Proc. Estonian Acad. Sci. Eng., 2007, **13**, 2, 105–116

Reprocessing technology of composite plastic scrap and properties of materials from recycled plastics

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Received 8 November 2006, in revised form 13 February 2007

Abstract. This study had two aims: to develop prospective techniques for recycling of composite plastic scrap and to find potential application areas for secondary raw materials. The method of collision was selected to treat composite plastic wastes, using a disintegrator mill. In our experiments, the particle size of acrylic plastic was reduced and glass fibres were separated. The paper describes the results of materials separation, granularity of the milled material and morphology of the plastic powder particles. To develop new filler materials for filler–resin systems, plastic powders with different granularity were used. Mechanical properties of new composite materials were examined. The developed new acrylic powder filler materials are prospective for use in the filler–resin systems to reinforce acrylic shells.

Key words: environment-friendly technology, scrap management, composite plastic scrap, recycling, disintegrator mill.

1. INTRODUCTION

Recent studies [1,2] show that through certain processes all types of plastics are suitable for recycling. Besides mechanical recycling, chemical recycling, gasification and liquefaction can be used [3,4]. Fibre-reinforced polymeric waste can be treated by pyrolysis [5]. It is equally clear, however, that no single method provides a universal answer and a sensible recycling policy will probably involve different approaches [6].

According to EU waste directives, the hierarchy of waste management is: 1) prevention, 2) reuse, 3) recycling, 4) energy recovery, 5) incineration without energy recovery, and 6) landfill. From directives it follows that the producers are responsible for environment protection during the lifecycle of their products [7].

The producers should form organizations in charge of managing collection and recycling of post-consumer products.

This leads on to a general policy regarding the use of materials, where there is growing support for a cascade philosophy, in which materials have a high-grade first use, followed (possibly) by a lower-grade second use, after which they may be disposed of by safe incineration with recovery of energy, thus giving a threefold benefit [8]. To meet these requirements, two solutions can be proposed. Firstly, to extend the lifecycle of the product in combination with durable materials and durable design. Secondly, to extend the lifecycle of the materials to reduce environmental impacts related to materials manufacturing and transportation.

The interest of this study lies with Estonian bathroom equipment manufacturing companies. Their approach is that the composite plastic scrap (vacuum formed acrylic plastic with glass fibre reinforcement) has low density and thus has to be precrushed to save transportation and landfilling costs.

The aim of this investigation is to study the reprocessing of problematic plastic scrap (composite plastics) by using mechanical methods, milling by collision. Very important is the recovery of the obtained secondary plastic product with optimization of the technology for the production of plastic powders with predetermined properties (granularity, morphology and technological properties) and to develop a new filler material of the PMMA plastic powder of optimal density and with needed properties of flowability.

2. THE METHOD

The material was treated with the collision method. Theoretical studies on milling by the collision method, which were conducted at Tallinn University of Technology, were followed by the development of devices, called disintegrators, and types of disintegrator milling (DS-series) systems [9]. The separation systems in the DS-series disintegrators are based on aerodynamic forces. Depending on the design of the disintegrator systems, direct, separative and selective types of milling are available and used in powder production [9].

3. EXPERIMENTAL

3.1. Studied materials

Industrial PMMA scrap can be divided into two groups: pure acrylic plastic scrap forms about 20% and reinforced acrylic plastic scrap about 80% of the total amount. PMMA scrap without technological additives cannot be recycled and reextruded to produce new PMMA sheet material because of the amorphous structure of this thermoplastic material. Heating up an acrylic plastic material over glass transition temperature (100 °C) converts the plastic into a rubber-like state, which makes this material ideal for vacuum forming. Continued heating causes thermal degradation of the material instead of melting. Physical and mechanical

Table 1. Physical properties of the studied plastics at 23 °C

Material	Tensile strength R_m, N/mm^2	Modulus of elasticity E, MN/mm^2	Impact strength, kJ/m^2	Density ρ, kg/m^3	Elongation after fracture A, %
PMMA	78	3.33	12	1200	4
Polyester resin	50	4.60	5	1200	2.3
GFP	75	7.70	9	1700	3

properties of the plastics to be recycled are given in Table 1. PMMA sheet material and vacuum-formed polyester resin, reinforced with glass fibre plastic (GFP), were used as the composite plastic scrap.

