratio of fine (0 mm – 0.16 mm) and coarse filler (1.25 mm – 2.5 mm) fractions was 1/1. After manufacturing the batch of specimens was divided into two groups. The first group was intended for post-cure in the oven at 50 °C for 12 hours and second one at room temperature 20 °C for 12 hours. The results of the tensile strength test showed that the post-curing at higher temperatures will increase tensile strength and modulus while elongation at break decreases (see Table 1). As the influence of post-curing temperature was clarified with testing the first tensile tests the specimens manufactured with second and third batch were post-cured in the oven at 50 °C for 12 hours.

Table 1. Chemical composition

No.	Post-cured at 50 °C	Post-cured at 20 °C	Stress, MPa	Strain, %	Tensile modulus, MPa
1	–	12 hours	9.6	1.1	1300
2	12 hours	–	18.0	0.5	3900

The tensile strength results of composite plastic materials with different resin wt.% and ratio of fine (0 mm – 0.16 mm) and coarse filler (1.25 mm – 2.5 mm) fractions are presented in Fig. 1.

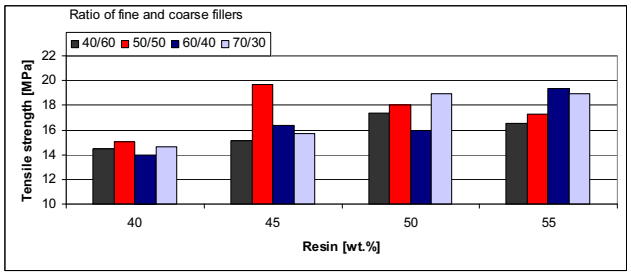

Fig. 1. Tensile strength of composite materials

The best tensile strength 19.7 MPA with tensile elongation at break 0.6 % belonged to the mixed composite consisting of 45 mass % of resin and 55 mass % of PMMA filler material (50 % of fine and 50 % of coarse fractions).

3.2. Surrogate models

A common technique for reducing computational cost in optimal design problems is to use surrogate models for the approximation of the objective and constraint functions. In this paper the surrogate models are used to guide the search towards a global optimum. The neural networks are applied for the approximation of the elongation at break and tensile strength of the material. An approach suggested is based on use of a two-layer network. The first layer has radbas neurons and the second layer has purelin neurons. In order to calculate the outputs for a concurrent set of input vectors, a network simulation function sim was employed. Using outputs generated by function sim the response surface was depicted. The obtained surface models corresponding to the elongation at break and tensile strength of the PMMA powder materials are given in Fig. 2 and Fig. 3, respectively.

In Figs. 2 and 3 the combination of fractions of the PMMA powder is fixed (in order to keep 3D figure) and

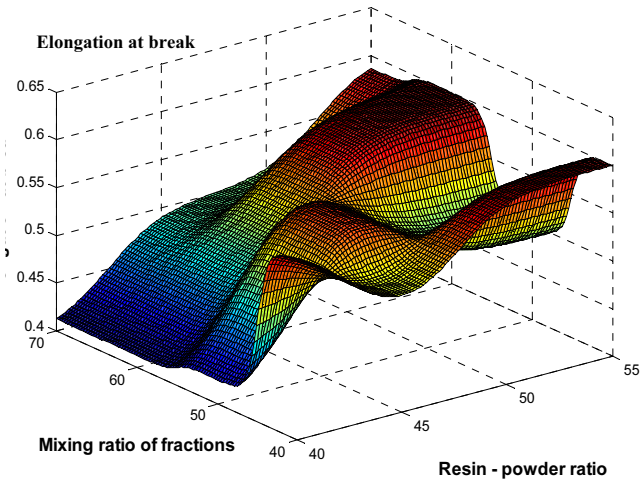

Fig. 2. Objective $F_1(\bar{x})$ – elongation at break

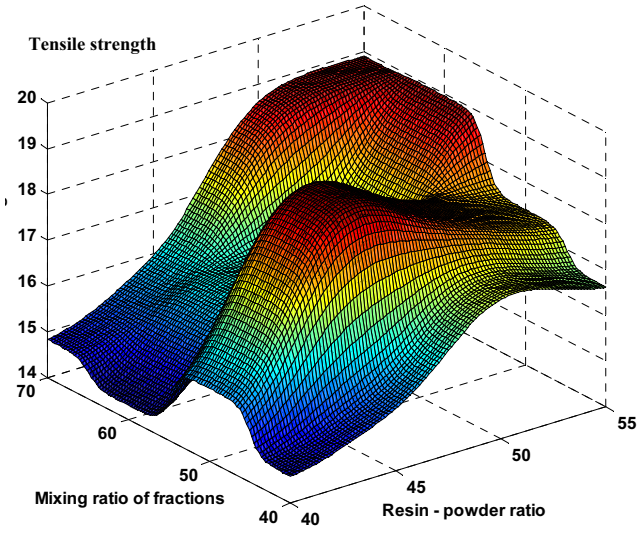

Fig. 3. Objective $F_2(\bar{x})$ – tensile strength

the dependence of objectives is shown with respect to the mixing ratio of fractions and the mixing ratio of resin and powder.

