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Comparison of the Hardness, Energy Absorption and Water Absorbability of Polymeric Materials Used in the Manufacture of Mouthguards

Porównanie twardości, absorpcji energii i nasiąkliwości materiałów polimerowych stosowanych w wykonawstwie ochraniaczy wewnątrzustnych

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A – research concept and design; **B** – collection and/or assembly of data; **C** – data analysis and interpretation; **D** – writing the article; **E** – critical revision of the article; **F** – final approval of article

Abstract

Background. Mouthguards constitute an inseparable feature of injury prevention for the head and mouth area. Due to growing expectations regarding comfort of usage and resistance parameters strictly determined quality standards must be established for such equipment. These resistance parameters are usually dependent on the type of the material they were made of and the technology applied.

Objectives. The aim of the present study was to compare the hardness, elasticity and absorbability of polymeric materials used to produce mouthguards as well as to identify which materials have the most favourable resistance and functional properties.

Material and Methods. Samples of polymeric material obtained during deep moulding, canning and thermal injection were utilised to measure hardness, resilience and absorbability.

Results. On the basis on the researched material, it is recommended that the following be used in the production of mouthguards: Impak® in 1 : 1 and 1.5 : 1 proportions, Elastosil®, double-laminated Erkoflex® and Corflex®, as these materials ensure optimal hardness and energy absorption. The studied material was shown to have an acceptable level of absorbability (up to 0.5% in mouthguards), but it was the Corflex Orthodontic material that exhibited the lowest values in this respect.

Conclusions. Corflex Orthodontic process using the thermal injection technique is the most suitable material for preparing mouthguards **(Dent. Med. Probl. 2015, 52, 1, 78–85).**

Key words: sport, orofacial injury, mouthguards.

Słowa kluczowe: urazy części twarzowej czaszki, sport, ochraniacze wewnątrzustne.

Participating in various kinds of physical activity has a positive impact on the functioning of the respiratory, circulatory, muscular and nervous systems. Practicing sports prevents diseases of affluence affecting our metabolic rate, reduces stress levels, and as a result, positively regulates the emotional state and mental health. Nowadays, however, contact sports are gaining more and more popularity, and participants are more prone to injury. Particularly dangerous are the effects of injuries sustained in the facial and mouth area. Their complications can lead to a deterioration in both the functioning of the chewing organ (speech, food intake, breathing), and, to an even greater degree, facial esthetics. Beside head gears protecting the head, mouthguards have become an essential factor in sports injury prevention. Their role is to provide direct protection for the frontal segment of the jaw and to separate opposing teeth and the mucous membrane of the lips and cheeks from teeth arches [1–4]. The basic component guaranteeing cushioning of the mouthguards is the clammy and springy nature of the polymeric materials applied in their manufacture. Depending on the type and mechanical qualities of the material used, the protector gear possesses changing resistance and an impact-absorbing ability. This is because the flexible polymeric materials, thanks to their complex chain structure, have an ability to transform the energy from impact into a different type of energy. When a deformation occurs, the polymer's components begin to migrate amongst themselves, which in turn converts some of the mechanical energy into molecular friction and heat. What occurs is vibration suppression [5–8], favorable from the point of view of oral cavity injury prevention.

The objective of the study was to compare the hardness, elasticity and absorbability of polymeric materials used in the manufacture of mouthguards and to identify the material with the most suitable resistance and utility features.

Material and Methods

The research material was made up of samples of disc-shaped polymeric materials that were 50 mm in diameter and 4 mm thick and which were obtained through the following process:

– the thermoforming pressing technique with one-layer samples made out of Erkoflex® 5 mm tiles, two-layer samples composed of Erkoflex 3 and 2 mm (hereinafter called Erkoflex 2) and Erkoflex 3 mm and Erkodur® 2 mm – ethylene copolymers and vinyl acetate (Erkodent, Germany),

– the conventional flasking technique, using commercially-labeled Impak® material (Vernon-Benshoff Comp., USA) in different powder to liquid ratios: 2 : 1 (Impak 2), 1.5 : 1 (Impak 1.5), 1 : 1 (Impak 1),

– the injection molding, involving the use of Corflex Orthodontic® (Pressing Dental, Italy) – ethylene copolymers and vinyl acetate and Elastosil® – HTV silicone (Wacker, Germany).