3.2. Reprocessing technology

For the milling of composite plastic scrap, different disintegrator mills were used [9]. As a result of our previous study, the 20% mass of industrial acrylic plastic scrap was reprocessable by high-energy disintegrator mills [10]. Thus we assumed that the high-energy mill can be used for the remaining 80% of the mass. To recycle composite plastic scrap, we then focused on the size reduction of the acrylic plastic constituent and on the separation of the glass fibre constituent.

Disintegrator milling enables milling with simultaneous separation of components of low toughness [11]. Composite plastic strips (PMMA+GFP) with dimensions of 100 × 100 × 5 mm were retreated with milling by collision.

The reprocessing technology for composite plastic scrap in disintegrators consisted of two steps:

1) preliminary milling of reinforced acrylic strips with the experimental DSL-158 disintegrator in direct milling conditions (sieving, as used for separating the glass fibre from the milled material) or with the semi-industrial DSA-2 disintegrator in the conditions of multi-stage milling (powder samples for sieve analysis were taken and the percentage of the separated glass fibres was determined),
2) final milling with the DSL-115 disintegrator milling system, using the direct or separative milling conditions to remove glass fibres from the milled material.

3.3. Study of the granularity and morphology

Geometrical characteristics of the milled material can be divided into size and shape parameters. Size parameters (e.g., area perimeter) describe the geometrical object independently of its shape. On the other hand, shape characteristics describe mainly the shape independently of the size. In this study, the particle size of acrylic plastic powder was characterized by sieving analysis (SA) and image analysis (IA). Particle shape was characterized by image analysis. Coarse powder granularity (particle size over 50 μm) was evaluated by sieve analysis to ensure sufficiently good results. Particle size distribution is adequately described by the modified Rosin–Rammler distribution function $f_m(X)$. This method can be used to characterize powders, produced by collision [12]:

$$f_m(X) = \frac{n-1}{m}\left(\frac{x-x_0}{m}\right)^{n-1} e^{-\frac{n-1}{n}\left(\frac{x-x_0}{m}\right)^{n}}, \tag{1}$$

where n, m and x_0 are parameters of the distribution. Logarithmic size of the particle, x, is given as

$$x = \log_k \frac{X_0}{X}, \tag{2}$$

where x is the natural size of the particles of the material, X_0 is the upper limit of the possible particle size, X is the natural size of the particles and k is the coefficient (ratio) of the sieve system used in the experiments $(k = 2, 2^5, 2^{25})$.

Data about particle size, obtained with the image analysis method, were primarily described through the arithmetical mean diameter d_m of the measured values. The values of d_m depend on the number of particles. Particle shape was characterized by the IA method and following shape factors were calculated: 1) the elliptic parameter to characterize ellipticity, aspect ratio AS, calculated as

$$AS = a/b, \tag{3}$$

where a and b are the axes of the Legendre ellipse (it is an ellipse with the centre in the object centroid and with the same geometrical moments up to the second order as with the original object area); 2) surface smoothness is characterized by the roundness RN, calculated as

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

where P is the perimeter and A is the area of the particle. Roundness of a circle is equal to 1, in all other cases roundness is greater than 1 [13].

4. RESULTS AND DISCUSSION

4.1. Recycling of the composite plastic scrap

The results, obtained from preliminary size reduction of the composite plastic PMMA+GFP in disintegrator mills, are shown in Fig. 1. Particle size of the output from the DSA-158 disintegrator was approximately 13–25 mm. The material preliminarily crushed was suitable for direct milling in the DSA-2 disintegrator. Table 2 shows the results of the separation of the glass fibre plastic from the composite plastic scrap.

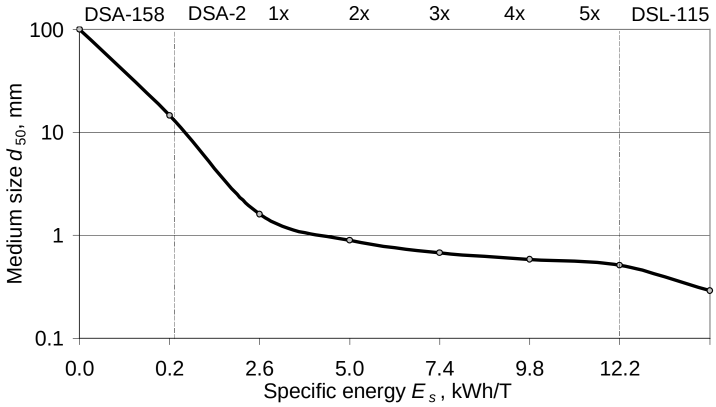


Fig. 1. Dependence of the particle size of the milled composite plastic PMMA+GFP on the specific energy of treatment.

