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Comparison of Impact Resistance on a Knitted Prosthesis Based on Polypropylene and Acrylic Cements Based on Poly(methyl methacrylate)

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Abstract
The aim of the study was to compare the physical and mechanical properties of known prostheses for cranioplasty: knitted Codubix based on polypropylene and Modela-cryl resin based on PMMA. It was expected that the study would allow to check whether it is possible to combine their properties, which should enable the preparation of a new material with properties combining the best features of both components. Physico-chemical and mechanical properties were evaluated. It was found that the two materials meet the requirements for chemical purity, ensuring the safety of their use. Regarding the mechanical properties, the energy of impact diffusion for two types of prostheses was determined applying the Drop Tower technique. The polymerisation heat of Modela-cryl resin was determined in real time using the DSC technique.

Key words: *Cranioplasty materials, acrylic cements, drop tower, impact resistance.*

Introduction

In a typical implantation environment, biomaterials applied must perform their function in a changeable state of tension and movement, as well as with reactive tissue and in a biological fluid environment, which can lead to irreversible changes in the material and, as a consequence, to loss of their function. Taking the above-mentioned data into account, introducing a new material for medical purposes is connected with the necessity to conduct a series of mechanical, chemical and biological tests. The usefulness of the new material is first checked in experimental laboratory conditions and then in an artificial biological environment *(in vitro*). Initial research provides information about physical and chemical features, structure stability, toxicity for tissues, behaviour in the bloodstream, and many others. Materials which receive a positive evaluation in the physio-chemical and biological *in vitro* tests can be tested *in vivo*. In the i*n vivo* tests, the material activity is analysed after implantation in the organism of experimental animals. Because of the 3R directive guidelines and as well as for ethical reasons, the aim is to extend the range of *in vitro* tests that would allow the prediction and assessment of biomaterials tested *in vivo* conditions. Consequently, the possibility of use of biomaterial in surgical practice is determined by the positive output of clinical examination.

In the human organism soft tissues (skin, blood vessels, cartilage, ligaments) and hard tissues (bones, teeth) can be distinguished. Bones are built of two main ingredients: collagen fibres, which provide flexibility and elasticity, and mineral factors, mainly calcium and phosphorus compounds (e.g. hydroxyapatite), which are responsible for hardness and stiffness. The two basic tissues which form a bone are of a hard (cortical) and spongy (cancellous) type. Cortical bone with high density and very good mechanical features is created in places of the highest burden. It is made of lamina and osteons with a Haversian Canal, which contains blood vessels, nerves and connective tissue. Spongy bone is the bone filler, which is not as hard as cortical bone, but it is lighter and does not need so many minerals. It is made of short, variously oriented bone trabecules. Constant tension, shortening and prolonging of the bone leads to fluid suction to its canals. Oxygen is transported in the same way, which means that stress and strain has an influence on the inner bone structure, and along with the stress, the bone density changes. Because of the complicated and various bone structures, as a bone-substitute various types of synthetic materials are used. According to Kumar [1], materials used for cranial bone implant production can be divided as follows: (a) metallic prostheses e.g. based on noble, tantalum, stainless steel and titanium, or the composite material 'vitallium' (alloy of cobalt, chrome and molybdenum); (b) bio-ceramic prostheses based on aluminium oxide or hydroxyapatite; (c) bone cements based on polymethacrylate methyl (PMMA) or calcium carbonate (CPCs); (d) polymer materials such as polyether ether ketone (PEEK), polyethylene (PE) and (e) mineralised collagen.

Materials used in cranial reconstruction should meet the following requirements [2]: radiotranslucency, resistance to infections, permanent stability, resistance to heat and cold, be easy to shape and ready to use, should fit the cranial defect perfectly in order to achieve total closure, and have a reasonable price.

The use of metal implants for a cranial prosthesis was described by Garcia-Gonzalez [3]. Tantalum mesh was described as useful for huge cranial defect repair. The prosthesis was implanted in 8 patients. For prosthesis fixing bone cement was used which was made of calcium phosphate. Clinical examination results

showed that two patients suffered from infection and the prosthesis had to be removed in the first and third month after the surgery had taken place. Austenitic Cr-Ni stainless steel (AISI Type 304) in the form of files formed spatially with the use of a laser beam, which resulted in the heating up of the material point and enabled plate deformation and obtaining of the projected prosthesis shape, was proposed in [4]. A metal cranial prostheses, especially titanium ones, made by the print spatial method with selective laser sintering (DLMS – Direct Laser Metal Sintering) was described by Staffa et al. [5]. The use of an aluminium alloy in prostheses for cranioplasty allows to obtain materials with high chemical stability and a low number of post-operational infections [6]. Another group of materials used in cranioplasty are bio-ceramic ones, especially aluminium oxide and hydroxyapatite [5]. Hydroxyapatite was used for manufacturing a personalised implant for a large cranial bone defect [7]. Anchieta and others [8] point out that individual cranial implants made of hydroxyapatite show osteogenesis and osteointegration with the patient's bone; however, total implant healing is a long-lasting process.