The hardness test was conducted with a clock durometer in the Shore A scale – Durometer A (Wilson Wolpert, ISO 7619), [3, 4, 9, 10]. Each sample was fretted with a bluntly ended pin, 0.8 mm in diameter, at 5 different spots. The measurement was taken at the moment when the hands had completely stabilized, i.e. after 3–15 s. The hardness of the examined sample was read out on the durometer's scale in Shore's A degrees, from 0° to 100°. The measurements were taken at room temperature (Fig. 1). The results of hardness examination were subjected to single variant analysis. The assumption of variance equality was verified by means of the Brown-Forsythe test. As a multiple test, Neuman-Keuls test was used.

The energy-absorbing qualities were evaluated by carrying out a test for shock elasticity by means of the Schob's method [3, 4, 11–13] and VEB TIW Ranenstein (Heckert) apparatus. This involved pounding the sample with a deadweight fixed to a pendulum at an angle of 90° from a specified location and measuring the altitude percentage ratio on the apparatus' scale. The material samples were pounded 5 times. The span (%) of the rebound represented the value of cumulated energy (the lower the rebound the bigger the loss). The subject of the evaluation was the ratio of the altitude of the rebounded pendulum from the sample to its initial altitude (E's rebound) and on this basis – a reduction in the impact-generated energy, that is the differential between the initial E and the rebounded E, in accordance with the rule of energy conservation (Fig. 2). The results of energy absorption were compared using a single variant analysis. The assumption of variance equality was verified using Brown-Forsythe test. As a multiple test, Neuman-Keuls test was used.

In order to evaluate water absorbency, polymer samples were initially placed for 24 h in a vacuum dryer at a temperature of 37°C. Next, they were weighed and transferred to receptacles with distilled water, then closed in a thermal chamber at a temperature of 37°C. After 24 h they were weighed once again at room temperature (23–25°C). The percentage increase in weight was then calculated [% = (wet weight – conditioned weight/conditioned weight) × (100)], (Fig. 3), [10].

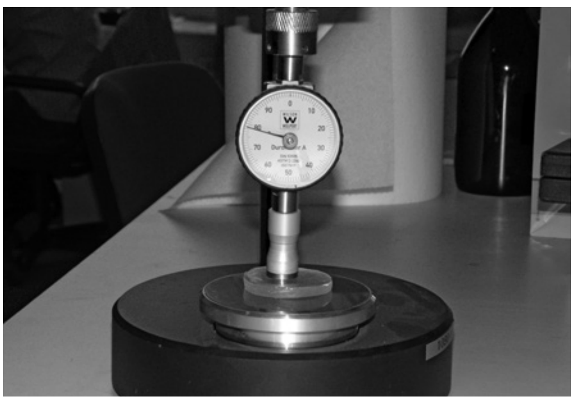

Fig. 1. The durometer with polymeric material sample embedded

Fig 2. The pendulum used for testing shock elasticity using Schob's method

Fig 3. Pomymeric samples in reptacles with distilled water

$$W_a = \frac{W_w - C_w}{C_w} \times 100\%,$$

where:
W_a –water absorption [%],
W_w – weight of wet sample,
C_w – weight of conditioned sample.

Results

Measurements of the studied polymeric material in terms of its hardness show (Table 1, 2) that the highest average hardness on the Shore A scale was achieved by samples that combined Erkoflex and Erkodur materials (89.5°), while the Impak material came up as the softest one in a powder to liquid ratio of 1 : 1 (47.5°).