3.3. Optimal design

The problem considered above contains three objectives: the elongation at break and tensile strength subjected to maximization and the cost of the materials subjected to minimization. Thus, the multicriteria optimization problem can be formulated as

$$f(\bar{x}) = \min(f_1(\bar{x}), f_2(\bar{x}), f_3(\bar{x})), \tag{5}$$

subjected to linear constraints

$$x_i \le x_i^*, \qquad -x_i \le x_{i*}, \ , \qquad i = 1,...,n, \tag{6}$$

where $f_1(\bar{x})$ and $f_2(\bar{x})$ stand for the elongation at break and tensile strength (taken with minus sign) and $f_3(\bar{x})$ for the cost of the materials, respectively. It is also assumed that the objectives are normalized as

$$f_1(x) = \frac{\max F_1(x) - F_1(x)}{\max F_1(x) - \min F_1(x)};$$

$$f_2(x) = \frac{\max F_2(x) - F_2(x)}{\max F_2(x) - \min F_2(x)}, \tag{7}$$

$$f_3(x) = \frac{F_3(x) - \max F_3(x)}{\max F_3(x) - \min F_3(x)},$$

since the magnitudes and the units used to measure the objectives are different. Note, that the formula for computing $f_3(\bar{x})$ differs from those for computing $f_1(\bar{x})$ and $f_2(\bar{x})$, since the objective $F_3(x)$ is subjected to minimization, the objectives $F_1(\bar{x})$ and $F_2(\bar{x})$ to maximization, respectively. The design variables considered are the combination of fractions of the PMMA powder, the mixing ratio of fractions and the mixing ratio of resin and powder.

Analysing the behaviour of the objectives considered above it can be concluded that contradictionary behaviour can be perceived between the tensile strength and cost, also between the elongation at break and cost. However, the tensile strength and elongation at break behaves similarly. In that reason in the following the two objectives – tensile strength and elongation at break are combined into one objective employing the weighted summation and compromise programming techniques. The relationship between the two combined criteria and cost (third criteria) is clarified by use of Pareto optimality concept.

According to the weighted summation technique, all the criteria are scaled, multiplied by weights and summed into the general objective f_{ws} as

$$f_{ws} = \sum_{i=1}^{m} w_i f_i, \tag{8}$$

where m is the number of the optimality criteria used, w_i is the weight of the i-th criteria and

$$\sum_{i=1}^{m} w_i = 1, \qquad 0 < w_i \le 1. \tag{9}$$

The tensile strength and elongation at break are combined into one objective, thus $m = 2$.

The objective function in compromise programming is defined as the family of distance functions

$$f_{cp} = \left[\sum_{i=1}^{m} (w_i d_i)^c \right]^{1/c}, \tag{10}$$

where w_i weights the importance of the discrepancy between the i-th objective and its ideal value and c reflects the importance of maximal deviation from the ideal solution. Obviously, if $c = 1$ the formula (10) reduces to formula (8), i. e. the compromise programming includes the weighted summation technique as a special case. If $c > 1$, then the larger distances from an ideal solution are penalized more than smaller distances.

As mentioned above the contradictionary behaviour can be perceived between the tensile strength and cost, also between the surface hardness and cost. This is the case when use of Pareto optimality concept is justified.

The multiple criteria analysis (MCA) techniques considered above (see [18] for details) are based on combining multiple objectives into one objective and solving the latter problem as a single objective optimization problem. Independent of the methodology

