A Comparative Study on Mechanical Properties of Some Thermoplastic and Thermo Set Resins Used for Orthodontic Appliances

LIGIA VAIDA[1], LIVIU MOLDOVAN[2]*, IOANA ELENA LILE[3]*, BIANCA IOANA TODOR[1]*, ANCA PORUMB[1], IOAN TIG[1], DANA CRISTINA BRATU[4]

[1] University of Oradea, Faculty of Medicine and Pharmacy, Department of Dentistry, 1 Universitãii Str., 410087, Oradea, România

[2] University of Oradea, Faculty of Electrical Engineering and Information Technology, Department of Electronics and Telecommunications, 1 Universitătii Str., 410087, Oradea, România

[3] Vasile Goldis" Western University of Arad, Faculty of Medicine, Pharmacy and Dental Medicine, Department of Dentistry, 94-96 Revolutiei Blv., 310025, Arad, România

[4] Victor Babes" University of Medicine and Pharmacy, Dental Medicine, 2 E. Murgu Sq., 300041, Timisoara, România

The orthodontic appliances can be built in a great diversity of resin that could be classified by one of the criteria, in thermoplastic and thermo set. This paper has as purpose to compare three resins used for orthodontic appliances, one thermoplastic and two thermo set –Biocryl C (Scheu Biostar), Orthocryl (Dentaurum), Orthoplast (Vertex Dental) – from the mechanical properties respect such as surface hardness and indentation elastic modulus. We tested six specimens; two from each type of these resins. Each specimen was fixed on a support and they were tested with Nano Indenter G200 from Keysight (Agilent). We obtained as a result that the thermoplastic material has a lower elastic modulus than the other thermo set.

Keywords: thermoplastic resin, thermo set resin, elastic modulus, hardness, nanoindentation

The orthodontic appliances have a great diversity of resins they can be made of and therefore, for practitioner is important to wisely choose the advantages and disadvantages of each type. There are many ways of classifying these resins, but starting from their thermal behavior they can be thermoplastic and thermo set.

The thermoplastic resins, as the name explains, are shaped at heat and pressure without chemical changes. They get hard after cooling and can be softened again at heat and are soluble in solvents. The thermo set resins are obtained by the chemical reaction of two substances (for example a powder and a liquid), cannot be resoftened by exposure to heat and are not soluble in solvents [1, 2].

Examples of thermoplastic resins are: polymethyl methacrylate, polyvinyl acrylics and polystyrene, and examples of thermo set resins are: cross-linked polymethyl methacrylate, silicones.

Pros for thermo-cured orthodontic appliances are: lower cost, the ability to introduce multiple active elements in the acrylic base, large offer of models.

Cons are represented by the irritating and allergenic potential due to the presence of unpolimerized monomer, which give also their porosity, increased working time, water uptake, more liable to break, uneven thickness.

The vacuum-thermoformed orthodontic appliances have no residual monomer, even thickness and better finishing but cost more, reduced color offer and fewer active elements possible to be introduced in their structure.

This paper has as purpose to compare three resins used for orthodontic appliances, one thermoplastic and two thermo set: Biocryl C (Scheu Biostar), Orthocryl (Dentaurum), Orthoplast (Vertex Dental).

Biocryl C – Scheu consists in break-resistant acrylic blanks, made of pure thermoplastic PMMA material, without monomer, which bonds to acrylic resins and which can be used for a large variety of removable appliances designed for retention of minor tooth movement, orthodontic plates and retainers [3].

Orthoplast (Vertex Dental) is a self curing acrylic resin available as powder and liquid (curing time 20 min at 55 degrees and 2.5 bar, dough time 9 min, working time 6 min) [4].

Orthocryl (Dentaurum) is another self curing acrylic resin available as powder and liquid (curing time 20 min, 40-46 degrees at 2.2 bars) [5].

The instrumented indentation technique is a method used to measure mechanical properties of a material like surface hardness and indentation elastic modulus (e-modulus). The method can be used on resins and polymers at micro or nano scale, materials with qualities that can vary from point to point [6].

In a traditional indentation test (macro or micro indentation), a hard tip whose mechanical properties are known (frequently made of a very hard material like diamond) is pressed into a sample whose properties are unknown. The load placed on the indenter tip is increased as the tip penetrates further into the specimen and soon reaches a user-defined value. At this point, the load may be held constant for a period or removed. The area of the residual indentation in the sample is measured and the hardness is defined as the maximum load, divided by the residual indentation area.