Statistical analysis based on the Newman-Keuls test, as shown in Table 3 and 4, proved no significant statistical differences between Corflex and single and double-laminated Erkoflex materials (Erkoflex 2) in terms of hardness parameters. The materials that differed most from one other in the same terms were Impak in a 1 : 1 ratio and Erkoflex in conjunction with Erkodur (penetrator was applied to Erkodur).

The studied materials were described in terms of shock elasticity figures (Table 5, 6) and the energy-absorbing capabilities resulting from them. Impak achieved the highest value for this parameter with ratios of 1 : 1 and 1.5 : 1.

Table 7 and 8 shows that Corflex, double-laminated Erkoflex and Erkoflex combined with Erkodur had similar abilities to absorb energy from an impact. A statistical analysis based on the Newman-Keuls test did not show any key differences in the case of these materials. A similar convergence was shown by Impak at a ratio of 2 : 1 and Erkoflex, both of which additionally marked the biggest differential from Impak at a 1 : 1 ratio, possessing the greatest ability to absorb energy from an impact.

The relationship between impact absorption and hardness is determined by the following model: absorption = a + b/(hardness^3). The model parameters were estimated using the Levenberg-Marquardt method. The sum of the smallest squares assumed the role of the loss function. Figure 4 provides a graphic presentation of the correlations.

The hardness of the researched materials has a significant influence on their ability to absorb

Table 1. Results of hardness measurements

Material	Erkoflex	Erkoflex 2	Erkoflex + Erkodur	Impak 2 : 1	Impak 1.5 : 1	Impak 1 : 1	Corflex	Elastosil
Hardness [^{0}Shore]	74	65	85	85	58	45	73	57
	74	70	95	94	60	49	70	57
	75	73	88	80	65	45	71	58
	72	71	85	80	63	48	75	57
	74.5	68	96	83	65	48	71	59
	74.5	72	88	89	60	50	72	59
Average	74	69.8	89.5	85.2	61.8	47.5	72	57.8

Table 2. Hardness measurement; basic statistics

Material	n	Average	std	Min	Median	Max
Impak 1	6	47.50	2.07	45.0	48.00	50.0
Elastosil	6	57.83	0.98	57.0	57.50	59.0
Imapak 1.5	6	61.83	2.93	58.0	61.50	65.0
Erkoflex 2	6	69.83	2.93	65.0	70.50	73.0
Corflex	6	72.00	1.79	70.0	71.50	75.0
Erkoflex	6	74.00	1.05	72.0	74.25	75.0
Impak 2	6	85.17	5.49	80.0	84.00	94.0
Erkoflex + Erkodur	6	89.50	4.85	85.0	88.00	96.0
All	48	69.71	13.45	45.0	71.00	96.0

Table 3. Hardness measurement. Newman-Keuls test; significant differences – values p

Corelation	Impak 1	Elastosil	Impak 1.5	Erkoflex 2	Corflex	Erkoflex	Impak 2	Erkoflex + Erkodur
Impak 1		0.0001	0.0001	0.0002	0.0001	0.0001	0.0001	0.0001
Elastosil	0.0001		0.0348	0.0001	0.0002	0.0001	0.0001	0.0001
Impak 1.5	0.0001	0.0348		0.0002	0.0001	0.0002	0.0001	0.0001
Erkoflex 2	0.0002	0.0001	0.0002		0.2435	0.0709	0.0002	0.0001
Corflex	0.0001	0.0002	0.0001	0.2435		0.2811	0.0001	0.0002
Erkoflex	0.0001	0.0001	0.0002	0.0709	0.2811		0.0001	0.0001
Impak 2	0.0001	0.0001	0.0001	0.0002	0.0001	0.0001		0.0229
Erkoflex + Erkodur	0.0001	0.0001	0.0001	0.0001	0.0002	0.0001	0.0229	