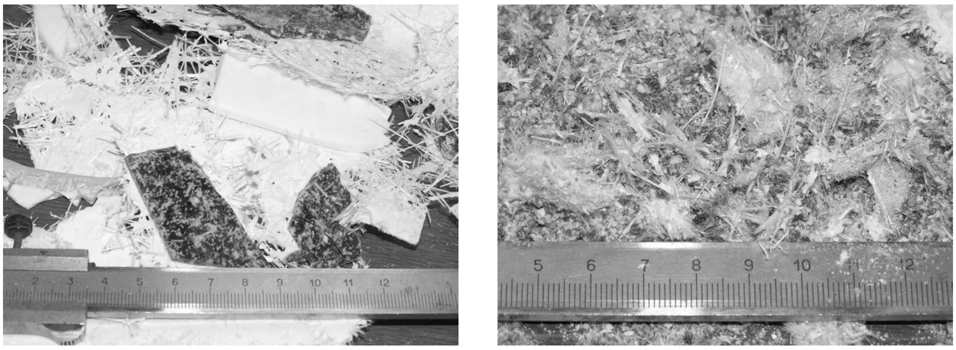
Table 2. Separation of the GFP

Milling stages	Milling device	Separation method	Separated GFP, mass %
I	DSA-158	Sieving	16.3
	DSA-2	Sieving	12.2
II	DSL-115	Air classifying	16.5

As it follows from Table 2, the total amount of separated GFP was 45 mass %. As a result, we can use 55 mass % of acrylic plastic from the composite plastic scrap. GFP can be reused in the production of polymeric concrete products as reinforcement.

4.2. Investigation of the particle shape

The data, necessary in the investigation of the particle size, were obtained using an image processing system, which consisted of a Nikon Microphot-FX, an optical microscope (OM) and a video transfer system. Measurements were performed in the transmission regime of the OM to obtain more accurate results for the particle size as compared to a reflection regime. Size and shape parameters were determined using image analysis (Image-Pro Plus 3.0 system). Acrylic plastic powder particles with an average size less than 5 mm are cubic-shaped and their mean aspect and roundness are measured only flatwise. Plastic powder particles over 5 mm are plate-shaped and their aspect and roundness are calculated as the arithmetical average of two images (flatwise and alongside). For example, medium size particles between 5–11.2 mm have the aspect flatwise 1.54 and alongside 3.25, an average aspect being 2.40 (Fig. 2). Shape factors of the milled PMMA powder particles are given in Table 3.



(a) (b)

Fig. 2. (a) PMMA+GFP composite product, preliminarily milled in DSA-158; (b) PMMA+GFP product, milled in DSL-115.

Table 3. Mean diameter, aspect and roundness of acrylic plastic powder fractions

Fraction, mm Parameter	<0.32	0.32–0.63	0.63–1.25	1.25–2.50	2.50–5.00	5.00–11.20	>11.20
d_m, mm	0.111	0.490	1.16	2.2	4.45	8.08	15.7
Aspect *AS*	2.07	1.91	1.71	1.61	1.55	2.40	3.01
Roundness *RN*	1.63	1.69	1.79	1.71	1.44	1.77	2.00