In nanoindentation small loads and tip sizes are used, so the indentation area may only be a few square micrometers or even nanometers. This presents problems in determining the hardness, as the contact area is not easily found. Atomic force microscopy or scanning electron microscopy techniques may be utilized to image the

* email: liviuuoradea@yahoo.co.uk; drlileioana@yahoo.com; biancalucan@yahoo.co.uk

indentation, but can be quite cumbersome. Instead, an indenter with a geometry known to high precision (usually a Berkovich tip, which has three-sided pyramid geometry) is employed. During the course of the instrumented indentation process, a record of the depth of penetration is made, and then the area of the indent is determined using the known geometry of the indentation tip. While indenting, various parameters such as load and depth of penetration can be measured. A record of these values can be plotted on a graph to create a load-displacement curve. These curves can be used to extract mechanical properties of the material. The indentation curves have often at least thousands of data points. The hardness and elastic modulus can be quickly calculated by using a programming language or a spreadsheet.

Experimental part

Materials and method

Three resins were put in test. From each of them were made two squared specimens, one transparent and one coloured: Biocryl transparent, Biocryl blue, Orthoplast transparent, Orthoplast pink, Orthocryl transparent, Orthocryl yellow. The resin specimens were prepared according to the manufacturer recommended instructions. All of those six specimens were designed at the same dimensions size 20x20x4 mm, using a sandblaster. Each specimen was fixed on a support and they were tested with Nano Indenter G200 from Keysight (Agilent) (fig. 1-4). For each specimen it was analyzed the mean modulus at maximum load and the mean hardness at maximum load.

The method uses a single load/unload cycle to a specified depth. Hardness and modulus are determined using the stiffness as calculated from the slope of the load displacement curve during the unload cycle. The indenter tip begins approaching the surface from a distance above the surface of approximately Surface Approach Distance. The approach velocity is determined by Surface Approach Velocity. When the indenter determines that it has contacted the test surface, according to the criteria Surface Approach Sensitivity, the indenter penetrates the surface at a rate determined by Strain Rate Target. When the surface penetration reaches the Depth Limit, the load on the indenter is held constant for Peak Hold Time. The load on the indenter is then reduced by an amount defined by Percent to Unload at a rate equal to the maximum loading rate. Then, if Perform Drift Test Segment is set to "1", the indenter is held in contact with the sample under constant force for 75 seconds (otherwise, this test segment is skipped). Each specimen had received 25 indentations (fig. 5), and for each indentation were around 800 measurements of load on sample (mN) versus displacement on surface (nm). The mean e-modulus and hardness for the specimens were obtained with the software of the Nanoindenter according to these data pairs (fig. 6-8) [7, 8].

Statistical analysis

Data for each mechanical property were analyzed to compare statistical difference using Student t-test, summary statistics and Student Newman Keuls test with Med Calc software (table 1).

Results and discussions

Biocryl got the closest values of mean e-modulus to those presented in technical sheet by the producer for both samples, the transparent and blue one (3.3 GPa given by producer, 3.202 GPa for Biocryl transparent, 3.329 GPa for Biocryl blue, $p>0.05$). Orthoplast had received bigger values in test comparing with those given by the producer (3.628 GPa for Orthoplast transparent and 3.719 GPa for Orthoplast pink comparing with 1.985 in technical sheet, $p<0.001$). Orthocryl had intermediate values (3.543 GPa for Orthocryl transparent and 3.608 GPa for Orthocryl yellow). The producer has not given values in this case. The statistical difference for Orthoplast can be explained by the different testing of e-modulus. The producer has not given details about the method used for testing.

The mean e-modulus is bigger in both thermo set resins than in thermoplastic one. For all resins, the coloured specimen had similar values with the transparent one ($p>0.05$).

Fig. 1. The support for the specimen exposed to heat, while the adhesive resin is melting