Table 4. Hardness measurement. Newman-Keuls test; homogenous groups

Material	Hardness	A	B	C	D	E	F
Impak 1	47.50	***					
Elastosil	57.83		***				
Impak 1.5	61.83			***			
Erkoflex 2	69.83				***		
Corflex	72.00				***		
Erkoflex	74.00				***		
Impak 2	85.17					***	
Erkoflex + Erkodur	89.50						***

Table 5. Results of energy-absorption study

Material	Erkoflex	Erkoflex 2	Erkoflex + Erkodur	Impak 2	Impak 1.5	Impak 1	Corflex	Elastosil
Shock- -elasticity (%)	35	30	32	33	21	11	32	28
	34	30	32	34	22	11	32	26
	34	32	32	33	22	9	32	28
	34	31	32	33	20	9	32	30
	34	32	31	32	20	9	30	28
	34	32	32	34	22	10	32	30
Average %	34.2	31.2	31.8	33.2	21.2	9.8	31.7	28.3
Energy absorption (%)	65.8	68.8	68.2*	66.8	78.8	90.2	68.3	71.7

* The pendulum pounded against Erkoflex.

Table 6. Study on energy absorption; basic statistics

Material	n	Average	std	Min	Median	Max
Erkoflex	6	65.83	0.41	65.0	66.00	66.0
Impak 2	6	66.83	0.75	66.0	67.00	68.0
Erkoflex + Erkodur	6	68.17	0.41	68.0	68.00	69.0
Corflex	6	68.33	0.82	68.0	68.00	70.0
Erkoflex 2	6	68.83	0.98	68.0	68.50	70.0
Elastosil	6	71.67	1.51	70.0	72.00	74.0
Impak 1.5	6	78.83	0.98	78.0	78.50	80.0
Impak 1	6	90.17	0.98	89.0	90.50	91.0
All	48	72.33	7.86	65.0	68.00	91.0

Table 7. Study on energy absoption; Neuman-Keuls test; significant differences – values p

Corelation	Impak 1	Impak 1.5	Elastosil	Erkoflex 2	Corflex	Erkoflex + Erkodur	Impak 2	Erkoflex
Impak 1		0.0001	0.0001	0.0002	0.0001	0.0001	0.0001	0.0001
Impak 1.5	0.0001		0.0001	0.0001	0.0002	0.0001	0.0001	0.0001
Elastosil	0.0001	0.0001		0.0001	0.0001	0.0002	0.0001	0.0001
Erkoflex 2	0.0002	0.0001	0.0001		0.3510	0.4266	0.0029	0.0001
Corflex	0.0001	0.0002	0.0001	0.3510		0.7548	0.0194	0.0003
Erkoflex + Erkodur	0.0001	0.0001	0.0002	0.4266	0.7548		0.0161	0.0003
Impak 2	0.0001	0.0001	0.0001	0.0029	0.0194	0.0161		0.0664
Erkoflex	0.0001	0.0001	0.0001	0.0001	0.0003	0.0003	0.0664	