4.3. Using of the milled product

Preliminary tests to find areas for acrylic powder applications as a new filler material were made by using the *Solid Surface* casting technology. For example, most of the bathroom washbasins are produced by the casting technology. Commonly, washbasins are made from a composite material consisting of a binder agent (unsaturated polyester resin), a filler material (dolomite powder), and a catalyst agent added to the resin to accelerate hardening. The mixing ratios of the binder agent and the filler material are 25/75 mass %. The traditional filler material, used in the casting technology, is a high-white dolomite filler, composed of $CaMg(CO_3)_2$ with a density of 2850 kg/m^3 and particle sizes of coarse fractions 0.2–0.6 mm and 0.1–0.3 mm, and of the fine fraction less than 0.1 mm. For this purpose, composites with different mixing ratios of the binder matrix (unsaturated polyester resin) and the filler (acrylic powder) were designed. Filler volumes varied from 50 to 65 mass %. The filler consisted of 50 mass % of coarse fractions (0.7–1.4 mm) and 50 mass % of fine fractions (0.2–0.4 mm) of acrylic powder material. Peroxide catalyst (1 mass % of the matrix) was added to accelerate polymerization, to ensure transforming from the liquid to the solid state with desired physical properties. The liquid mixture of the composite was cast into a plate-shape mould (500×500 mm^2) with a layer thickness of 15 mm. We assumed that by increasing the acrylic filler content, the mixed polyester resin would ensure hardness and good wear resistance properties of the working surface of the washbasin. The hardening time of the composite was four hours. The best flow characteristics of the mixture were obtained with 50 mass % of acrylic filler and 50 mass % of matrix, but the best surface quality and hardness after polishing was achieved with a mixture of 66 mass % of the acrylic filler and 34 mass % of the resin matrix. Flow characteristics of the mixture 66/34 could be improved by using a lower viscosity matrix.

4.4. Mechanical testing of the new composite material

4.4.1. Tensile test

Mechanical properties of the new composite material were determined. Specimens of plastic composites (in different compositions of the filler and binder agent) were prepared according to ISO and DIN standards. Mechanical properties of a plastic are primarily defined by the tensile strength of the material. Unlike metals, the most important factor, influencing plastics, is temperature. Therefore it is important to know the minimum and maximum working temperatures of the plastic, which are not entailing changes in physical and mechanical properties of the material. The tensile strength of composite plastic materials mainly depends on the adhesion strength between the matrix and reinforcement. For glass fibre reinforced plastics, the direction of reinforcement is important (uni-axial, bi-axial, multi-axial). In our case, instead of fibres, the new composite plastic material consists of the polyester resin matrix and granular filler (reinforcement, acrylic plastic) instead of fibres. Test specimens of type 1B were machined from the cast plate material in accordance with ISO 527-2/1A/50 standard. To compare test results, specimens of pure acrylic sheet material were made. Table 4 gives the tensile test results.

The tensile test of the 38/62-composite gave an average tensile strength of 20.7 N/mm^2 while the tensile strength of the 0909-acrylic plastic specimen was 41.6 N/mm^2. We assume that the pores inside the material influence the tensile strength of the new composite material.

Table 4. Results of the performed tensile tests with pure acrylic sheet material

Test piece material	Elongation after breakage ε_B, %	Tensile strength R_m, N/mm^2
35/65-composite	0.66	10.1
34/66-composite	0.36	13.2
40/60-composite	0.87	17.7
45/55-composite	1.28	15.9
50/50-composite	0.95	18.2
38/62-composite	1.30	20.7
0909-acrylic plastic	2.02	41.6

4.4.2. Hardness test

Hardness tests were performed according to the Brinell hardness test method for metals EVS-EN-ISO 6506-1 [14]. A typical test uses a 10 mm diameter steel ball as an indenter with a 29 kN force. For softer materials, a smaller force is used; for harder materials, a tungsten carbide ball is used. The indentation is measured and hardness is calculated as

$$HBS = \frac{2F}{\pi D(D - \sqrt{(D^2 - d^2)})}, \tag{5}$$

where F is applied force (N), D is the diameter of the indenter (mm) and d is the diameter of the indentation (mm). The Brinell indentation hardness test was performed with a 1 mm diameter steel ball, with loads 49 and 98 N and loading time 30 sec:

- *HB* (1 mm diameter steel ball and load 49 N) to test materials 1–2 and 4–7 (Table 5);
- *HB* 1/10 (1 mm diameter steel ball and load 98 N) to test material 3 (because the load 49 N did not make observable indentation on the measured surface and thus the load 98 N was used). Results of the Brinell indentation hardness test are shown in Table 5.