The application of bone cements is widely described in literature. Bone cements made of polymethacrylate methyl (PMMA) are used in cranioplasty [9], but their main disadvantage is the exothermic process of hardening, which can lead to the thermic necrosis of a patient's healthy bone. Cortoos material, containing bis-glycidyl methylmethacrylate, bisphenol, triethylene glycol, dimethylacrylate monomer, and bioactive glass was initially used in dentistry, but it has been found useful in cranial bone surgery and is an alternative for PMMA. Methacrylate methyl (MMA) is described as the perfect material for cranial reconstruction as it guarantees implantation success [10]. To prevent thermic bone damage, the dura mater and neighbouring tissues were covered with cotton gauze dressing, which was located under the formed bone cement. Nourishing the dressing with salt solution along the implant edge was continued till the end of the polymerisation process and drying of the implant.

Bone cement on the basis of PMMA with a titanised plate was used as implants in seventeen patients with bone loss. Only in the case of 1 patent was the implant rejected because of infection. In 97% of cases the prosthesis was well tolerated and a very good cosmetic effect achieved [11]. PMMA based prostheses were used in studies of 131 patients [12] and the results of all 131 patient tests described. Patients were divided into 3 groups depending on the cranioplasty technique used. The first group of patients were those whose implanted prosthesis was a frozen cranial bone obtained from craniotomy, kept at a temperature of -80 ^{o}C. The second group of patients were those who had the prosthesis implanted intraoperatively. The prostheses were made of PMMA. In the third group, the patients had a custom-made prosthesis of PMMA, whose shape was created on the basis of a CT scan and using CAD/CAM technology. It was found that the second group of patients required prolonged post-operational time compared with the first and third, while the operational time did not differ between the first and third groups. The average blood loss was significantly higher in the second group than in group one, while there were no significant differences between groups one and three. The infection rate for the PMMA prosthesis before the operation was higher than for the PMMA prosthesis formed in the surgical field, and it was comparable to plates made of autogenic material. Plates made by CAD/CAM technology and from PMMA material were the perfect alternative when there was no autogenic material available for cranioplasty. The method of using a computer model for projecting and creating a custom-made cranial bone prosthesis [13] is increasingly used. This technique can also be used in the case of custom-made cranial prostheses based on PMMA [14-16].

Quite new materials used in cranioplasty are those based on polymers. A comparison of mechanical features of polyether ether ketone (PEEK) and titan was done [17], and it was found that the mechanical properties of PEEK implants are better than those of titanised ones. An overview of PEEK use as a pure polymer and as a composite element for creating medical devices with the print spatial method was described in [18]. A numerical analysis of cranial implants made of macro-hydroxyapatite and PEEK in impact conditions was described by Simon [11]. In order to study the implant's usefulness, a head model was constructed including finished elements surrounding the head skin, a skull, cerebrospinal fluid, brain tissues and a cranial implant substituting the part of the skull. To sum up, the authors state that PEEK and macro-hydroxyapatite meet the criteria for implant materials.

Other materials tested for cranial prostheses include polymerised silicone [19], acryl-nitrile-butadiene-styrene (ABS) [20] and polymer carbon fibre [18].

Currently, polypropylene fibres (PP) are widely used in surgical practice [21]. Taking into consideration their physio-mechanical and chemical properties, PP is used in medical devices (surgical sutures, hernia meshes, cranial prosthesis) [22]. Compared to other synthetic materials used in medicine, PP fibres are characterised by tissue tolerance and the highest biocompatibility, just like devices made of polytetrafluoroethylene. Polypropylene surgical sutures are used in general surgeries of soft tissue, including cardio-vascular, ophthalmic, neurological and others. Cranial bone prostheses, meshes and sutures based on polypropylene became a real treatment breakthrough because of their high resistance, biological neutrality and resistance to tissue fluids. Of course, just like every implant, medical devices made of polypropylene can evoke a tissue reaction, especially in patients with a low immunological system and systemic diseases [23]. In a typical procedure of preventing infection, cleansing of the surgical field with antibiotic solutions or antibacterial agent soaking is performed. The study results state that meshes saturated with antibiotics or antiseptics show lower susceptibility to infection and have more prominent bactericida; activity during the patient's healing process.