Fig. 2. The specimen glued on the support with the melted glue resin

Fig. 3. Three specimens and reference specimen of the Nano Indenter

Fig.4. The Nano Indenter G 200 used during testing

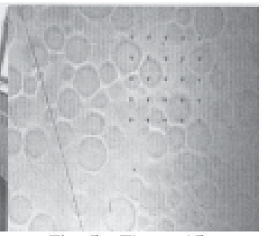

Fig. 5. Those 25 indentations on each specimen

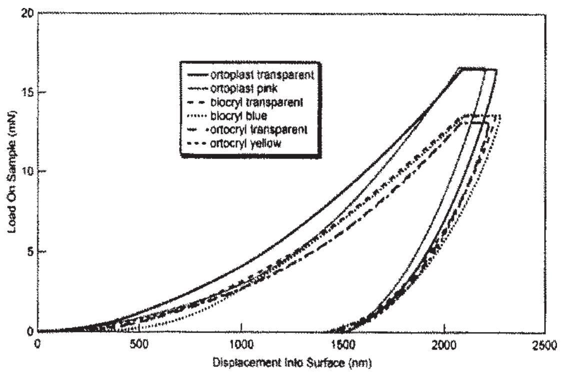

Fig. 6. Results of the test

Material tested	Mean e modulus at maximum load (MPa) p=0,81*	Standard deviation	Mean hardness at maximum load (MPa), p=0,41* *	Standard deviation
Biocryl transparent	3202	197,87		17,54
Biocryl blue	3329		130	
Orthoplast transparent	3628		169	
Orthoplast pink	3719		159	
Orthocryl transparent	3543		130	
Orthocryl yellow	3608		129	

Table 1
MEAN RESULTS FOR E-MODULUS AND SURFACE HARDNESS

*Kolmogorov Smirnov test for normal distribution

**Student t test p<0,001

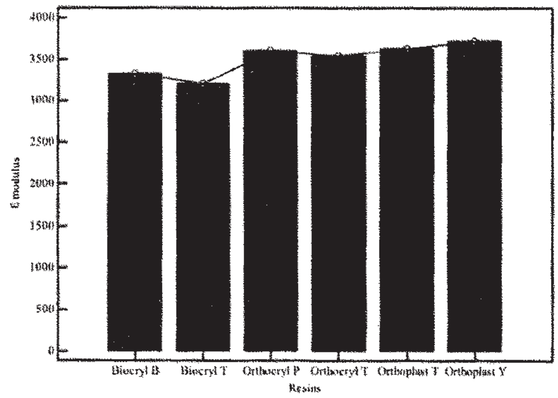

Fig. 8. E-modulus for tested resins

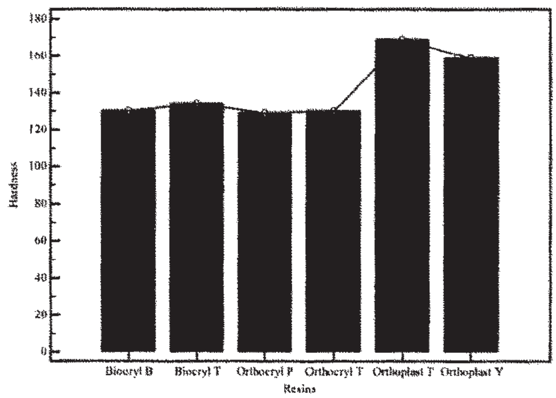

Fig. 9. Hardness for tested resins

The literature written about mechanical properties of materials used for orthodontic appliances determined with nanoindentension or other methods is not very extensive. The results are obtained with different methods, so they can not be in all cases compared.

One study has measured flexural modulus for 6 acrylic PMMA resins cold and heat cured and found values between 1.7-2.5 GPa [9]. The method used was three point bending test in water bath at 37 degrees under the conditions specified by ISO 1567:1999.

Another study observed three resins obtained with thermal polymerization and two with microwave polymerization. The e-modulus for thermo polymerized resins was 3724, 2925, 2613 MPa and 2945 and 3737 MPa for microwave group microwave. The method used was nanoindentation [10]. Our data for e-modulus and working method are close to these results.

Elastic modulus was significantly higher for heat-polymerized acrylic resins than for auto polymerized acrylic resins in a study conducted by American researchers [11].

According to the brand used, flexural (e) modulus in another research ranged from 2550 MPa for heat-curing denture base polymer to 2418 MPa for auto polymerizing denture base polymer, so lower results than in our study [12].

Lower results had also Ali et al. using 3-point bending test. The flexural modules (MPa) were 1969 +/- 55, and 1832 +/- 89 for Meliodent (heat-cured PMMA), and Probase Cold (auto-cured PMMA) materials, respectively [13].

On the other part, Danesh et al. had a larger range of results for auto and light polymerized PMMA then our study, using a different method. Flexural modules lay between 1.3 and 5.3 GPa [14].

Hardness is also a mechanical property tested by several studies. It has many facets, regarding the measuring characteristics. Hardness Vickers, Rockwell, Barcol, nanoindentation hardness are just a few of the parameters found in research.

In our study the mean surface micro hardness was the biggest in Orthoplast (169 MPa for Orthoplast transparent and 159 MPa for Orthoplast pink), followed by Biocryl (134 MPa for Biocryl transparent and 130 MPa for Biocryl blue) and with very closed values by Orthocryl (130 MPa for Orthocryl transparent and 129 MPa for Orthocryl yellow). Only Scheu Gmbh has provided values for surface hardness without explaining the type of test used 195 MPa. The values obtained by our test for both specimens of Biocryl are smaller.