4.5. Abrasive wear resistance

Abrasive wear resistance tests were made according to the standard test method for measuring abrasion using dry sand/rubber wheel apparatus. This test method covers laboratory procedures for determining the resistance of metallic materials to scratching abrasions by means of the dry sand/rubber wheel test. Dry sand/rubber wheel abrasion tests involve the abrading of a standard test specimen with a grit of controlled size and composition. The abrasive is introduced between the test specimen and a rotating wheel with a chlorobutyl rubber tire or rim of definite hardness. This test specimen is pressed against the rotating wheel at a specified force by means of a lever arm, while a controlled flow of grit abrades the test surface. The rotation of the wheel is such that its contact face

Table 5. Brinell hardness of composite materials

No.	Type of the material	Load *F*, N	*HBS*
1.	5050-composite (filler PMMA 50 mass % and binder 50 mass %)	49	21.5
2.	3565-composite filler PMMA 65 mass % and binder 35 mass %)	49	13.3
3.	3466-composite (filler PMMA 25 mass %, $CaCO_3$ $MgCO_3$ 41 mass % and binder 34 mass %)	98	47.4
4.	4555-composite (filler PMMA 55 mass % and binder 45 mass %)	49	15.2
5.	40/60-composite (filler PMMA 45 mass % and binder 55 mass %)	49	21.1
6.	38/62-composite (filler PMMA 62 mass % and binder 32 mass %)	49	13.4
7.	0909-acrylic plastic sheet	49	26.1

Table 6. Abrasive erosion wear resistance of plastic composite materials

Material	Density, g/cm^3	Wear rate		Relative wear resistance, ε_v
		mg	mm^3/Nm × 10^{-5}	
0909-PMMA sheet	1.19	95.0	858.6	1.0
34/66-composite	1.57	148.9	1346.2	0.64
40/60-composite	1.08	101.5	917.3	0.94

moves in the direction of the sand flow. Specimens are weighed before and after the test and the loss in mass is recorded. The rubber wheel abrasion test was performed according to the standard ASTM-G-65-94 [15]. The test parameters of the rubber wheel were as follows: rubber wheel (diameter 228.6 mm, width 12 mm), abrasive (quartz sand, grain size 0.01–0.30 mm, mass 0.5 kg), normal force (140 N) and rotation speed 60 rpm. The results of the abrasive erosion test are presented in Table 6. The relative wear resistance ε_v of plastic composites was calculated from the ratio of the volume wear rates of the reference material PMMA.

4.6. Porosity of the composite material

To study the porosity of the cast composite material, specimens of the size 50 × 50 × 10 mm were made. The surfaces of the specimens (top, bottom and cross-section) were ground and polished. Specimen surface photos were taken and the pictures were processed (Fig. 3). The images were analysed with Image-Pro Plus 3.0. Firstly, the surface areas of the matrix and the pores were calculated. The total area of the pores was 6.5%. Data concerning pore size, obtained by the image analysis method, were primarily described through the arithmetic mean diameter d_m of the measured values (Fig. 4). The mean diameter of the pores was 97 μm.

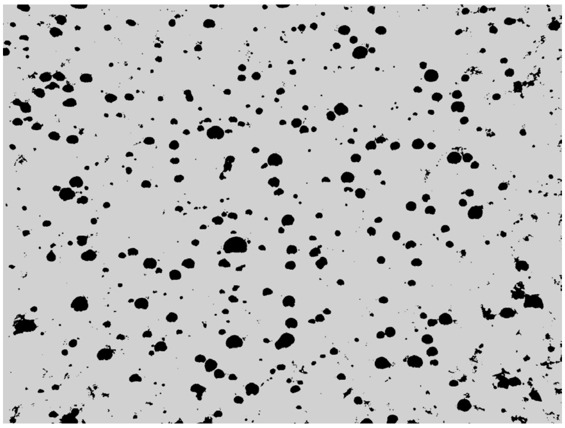


Fig. 3. Porosity of the composite material.

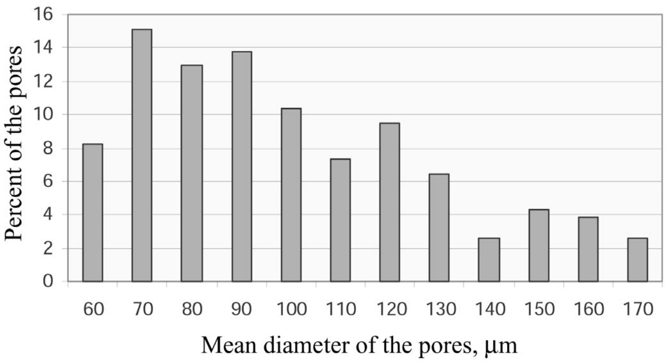


Fig. 4. Distribution of the mean diameter of the pores.