The aim of the research was to compare the physical and mechanical properties of selected materials used in cranioplasty. Materials used for testing were Codubix based on polypropylene and Modela-cryl, and a polymer set consisting of acrylic resin based on PMMA. Comparison of the properties of PMMA bone cement and material based on PP should give an answer as to which material has better mechanical properties, which translates into the functional parameters of the prosthesis. It was expected that the study would allow to check whether it is possible to combine the properties of PP and PMMA, which should permit the preparation of a new material with properties combining the best features of both components.

Materials and methods

Materials tested

Modela-Cryl – a trade product by Protechno, was used as stated in the Instructions for Use supplied by the manufacturer. This resin can be considered as an equivalent of MED-acryl resin used for the reconstruction of cranial bone. Codubix cranial bone prostheses were manufactured out of isotactic polypropylene-polyester filaments – a commercial product by Tricomed SA. To form the final prosthesis applied, continuous multifilament polypropylene yarn – a commercial product by Chemosvit-Fibrochem, Slovenia, with linear mass 233 dtex and accurate resistance 38.3 cN/tex and continuous multifilament polyester yarn – a commercial product by Torlen, Poland, with linear mass 110 dtex amd accurate resistance 39.0 cN/tex, were used.

Codubix cranial bone prostheses are characterised by the following physical parameters: average pore size – 250 μm, lack of liquid absorption, density of 0.92 g/cm^3, linear mass of 1.9 kg/m^2, minimal bending strength of 60 N, elasticity module at compression – 2600 Pa, and crystallinity index – 0.53.

Research methods

Chemical parameters of the implants

Tests were carried out in accordance with the following standards: pH – PN–EN ISO 3071; permanganate oxidation – PN–P 04896; max. UV absorbance in a wavelength range of 230 and 245 nm – PN–P 04990; Cl^- ion content – PN–P 04781-03; SO_4^{2-} ion content – PN–P 04781–04; NH_4^+ ion suspension – PN–P 04992; and content of substances soluble in isopropyl alcohol – PN–P 04607. All tests were based on water extract prepared in accordance with the PN–P 04894 standard.

Physical parameters of the implants

While assessing the utility of the yarn in terms of its mechanical properties, the following parameters were assessed: the mean linear mass, coefficient of linear mass variation, humidity level – ASTM D 885-03, accurate resistance, elongation at break, and tensile force – PN-EN ISO 2062.

Structural analysis of the implants

The chemical composition of the Codubix knitted implant and Modela-cryl resin based implant was confirmed by FTIR tests carried out with the use of a Genesis Series FTIR^{TM} device by Unicam. For the structural test a Nova NanoSEM 230 scanning electron microscope (SEM) by FEI was used (FEG electron gun – polar emission) as well as an EDS Apollo 40 SDD RTG microanalyser by EDAX.

Study of polymerisation heat of Modela-cryl resin

In order to determine the polymerisation heat of Modela-cryl resin, the DSC technique was applied. The DSC measurements were taken with a DSC "Diamond" device by Perkin Elmer and according to the PN-EN ISO 10993-18:2006 and ISO 10993-19 standards.

The typical procedure of acrylic resin polymerisation heat measurement was carried out as described below. In a 20 ml crucible, 5 g of powdered acrylic resin containing pre-polymer was placed. The crucible containing the pre-polymer was placed in the measuring chamber of the DSC device and held there for 20 minutes in isothermal conditions. Such a procedure allowed to obtain a stable temperature of the pre-polymer. After 20 minutes, the DSC chamber was opened and 5 ml of the liquid part of the acrylic resin, containing the monomer and initiator, was added using a micro syringe. After the introduction of the liquid, measurements of the heat emanating from the crucible were taken.

Determination of polymerisation heat of Modela-cryl acrylic resin

In order to determine the polymerisation heat of Modela-cryl, a semi-open – diathermal calorimeter was used. The construction of the device may vary, but its most essential parts are a calorimetric shield, a calorimetric dish containing the sample tested, and thermometer sensor. The function of the calorimetric shield is to prevent heat exchange between the surroundings and dish with the sample. A scheme of the calorimeter used for polymerisation heat measurement of Modela-cryl resin is presented in ***Figure 1***.

After assembling the measuring device, the stirrer was switched on. After 10 minutes, when the temperatures of all elements were levelled off, it was possible to start the main measurements. The calorimetric measurement consists of three phases: the initial, main, and final one. During each phase, temperature measurement was taken and recorded each 0.5 minutes to within 0.001K. In the initial phase at least 10 temperature measurements were taken. After the last recording of the initial phase but before the first one of the main phase, testing of the process for 0.5 min was initiated. Next, systematically every 0.5 min, further values were recorded until the temperature changed insignificantly or it became unchanged (the so-called thermometer performance). It is the final phase of the measuring process, during which at least 10 temperature measurements were taken. The polymerisation heat of the sample was determined using measurements of the temperature changes surrounding the polymerisation mass. Moreover, in order to determine the Modela-cryl resin polymerisation heat, the DSC technique was used. Into a platinum DSC crucible, 5 mg of the Modela-cryl powdered component was introduced. The filled crucible was placed in the DSC device and then held there in isothermal conditions, at a temperature of 25 °C. The sample was thermostated for 30 min. After 30 minutes, the liquid component of Modela-cryl resin was added into the crucible. The whole content of the crucible was stirred and immediately DSC measurement started in isothermal conditions of 25 °C.