Biocryl was also tested by some Serbian authors [15] for parameters like tensile strength, 3 point bending strength, fracture toughness and hardness Vickers. The hardness Vickers was 22.43 HV0.3 and 21.96 HV0.3 but the data are not comparable because of different work method and type of formula used comparing to our study.

Other authors have studied the hardness of light cured resins and auto polymerized resins (including Orthocryl) and the auto polymerized resins had lower hardness than the light polymerized resins [14].

Another study that tested five resins with nanoindentation found 236, 156 and 145 MPa micro-surface hardness for thermo polymerized ones and 158 and 226 MPa for microwave polymerized resins. The results are for three of them close to our study, but still two of them were higher [10]. Other materials tested were Meliodent (heat-cured PMMA), and Probase Cold (auto-cured PMMA) with hardness Vickers (VHN) values 17.0 +/- 0.4, and 16.0 +/- 0.4 [13].

Zafar et al. made another evaluation of micro-hardness with a nanoindenter. The absolute hardness was recorded 297.72±19.04 MPa and 229.93±18.53 MPa for heat cured PMMA and cold cured PMMA, so values higher than in our study [16].

A group of six heat and auto cured PMMA resins got hardness Vickers between 11.88 HV0.3 and 17.24 HV0.3, 12.16-16.48 HV0.03 and 23.6-39.1 hardness Barcol [9].

Conclusions

The thermoplastic material examined had a lower e-modulus than the other thermo set PMMA. The micro-surface hardness values are different in the case of all tested PMMAs and they are not influenced by the type of resin-thermoplastic or thermo set.

Acknowledgment: Our gratitude to "Hungarian-Romanian Research Platform for Smart-Materials Research Project Support", cod HURO/tto1/1g1/2.2.1, Hungarian-Romanian Cross-border Cooperation Programme 2007- 2013, for the help in acquiring the device used.

References

1. BECHIR A., PĂCURAR M., BECHIR E., et al., Mat. Plast., **51**, no.1, 2014, p.57
2. NEGRUIU M., SINESCU C., ROMÂNU M., POP D., LAKATOS S., Temporo Mandibular Joint, **55**, no. 3, 2005, p.295
3. *** http://www.scheu-dental.com/fileadmin/medienablage/SCHEU-DENTAL/Downloads/ Produkt datenbl%C3%A4tter/Englisch/Datasheet_BIOCRYL_C.pdf accessed at 15.06.2015
4. *** http://www.vertex-dental.com/en/products/19-en/26/168-vertex-orthoplast/ accessed at 15.06.2015
5. *** http://www.dentaurum.de/eng/polymerisation—finishing-17511_17966.aspx accessed at 15.06.2015
6. CANTARAGIU A., FETECĂU C., PARASCHIV G., Mat. Plast., **52**, no. 1, 2015, p. 69
7. MASOURAS K., AKHTAR R., WATTS D., SILIKAS N., J. Mater. Sci. Mater. Med., **19**, no. 12, 2008, p. 3561
8. *** http://www.keysight.com/en/pc-1678689/nanoindentersnid=-34000.0&cc=US&lc=eng accessed at 15.06.2015
9. LEE H.H., LEE C.J., ASAOKA K., Dent. Mater. J., **31**, no. 1, p.157
10. BINDO M.J., NAKAMAE A.E., SANTOS LDE B., ISHIKAWA K.H., GUARNIERI TDE C., TAMAKI R., Bras. Oral. Res., **23**, no.1, 2009, p.68
11. BERTASSONI L.E., MARSHALL G.W., DE SOUZA E.M., RACHED R.N., J. Prosthet. Dent., **100**, no. 6, 2008, p. 449
12. VALLITTU P.K., J. Prosthet. Dent., **81**, no. 3, 1999, p. 318
13. ALI I.L., YUNUS N., ABU-HASSAN M.I., J. Prosthodont., **17**, no. 7, 2008, p.545
14. DANESH G., LIPPOLD C., ZIEBURA T., REINHARDT K.J., SCHÄFER E., EHMER U., J. Orofac. Orthop., **67**, no.2, 2006, p.138
15. BALOS S., MILUTINOVIC M., POTRAN M., et al., J. Mechanical Engineering, **61**, no.2, 2015, p.138
16. ZAFAR M.S., AHMED N., Technol. Health Care, **22**, no. 4, 2014, p.573

Manuscript received: 8.07.2014