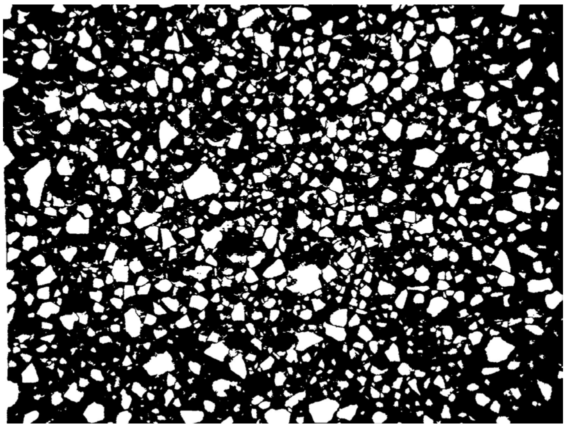


Fig. 5. Particles inside the composite matrix.

As mentioned above, an increase in the acrylic filler content in the mixed polyester resin ensures material strength and hardness and good wear resistance properties of the material surface. Therefore it is important to determine the optimal size and shape of particles in the composite.

As it follows from Fig. 5, the mean diameter of a surface particle was 105 μm. The mean roundness parameter RN of particles was 1.56 and the mean aspect AS was 1.67.

5. CONCLUSIONS

1. Plastic powder with a particle size of about 1–2 mm can be produced by two-step milling and 95 mass % of the glass fibre content can be separated by final selective milling.

2. The retreated material can be recovered in the same production process where it is generated. Milled PMMA powder is applicable as a filler material in the casting technology.
3. Based on the results of tensile and hardness tests, two composite materials, 34/66 and 40/60 were selected for the abrasive resistance test. This test showed that the composite 40/60 had the best relative wear resistance properties ($\varepsilon_v = 0.94$), which were closest to the reference material PMMA.
4. The aim of further studies is to design a composite material for washbasin production. Reprocessed plastics washbasins, produced from the new composite material, will increase the wear resistance of the working surface. At the same time, as compared to the dolomite filler, double reduction in weight can be achieved.

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Komposiitplastijäätmete töötlus ja taaskasutatud plasti omadused

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Komposiitplastijäätmed – nii tööstus- kui ka olmejäätmed – on probleemiks kogu maailmas, sest neid ei ole võimalik töödelda ega taaskasutada nagu enamikku termoplaste. Eestis on komposiitplasttooteid valmistavatel ettevõtetel (sanitaartehnika, paatide, suusabokside jms valmistajad) oma tootmisjäätmetega samuti probleeme. Praegu ladustatakse neid prügilasse, tulevikus on see aga keelatud. Komposiitplastijäätmetele, mis koosnevad akrüül- ja klaasplastist, ei ole maailmas siiani ühtki töötlemise ega materjali taaskasutuse meetodit välja töötatud ja sellest tulenevalt on artiklis võetud vaatluse alla komposiitplastist tootmisjäätmete mehaaniline töötlemine desintegraatorjahvatuse teel. On uuritud komposiitplastijäätmete töödeldavust desintegraatortehnoloogiat kasutades. Selleks on kasutatud mitut tüüpi desintegraatorveskeid ja jahvatussüsteeme (laboratoorseid ja pooltööstuslikke, otse-, selektiiv- ja separatsioonjahvatus). Materjalide jahvatusprotsess koosneb reeglina kolmest etapist: eelpurustus, eel- ja lõppjahvatus. On uuritud materjalide jahvatatavust, osiselist koostist ning osakeste kuju sõel- ja kujutisanalüüsi meetodeid kasutades. On läbi viidud katsed akrüülplastipulbri tehnoloogiliste omaduste määramiseks. On uuritud saadud täiteainete kasutatavust uute komposiitmaterjalide valmistamiseks *solid surface* tehnoloogiaga ja määratud komposiitplastide mehaanilised omadused (tõmbetugevus, kõvadus, kulumiskindlus).