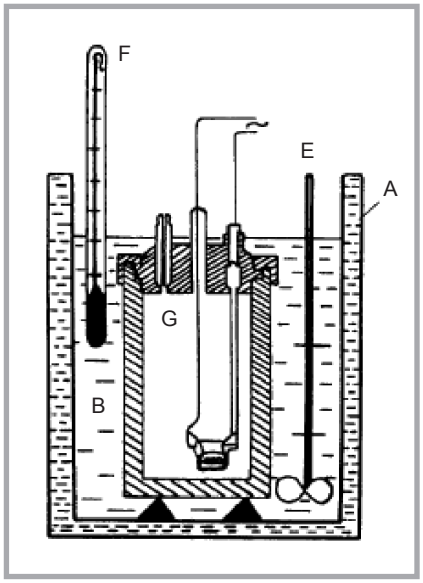

Figure 1. *General scheme of the calorimeter. A – isolation shield, B – calorimetric liquid, D – glass rod for crushing the ampules, C – ampule with the substance tested, E – stirrer, F – Beckmann thermometer.*

Study of Modela-cryl sample resistance to bending

Bending tests of acrylate resin samples were carried out according to the ISO 14125 standard. The molder, with dimensions of 5 mm x 5 mm x 50 mm,

Table 1. Chemical test results of water extracts from polypropylene yarn.

Input material			Polypropylene yarn		
No.	Parameters tested	Unit	Acceptable amount	Test method	Test result
					Sample
1.	Amount of substances soluble in petroleum ether	%	1.5	SOP-KJC.09 PN-P-04607:1983 /met. A	1.262

Table 2. Chemical test results of water extracts from the Codubix prosthesis.

No.	Parameters tested	Unit	Acceptable amount	Test method	Result
					Sample
1.	Organoleptic analysis of the extract: → transparency → colour	– –	Transparent colourless	SOP-KJC.02	Transparent colourless
2.	pH of sample tested	pH unit	5.5-8.0	PN-EN ISO 3071: 2007	6.51
3.	Permanganate oxidation	mg O_2/g	0.10	PN-P-04896:1984	0.005
4.	Max. ultraviolet absorbance	A_{max}	0.3	SOP-KJC.05 PN-P-04990:1989	0.0382
	In the wavelength range	ƛ, nm	230 230		
	Characteristic size	A	0.3		
	In the wavelength range	ƛ, nm	245 245		
5.	Frothing agents	Froth height, cm	none	SOP-KJC.03 PN-P-04781-14:1989	none
6.	Accurate conductivity	µS/cm	–	SOP-KJC.04	7.8 6.6
7.	Amount of substances soluble in petroleum ether	%	1.5	SOP-KJC.09 PN-P-04607:1983 /method A	4.35

Table 3. Chemical test results of water extracts from the Modela-cryl resin prosthesis.

No.	Parameters tested	Unit	Test method	Test result
1.	Organoleptic analysis of the extract → transparency → colour → scent	–	SOP-KJC.02	Transparent Light red Intense scent perceptible
2.	pH tested sample	pH unit	PN-EN ISO 3071:2007	3.08
3.	Permanganate oxidation	mg O_2/g	PN-P-04896:1984	1.816
4.	Max. ultraviolet absorbance	A_{max}	SOP-KJC.05 PN-P-04990:1989	4.3474
	In the wavelength range	ƛ, nm		
		230 230		
5.	Chloride ion suspension	mg Cl^-/g	PN-P-04895:1984 /met.2.1.	below 0.02
6.	Ammonium ion suspension	mg NH_4^+/g	SOP-KJC.07 PN-P-04992:1989	above 0.01
7.	Sulfuric ion suspension	mg SO_4^{2-}/g	SOP-KJC.06 PN-P-04781-04:1987	below 0.05
8.	Heavy metal ion suspension	mg Pb^{2+}/g	SOP-KJC.08 PN-P-04991:1989	Below 0.01
9.	Accurate conductivity	µS/cm	SOP-KJC.04	73.5
10.	Frothing agents	Froth height, cm	SOP-KJC.03 PN-P-04781-14:1989	None

Table 4. Mechanical properties of polypropylene yarn used for Codubix forming.