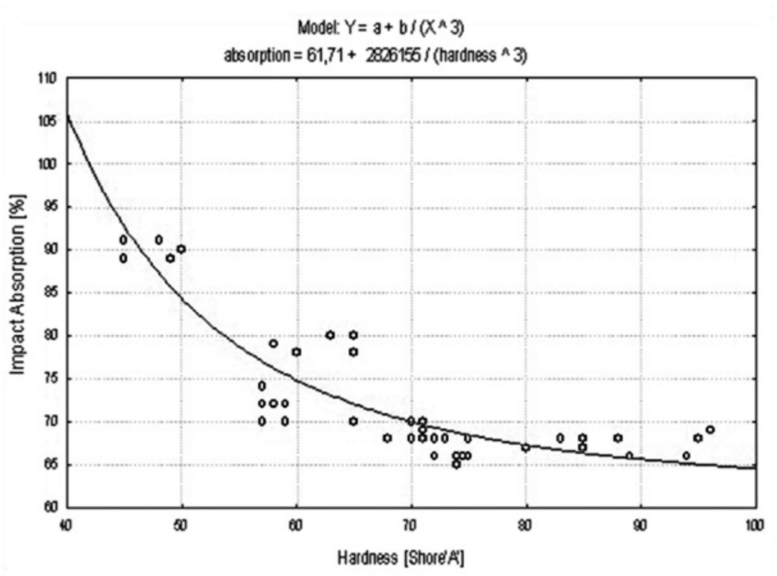

Fig 4. Relation between energy absorption and hardness

energy. Polymers with over 85° hardness on the Shore A scale have the ability to absorb energy below a level of 67%. Of the studied materials both Erkodur and Impak 2 match this description. Optimal hardness and energy absorption were detected in the following materials: Impak 1, Impak 1.5, Elastosil, Erkoflex 2 and Corflex.

The water absorption of the examined materials ranged from 0.072% (Corflex) to 0.49% (Impak 1 : 1), (Table 9). All the materials demonstrated a slight, though sufficient, grade of absorbability, ranging in intra-oral mouthguards up to 0.5%. The lowest value for this parameter was achieved by Corflex, and therefore it will perform best in the humid conditions within the oral cavity.

Hardness of polymeric materials has a significant effect on their ability to absorb impact induced energy. The greater the hardness, the lower

Table 8. Study on energy absorption; Newman-Keuls test; homogenous groups

Material	Shock elasticity	Energy Absorption	A	B	C	D	E
Impak 1	9.83	90.17	****				
Impak 1.5	21.17	78.83		****			
Elastosil	28.33	71.67			****		
Erkoflex 2	31.17	68.83				****	
Corflex	31.67	68.33				****	
Erkoflex + $Erkodur_1$	31.83	68.17				****	
Impak 2	33.17	66.83					****
Erkoflex	34.17	65.83					****

The pendulum pounded against Erkoflex.

Table 9. Results of water absorption study

Material	Corflex	Elastosil	Erkoflex 2	Erkoflex + Erkodur	Erkoflex	Impak 2	Impak 1.5	Impak 1
Conditioned weight C_w (g)	8.6049	10.7139	8.9234	9.4271	9.6734	9.9959	8.9607	9.4518
Wet weight W_w (g)	8.6111	10.7218	8.9328	9.4387	9.6864	10.0368	9.0035	9.4987
$W_w - C_w$ (g)	0.0062	0.0079	0.0094	0.0116	0.013	0.0409	0.0428	0.0469
Water absorption (%)	0.072	0.073	0.105	0.123	0.134	0.409	0.477	0.496

the energy reduction. Among the examined materials optimal hardness and energy absorption have: Impak material at ratios of 1 : 1 and 1.5 : 1, Elastosil, two-layered Erkoflex and Corflex. All the examined materials have a sufficient level of absorbability; in the case of intra-oral pads this level is 0.5%. The most suitable material for the conditions of the oral cavity is Corflex Orthodontic, as it has the lowest value for this parameter.

Discussion

Scientific studies on sports-related injury prevention aim to establish certain standards that materials used in the manufacture of mouthguards should meet [11, 14–16]. The literature in recent years shows that efforts have been made in recent years to identify the material with the most favorable mechanical properties, or, in other words, the greatest energy absorption, alongside a slight increase in the thickness of the layer, which would not affect the user's comfort. An interesting study to determine the optimal thickness that has often been used to produce ethylene copolymer and vinyl acetate mouth guards (EVA) was conducted by Westerman et al. [17]. Using a pendulum pounding with an energy level of 4.4 J and at the speed of 3 m/s, which could damage the facial part of the skull, they demonstrated that energy absorption paralleled the increase in the material's layer thickness, but only up to 4 mm, which they regarded as the most convenient. The authors then used the thickness of the material measured in their study in their own research on the mechanical and physical properties of polymers.