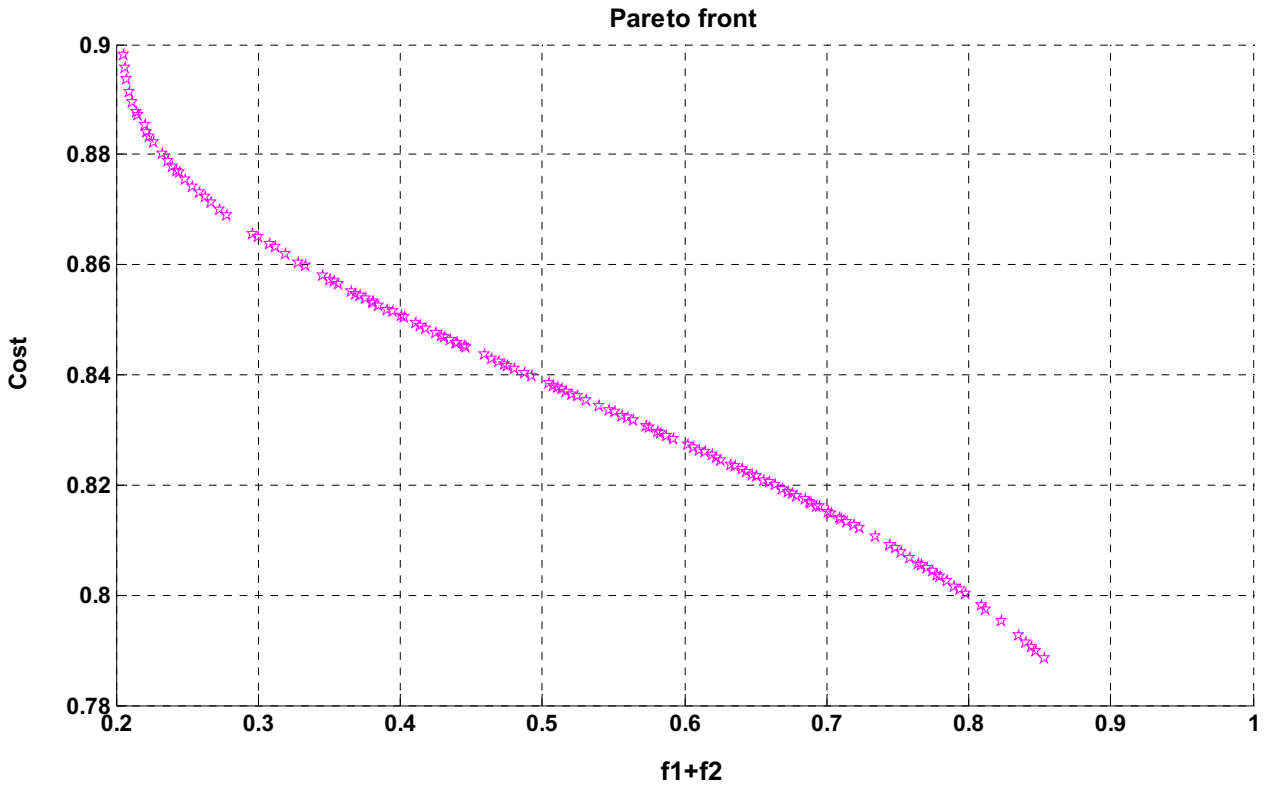

Fig. 4. The combined objective $f_{cp}(\bar{x})$ versus cost

how the objective functions are combined into one objective, such an approach has some drawbacks. Namely, the relative importance of the objectives is not generally known and the evaluation of the weights is complicated.

As an alternate approach, the Pareto optimality concept can be used according to which all solutions on the Pareto front are optimal (the Pareto front represents the set of all "non-dominated" points). The Pareto front of the combined objectives (10) and cost is given in Fig. 4.

Obviously, the Pareto front of the objective functions does contain more information than the physical programming approaches discussed above. The shape of the Pareto front provides valuable information. However, the selection of an optimal solution is still complicated and depends on a number of factors, like the specific problem considered, additional information available, etc. [19 – 21].

4. CONCLUSIONS

Mechanical reprocessing is continually the most commonly used technology for recycling thermosetting composite plastics. The reprocessing of the composite PMMA+GFP plastic scrap by using disintegrator milling will enable to produce the acrylic plastic powder with a determined granularity and technological properties (the apparent density).

The results of the tensile strength test showed that the post-curing at higher temperatures will increase tensile strength and modulus while elongation at break decreases.

The new composite is modelled on the basis of the properties of manufactured new composite materials. The target characteristics of the material considered are the tensile strength and elongation at break. Another important factor is cost of the new material. The combination of fractions of the PMMA powder, the mixing ratio of fractions and the mixing ratio of resin and powder are considered as design variables. The relation between the objectives and design variables is modelled on the basis of the experimental data. The surrogate models are used to guide the search towards a global optimum. The neural networks are applied for the approximation of the elongation at break and tensile strength of the material.

The problem considered is consisting of three objectives: the tensile strength and elongation at break subjected to maximization and the cost of the materials subjected to minimization. Analysing the behaviour of objectives considered it has been concluded that the contradictonary behaviour can be perceived between the tensile strength and cost, also between the elongation at break and cost. The relationship between the combined criteria (elongation at break and tensile strength) and cost is elucidated by use of Pareto optimality concept. Real-coded genetic algorithm in combination with gradient method has been utilized for finding global extreme values of the objective functions. The sensitivity analysis showed that the objective functions are most sensitive with respect to the mixing ratio of resin and powder.