No.	Parameter tested	Unit	Test method	Requirements	Test results
1.	Thread linear mass	dtex	PN-EN ISO 2060:1997 manner 1	215.6-237.6	229±2
	Coefficient of linear mass variation	%			1.16
2.	Accurate resistance in the acclimatised condition	cN/dtex	PN-EN ISO 2062:2010 Method A	min. 3.1	3.9
3.	Elongation at break	%		30-100	40±2

obtained was placed on two linear props, between which the distance was equal to L = 28 mm. Exactly in the middle of this distance, the sample was subjected to a bending test with a pivot of 2 mm radius.

Resistance to bending and curvature height tests of Codubix knitted cranial bone prostheses

The tests were carried out with an altimeter which was used to determine the curvature height to within 0.1 mm. Next, the thickness of the implant was measured at three points with a screw micrometer to within 0.01 mm. On the basis of the results, the mean thickness of the implant was determined. From the difference between the height and mean thickness of the implant, the height of the internal curvature was calculated.

The bending resistance test was carried out on an universal testing machine and with the use of bending test plates. The samples prepared were placed on the lower plate, and the upper plate was positioned in such a way so as to touch the implant lightly. Simultaneously, the traverse measurements were reduced to zero. The value of the internal curvature height of the implant was introduced into the software of the universal testing machine, then the machine was set in motion with a traverse velocity of 25 mm/min. The test continued until the implant was completely flattened. The determination was performed one by one for each sample. The bending force was registered by the machine's software at 50% of the curvature height value of the implant. The result of such determination was the mean bending force of the prosthesis.

Prosthesis impact tests using the "drop tower" method

A station for impact tests was designed and equipped in such a way to be compliant with the requirements stated in the EN 1621-1, EN 1621-2, EN 13594 & EN 14021 standards.

For each of the above-mentioned standards, hammer devices of appropriate weight and shape were prepared. The equipment also included three replaceable anvils with different shaping of the working surface. The maximum height of the hammer device drop was up to approx. 1.5 m (depending on the length of the device and thickness of the sample), and it covered the energy values stated by the standards previously mentioned.

Table 5. *Results of the physical properties of the Codubix polypropylene cranial bone implant formed in industrial conditions.*

No.	Parameters tested	Unit	Standard physical parameters of Codubix prostheses					Accepted tolerance	Study method	Measurement results
			S1	S2	S3	S4	S5			
1.	Sizes	mm	130/125	134/110	105/60	75/75	75/57	±10%	SOP-KJF.08/PN-P-04890-00:1983	103/63
2.	Curvature height	mm	22.0	24.0	11.5	10.3	8.6	±10%	SOP 49/PN-P-04890-00:1983	–
3.	Bending force	daN	10.0	10.0	6.0	6.0	6.0	Min.	SOP 50/PN-P-04890-03:1983	23.5

The essential part of the station is a hefty base (weighing more than one tonne), comprising a steel plate of 50 mm thickness submerged in a concrete foundation on which the anvil is placed. Above the anvil there are vertical guide bars along which the unrestrained fall of the hammer device takes place. Between the base and the anvil there is a quartz force transducer with a range of 200 kN, which is the most essential measuring device of the station.

The additional elements of the station are the cable-based mechanism raising the hammer device and a special magnetic gripper which releases the hammer device and initiates the unrestrained fall. Tests were carried out on a device equipped with detectors of both the impact force and the force released by the sample. During the preliminary tests, the weight of the hammer and the height at which it was released were determined. The optimal values for acrylate resin were a weight of the hammer equal to 500 g and an impact value of 50 cm or 25 cm.

Table 6. *Physical properties of samples of the prosthesis based on PMMA.* ***Note:*** **coefficient of variation – statistical dispersion of the feature, defined as $V = s/x$, where: s – sample standard deviation, x – arithmetic average for sample $x \neq 0$.*

No.	Sample no.	Max. bending force, N	Bending tension, MPa
1.	1	31.66	48.19
2.	2	26.29	57.83
3.	3	35.00	65.32
4.	4	24.10	43.99
5.	5	23.13	51.20
6.	Average	28.04	53.30
7.	Standard deviation	5.10	8.40
8.	Coefficient of variation*	18.21	15.76

Table 7. *Results of the energy transmitted to the sample through the hammer device, the speed of the impact, and the reflection for samples made of PMMA (Modela-cryl) and knitted polypropylene prostheses (Codubix).*

Sample marking	Modela-cryl sphere	Modela-cryl stick	Codubix oval	Codubix elliptical
Drop height, mm	250	500	500	500
Hammer device speed, m/s	2.25	3.2	3.20	3.21
Hammer device impact speed, m/s	0.76	0.53	1.08	1.418
Hammer device energy, J	6.33	12.77	12.81	12.87
Energy transmitted to the sample, J	5.51	12.39	10.57	10.40
Dispersed energy, %	12.91	3.01	17.54	19.22

Results and discussion

Chemical purity tests

A very significant aspect of the successful application of implants is their chemical purity. In order to be sure that the materials used are clean enough, tests were carried out on aqueous extracts after an eight-fold washing. It was assumed that this study would slowly evaluate the in vitro potentially dangerous compounds released from the prostheses after implantation. Before testing water extract parameters obtained from a knitted Codubix prosthesis based on polypropylene and from a Modela-cryl resin prosthesis, research was carried out using polypropylene yarn used as a substrate in the Codubix prosthesis manufacturing process.