The main objective was to determine the hardness of the materials available on the Polish market and used to produce mouthguard. Because they are by definition supposed to be flexible supplements, this parameter rules out hard materials that do not possess this quality. A study on material resistance was conducted by Craig and Godwin [18] in 1967. They tested pads obtained from ethylene copolymer and vinyl acetate (EVA), polyurethane, rubber latex material, 'Termoplastic' and 'Plastisol' (vinyl resin). The hardness of these polymers ranged from 35° to 90° on the Shore A (Sh) scale, which represents a broad span of results. Having tested 8 standard pads and 7 types of thermoplastic materials from different companies, the same authors concluded that at a temperature of 37°C pads should have a hardness within a range of 55° and 85° on the Shore A scale, and that their inner layer should vary between 40° and 60° [3]. A similar span of acceptable hardness levels (66°–86°) was noted by Going et al. [4] in 1974. They claimed that a pad that is too hard would not provide sufficient protection, since all the energy resulting from an impact would be transferred to the oral cavity structure. These allegations were confirmed by a study published by Auroy et al. [9], which additionally evaluated the correlation between impact induced energy absorption and the hardness of the material. The power, measured with the assistance of a transducer placed under the pounded sample, was highest in the hardest materials, a fact which did not result in its dispersal. Wilkinson and Powers [19], Jagger et al. [20] and Tran et al. [16] also channeled their efforts into comparing the hardness of materials. However, the results did not diverge from those previously published. The materials the authors tested in their own study, characterized by a degree of hardness beyond 85° Shore (Erkoflex + Erkodur, Impak 2), insufficiently absorbed the energy from an impact compared with the above quoted publications. Craig and Godwin [3] determined the optimal suppressing qualities of materials. They applied a method that involved a ball pounding against the material, and concluded that the material used to produce pads should reduce the energy from an impact to at least 70% of the initial figure (according to this method the higher the figure the greater the energy absorption). However, in a study that involved the use of pendulum, in which they compared the degree of its reflection in percentage terms, Going et al. [4] demonstrated that the highest level of energy absorption was achieved by acrylic resin and PVC. Loehman et al. [21] reported an identical result. The energy absorption values of 65% to 90% they obtained in their own study employing the Schobe method are similar to those achieved by the other above-mentioned authors, and indicate that, apart from Erkoflex and Impak at a 2 : 1 ratio, the other materials have a sufficient ability to absorb energy. Despite having the requisite hardness the most frequently used EVA material (Erkoflex), exhibited inadequate energy absorption, a fact which confirms the need, as was also suggested by other authors, to reinforce it with other materials or use multiple layers [22, 23].

To evaluate the physical features of pads in conditions resembling those inside the oral cavity, some authors have conducted tests on water absorption [2–4, 11, 12]. Materials with a higher degree of absorbability may contribute to salivary and bacteria retention and by doing so, stimulate the formation of tooth decay [4]. On the other hand, in the case of oral cavity pads, this factor is less important as they are worn only when the user desires to practice sport (training, tournament, recreation), i.e. approximately 2–3 h during the day. Craig and Godwin [3] recommend that the liquid absorption of a material does not exceed 0.5% at a temperature of 37°C.

Research on the mechanical properties of polymeric materials have demonstrated that their hardness has a significant effect on their ability to absorb impact induced energy. The greater the hardness, the lower the energy reduction. Among the examined materials used in the production of pads, the following are recommended: Impak material at ratios of 1 : 1 and 1.5 : 1, Elastosil, two-layered Erkoflex and Corflex, as they have shown optimal hardness and energy absorption. All the examined materials have a sufficient level of absorbability; in the case of intra-oral pads this level is 0.5%. However, it was Corflex Orthodontic that had the lowest value for this parameter, which makes it the most suitable material for the conditions of the oral cavity.

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