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REFERENCES

1. **Pickering, S. J.** Recycling Technologies for Thermoset Composite Materials – Current Status *Composites Part A* 37 2006: pp. 1206 – 1215.

2. **Broekel, J., Scharr, G.** The Specialities of Fibre-reinforced Plastics in Terms of Product Life-cycle Management. *Journal of Materials Processing Technology* 162 – 163 2005: pp. 725 – 729.
3. **Scheirs, J.** Polymer Recycling. Science Technology and Application. John Wiley&Sons Inc.; London, 1998.
4. **Al-Salem, S. M., Lettieri, P., Baeyens, J.** Recycling and Recovery Routes of Plastic Solid Waste (PSW): A Review *Waste Management* 29 2009: pp. 2625 – 2643.
5. **Kers, J., Majak, J., Goljandin, D., Gregor, A., Malmstein, M., Vilsaar, K.** Extremes of Apparent and Tap Densities of Recovered GFRP Filler Materials *Composite Structures* 92 (9) 2010: pp. 2097 – 2101.
6. **Tamm, B., Tümanok, A.** Impact Grinding and Disintegrators *Proceedings of the Estonian Academy of Sciences* 2 1996: pp. 209 – 223.
7. **Kers, J., Kulu, P., Goljandin, D., Kaasik, M., Ventsel, T., Vilsaar, K., Mikli, V.** Recycling of Electronic Wastes by Disintegrator Mills and Study of Separation Technique of Different Materials *Materials Science* (*Medžiagotyra*) 14 2008: pp. 296 – 300.
8. **Schwartz, C. J., Bahadur, S.** The Role of Filler Deformability, Filler-polymer Bonding, and Counterface Material on the Tribological Behavior of Polyphenylene Sulfide (PPS) *Wear* 251 (1 – 12) 2001: pp. 1532 – 1540.
9. **Xanthos, M.** Functional Fillers for Plastics. Wiley -VCH Verlag GMBH, Weinheim, 2005.
10. **Bartl, A., Hackl, A., Mihalyi, B., Wistuba, M., Marini, I.** Recycling of Fibre Materials *Transactions of the Institution of Chemical Engineering Part B* 83 2005: pp. 351 – 358.
11. **Asokan, P., Osmani, M., Price, A. D. F.** Assessing the Recycling Potential of Glassfibre Reinforced Plastic Waste in Concrete and Cement Composites *Journal of Cleaner Production* 17 2009: pp. 821 – 829.
12. **DeArmitt, C., Rothon, R.** Fillers and Surface Treatment. *Plastics*, *Additives and Compounding* 4 (5) 2002: pp. 12 – 14.
13. **Katz, H. S., Milewski, J. W.** Handbook of Fillers for Plastics. Van Notstrand Reinhold, New Work, 1987.
14. **Kulu, P., Tümanok, A., Mikli, V., Käerdi, H., Kohutek, I., Besterci, M.** Possibilities of Evaluation of Powder Particle Granulometry and Morphology by Image Analysis *Proceedings of the Estonian Academy of Sciences* 4 1998: pp. 3 – 17.
15. **Gerald, C. F., Wheatly, P. O.** Applied Numerical Analysis. Fifth Edition, California Polytechnic State University, 1994.
16. **Konak, A, Bartolacci, M. R.** Designing Survivable Resilient Networks: A Stochastic Hybrid Genetic Algorithm Approach. Omega *The International Journal of Management Science* 35 2007: pp. 645 – 658.
17. **Rowe, M. D., Pierce, B. C.** Sensitivity of the Weighted Summation Decision Method to Incorrect Application *Socio-economic Planning Science* 16 (4) 1982: pp. 173 – 177.
18. **Zeleny, M.** Compromise Programming. In: Multiple Criteria Decision Making. University of Southern Carolina Press, Columbia, 1973.
19. **Bassir, D. H., Zapico, J. L., Gonzales, M. P., Alonso, R.** Identification of a Spatial Linear Model Based on Earthquake-induced Data and Genetic Algorithm with Parallel Selection *International Journal of Simulation and Multidisciplinary Design Optimization* 1 2007: pp. 39 – 48.
20. **Pohlak, M, Majak, J, Eerme, M.** Optimization of Car Frontal Protection System *International Journal of Simulation and Multidisciplinary Design Optimization* 1 2007: pp. 31 – 38.
21. **Pohlak, M. Majak, J. Karjust, K. Küttner, R.** Multicriteria Optimization of Large Composite Parts *Composite Structures* 92 2010: pp. 2146 – 2152.

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