In ***Tables 1, 2*** and ***3*** results of measurements of the water extract obtained from polypropylene yarn (***Table 1***), the knitted Codubix prosthesis (***Table 2***), and the Modela-cryl resin prosthesis based on PMMA (***Table 3***) are presented.

The results presented in ***Tables 1-3*** show that for the samples of cranial bone prosthesis in the form of the three-dimensional structure of knitted polypropylene/polyester yarn tested (commercial product Codubix) (***Table 2***), the cranial bone implant made of acrylic resin (Modela-cryl) (***Table 3***) as well as polypropylene yarn used in the Codubix implant production (***Table 1***) meet the criteria required for the implantation materials.

Study of the tensile force of Codubix and the Modela-cryl resin

Implantation materials, especially constructional ones like cranial bone or cranial bone coating, have to possess appropriate mechanical properties like resistance to stretching and elongation at break. Marking these parameters is crucial for the evaluation and meeting the requirements of a prosthesis of a part of the human body. In ***Table 4*** mechanical properties of the polypropylene yarn used for Codubix formation are presented.

On the basis of the results presented in ***Table 4***, it was found that the polypropylene yarn used in the Codubix implant production meets the minimum requirements for yarns used in cranial bone prosthesis production. The accurate resistance in the acclimatised conditions (60 RH, 25 °C) was 3.9 cN/dtex, while the minimum value is 3.1 cN/dtex. The elongation at break is within the acceptable range; it is 40%. It confirms that the polypropylene yarn used has the appropriate elasticity and is predisposed for knitted technique modification.

Typical dimensions and the corresponding physical parameters of the Codubix prostheses are shown in ***Table 5***. For the selected sample obtained in industrial conditions, studies on the curvature height as well as the bending force were carried out.

Results of physical measurements of the Codubix cranial bone prosthesis (***Ta-***

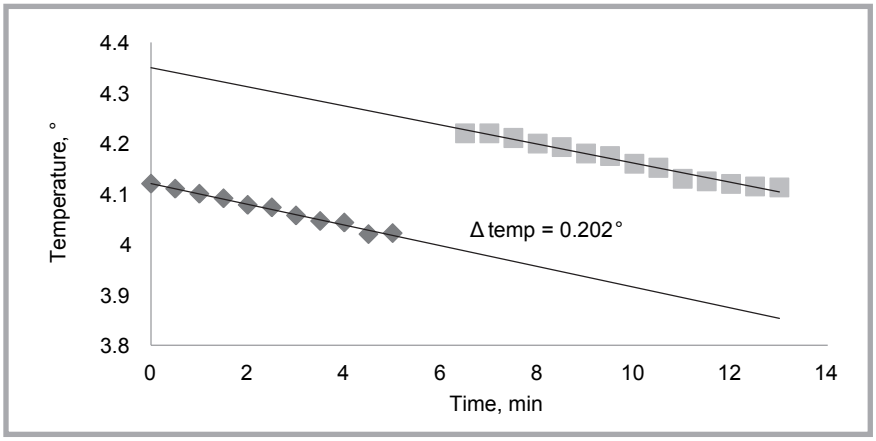

Figure 2. *Course of temperature of the adiabatic calorimeter during Modela-cryl resin polymerisation.*

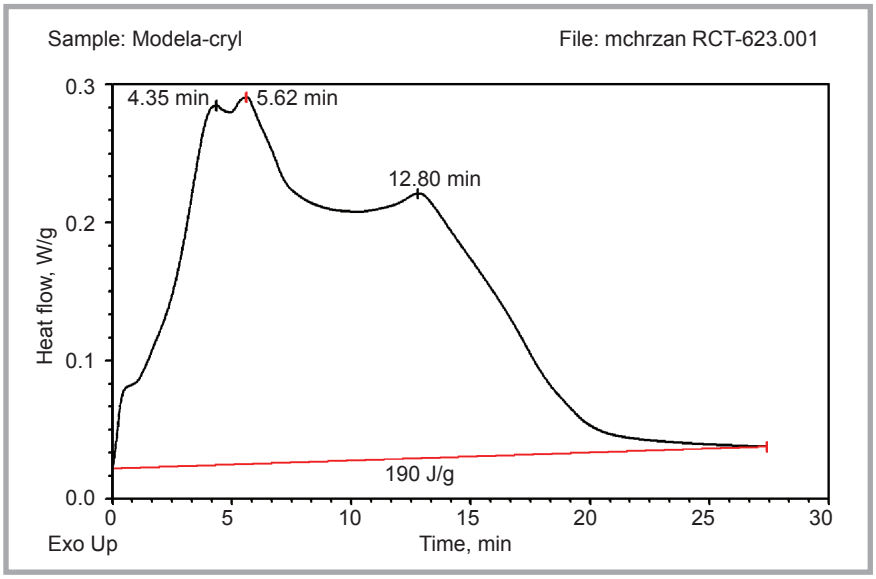

Figure 3. *Thermogram of polymerisation heat of Modela-cryl resin.*

ble 5) show that the industrial procedures applied allow to obtain materials with physical properties that meet the requirements for medical devices.

Comparative tests of physical properties using samples of skull prostheses formed from Modela-cryl resin based on PMMA were done (***Table 6***).

It was found that in the case of Modela-cryl resin, the average bending force was 28 N, which in comparison to 25.5 daN for the Codubix prosthesis, was about 9 times lower. Data presented in the table show that the bending force of the implant made of acrylic resin Modela-cryl oscillates around 53 MPa.

Impact study

In the next step, studies on the ability to disperse the impact energy were conducted. ***Table 7*** presents results of the energy transferred to the sample through the hammer device. In addition, impact and reflection measurements for the samples made of PMMA (Modela-cryl) in the spherical and stick forms were made. The same comparative tests were performed for a knitted Codubix prosthesis in an oval and elliptic form. The results are the average taken from at least 5 measurements of each sample.

According to the data presented in ***Table 7***, the knitted structure of Codubix in an oval shape disperses approx. 17.5% of the impact energy, whereas the elliptical – 19.2%. In the case of acrylic resin, the dispersed energy closely depended of the shape of the samples tested. For the sphere shape the dispersed energy was slightly lower (12.9%) in comparison to the knitted samples. While, for the flat samples of PMMA of square shape measuring 5 mm x 5 mm, the dispersed energy was 3%. It seems that the key parameter affecting the ability to dissipate energy is the spherical shape, guaranteeing the spatial volume of the sample.

The dispersed energy was calculated using the following ***Equation (1)***:

$$E_{dispersed} = \frac{E_{impact} - E_{transmitted}}{E_{impact}} \text{x100\%} \quad (1)$$

Analysis of the difference in hammer speed before and after the impact shows that the knitted structures have slightly higher elastic properties than the acrylic resin. The speed change of the hammer device after the impact for the knitted structures was 42.5% and 33% for the spherical form of Modela-cryl resin. Also, here the results for flat square PMMA samples were lower (16%) in comparison to those for the spherical ones.

Heat of polymerisation of Modela-cryl resin

The heat of polymerisation of the PMMA resin was established using an adiabatic calorimeter, and additionally the polymerisation heat value was confirmed by DSC.

Model-cryl resin heat polymerisation determined on the basis of temperature changes of the adiabatic calorimeter is -180 J/g. The heat polymerization value was determined based on the following formula:

$$\Delta H = \frac{-K \cdot \Delta temp \cdot M}{m} \quad (2)$$

Where, K – calorimeter heat capacity, $\Delta temp$ – calorimeter temperature increase during polymerisation process, M – methyl methacrylate molar mass, m – mass of Modela-cryl resin components of sample

In the DSC test, isothermal conditions (25 °C) were applied. ***Figure 3*** presents a DSC thermogram of polymerisation heat for Modela-cryl resin.

The heat of polymerisation of Modela-cryl resin established was -190 J/g (***Figure 2***), which is almost 2.9 times lower [24] than that of pure methyl methacrylate (the main ingredient of the component of liquid Modela-cryl resin -544 J/g). The polymerisation heat of Modela-cryl resin found might be con-

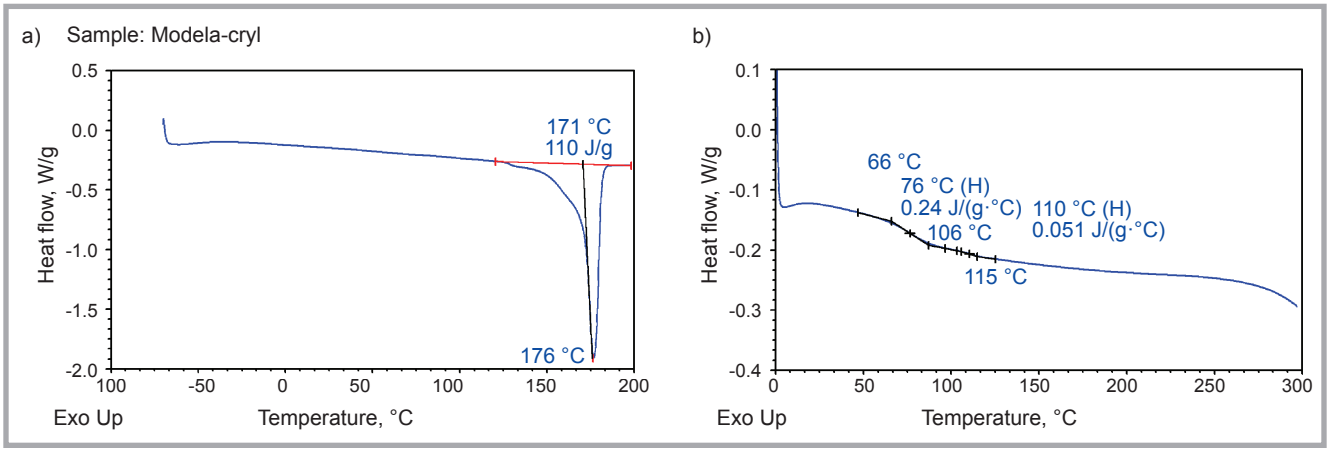

Figure 4. *a) DSC thermogram of knitted Codubix prophesies, b) DSC thermogram of Modela-cryl resin.*

nected with the presence of methacrylate groups in the reactive solution, which is one of the substrates of Modela-cryl resin. The use of a two-component substrate with ingredient A (containing a monomer) and ingredient B (an appropriate mixture of an initiator and filler) is responsible for the tri-modal process of polymerisation observed, which results in a slowing down of the release of polymerisation heat. Such a profile of releasing polymerisation heat could be beneficial in terms of the heat dispersion in the surrounding bones.

Thermal analysis of final Codubix and Modela-cryl prostheses

On the basis of the DSC analysis of the knitted sample of Codubix (***Figure 4.a***), it was found that polypropylene fibres used for the preparation of the prosthesis had a melting temperature of the crystal phase of 171 °C. On the thermogram glass transition is not observed.

On the DSC thermogram of Modela-cryl resin (***Figure 4.b***), no occurrence of crystal phase melting up to 300 °C is observed, which is connected with the cross linking character of Modela-cryl resin. The occurrence of two characteristic glass transition temperatures at 76 °C and 110 °C indicates that two types of monomers were used for preparation of the Modela-cryl resin. It can be assumed that the ingredient which is characterised by glass transition at temperature 110 °C and enthalpy at the level of 0.051 J/(g*°C) is the cross-linking component. The dominant component is characterised by Tg = 76.6 °C and enthalpy at the level 0.24 J/(g*°C), corresponding to methyl methacrylate.

Conclusions

Comparison of physio-chemical properties of textile material in the form of a knitted cranial prosthesis and the implant made from polymer acrylic resin shows that the basic chemical purity parameters established, such as pH, oxidation, max. ultraviolet absorption at a wavelength of 230 nm and 245 nm, and the accurate conductivity of the water extract, are at acceptable levels.

The mechanical properties of Codubix implants and acrylic resin show that both materials achieve appropriate parameters, predisposing them for applications as surgical implants.

The dispersion of impact energy for the knitted prosthesis was similar to that for the prosthesis with an oval shape and for the prosthesis an with elliptical one (17.5% and 19.2%, respectively). In the case of the acrylic resin, the dispersed energy was closely dependent on the shape of the samples tested. For the sphere shape the dispersed energy was slightly lower (12.9%) in comparison to that of theknitted samples. For the flat PMMA sample, significantly lower dispersed energy was observed (3%, respectively).

The measurements of the difference in hammer speed before and after the impact show that the knitted structures have slightly higher elastic properties than the acrylic resin.

The heat of polymerisation of Modela-cryl resin established using DSC showed that the appropriate composition of the components allows a uniform distribution of heat during the application time. The first maximum energy emission was observed at 4.3 min, the second maximum heat emission at 5.6 min and the last one at 12.8 min. Such a character of the polymerisation process enables to accurately shape the missing element of the cranial part before the curing process finishes. Moreover, the process of heating of the polymerisation emission enables to obtain the energy secreted through the patient's organs without the risk of heatstroke.

The research conducted showed the opportunity for application of both materials tested. It seems that their physical and mechanical properties should allow to establish medical procedures which enable the correction of small cavities accompanying the use of a knitted prosthesis, by using acrylic resins formed during surgical treatment.

The comparative study of the physio-chemical properties of products used for cranial bone implants based on the application of a knitted Codubix prosthesis and Modela-cryl resin prosthesis shows the possibility of complementary application of both of them, leading to a decrease in the level of complications and improvement of the success rate.

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