Chapter 1

Acrylates and Their Alternatives in Dental Applications

Lavinia Cosmina Ardelean, Cristina Maria Bortun,
Angela Codruta Podariu and Laura Cristina Rusu

Additional information is available at the end of the chapter

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Abstract

Acrylic resins dominated dentures technology for several decades. Due to their many disadvantages, new classes of resins, which promise better quality, constantly appear. Mechanical properties of acrylic resins, including fracture behaviour, water absorption and mechanical strength degradation caused by the exposure to saliva of classical heat-cured acrylic resins compared to alternative urethane-based light-cured resins, were carried out. The allergy potential of acrylic resins was evaluated by *in vivo* and *in vitro* tests. New choices of resins, like thermoplastic injected resins, light-cured or milled high-performance polymers, with better properties compared to acrylics, suitable for dental applications are being presented.

Keywords: acrylates in dentistry, alternative resins for dental use, thermoplastic resins, light-cured resins

1. Introduction

In dentistry, non-metallic materials for denture manufacturing have a long tradition [1]. Among the first materials used, wood, ivory and dentin from hippopotamus teeth or even human teeth may be found. These types of dentures were considered a luxury, due to their prohibitive price and only rich people could afford them. Charles Goodyear discovered vulcanized rubber in 1839. This was the premise for manufacturing dentures with rubber base, much more cheaper and accessible to any pocket [2]. Celluloid, which appeared in 1871, was the first artificial polymer competing with rubber. But, this was not able to overcome the drawbacks such as dimensional instability, deformability and problems in processing technology. Resins represented a huge step forward in dentistry and the first heat-cured acrylic was reported in 1936 [3]. First chemical studies regarding

diacrylic composite resins-type urethane polymers were also carried out at that time by Otto Bayer in the IG Farben Laboratories in Leverkusen. Acrylics, in fact poly(methyl methacrylate) (PMMA) mixed with methyl methacrylate, dominated denture technology for several decades. There were no competitors in manufacturing denture bases, artificial teeth, orthodontic appliances, single-tooth or provisional restorations or as veneering materials (**Figure 1**).

The toxicity of the residual monomer, the complex wrapping system, difficult processing and poor resistance are some of the disadvantages of these materials. Many new classes of resins/macromolecular compounds which promise better quality came on to the market such as diacrylic, styrene, polycarbonate, epiminic, polyurethane, vinyl, polyamide, acetal and polyglass. Besides classic heat-curing, alternative technologies namely, casting and injection moulding are nowadays available in manufacturing acrylic resins for dental applications. In the case of alternative resins, light-curing or microwave polymerization techniques are also used [4, 5]. Light-curing, as a polymerization method for dental materials, appeared in the 1970s. Initially, ultraviolet light was used. Afterwards, it was replaced by visible radiation (visible spectrum wavelength/electromagnetic waves), the light source being either a halogen bulb or xenon stroboscopic lamps [6, 7]. The classification of resins according to DIN EN ISO 1567 is presented in **Table 1**.

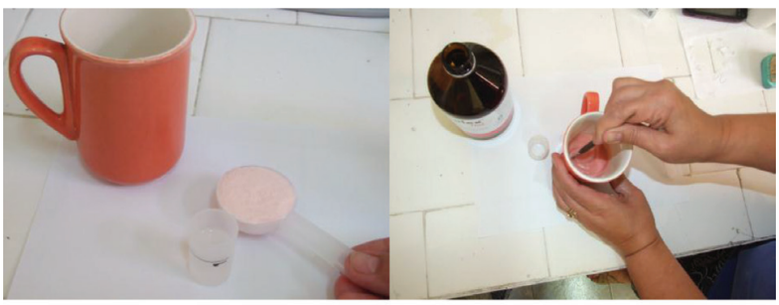

Figure 1. (a) Heat-curing acrylate powder and liquid and (b) mixing the acrylic paste.

Type	Class (manufacturing)	Group (presentation form)
Type 1	Heat-cured resins (>65°C)	Group 1: Bicomponent powder and liquid Group 2: Monocomponent
Type 2	Self-cured resins (<65°C)	Group 1: Bicomponent powder and liquid Group 2: Bicomponent powder and casting liquid
Type 3	Thermoplastic resins	Monocomponent system grains in cartridges
Type 4	Light-cured resins	Monocomponent system
Type 5	Microwave-cured resins	Bicomponent system

Table 1. The classification of resins according to DIN EN ISO 1567.

2. Mechanical properties of acrylic resins

2.1. Evaluation of water absorption and mechanical strength degradation caused by the exposure to saliva of classical heat-cured acrylic resins compared to alternative urethane-based light-cured resins

It is well known that acrylates for dental use have poor resistance and these degrade in the wet environment of the mouth. Our studies involve evaluation of water absorption and mechanical strength degradation caused by the exposure to saliva of classical heat-cured acrylic resins compared to alternative urethane-based light-cured resins, which are also used for dentures manufacturing. Twenty samples (plates: 2 mm in thickness, 30 mm in length and 5 mm in width) of Meliodent (Heraeus-Kulzer) heat-curing acrylic resin and twenty samples of two urethane-based light-curing resins from the same system-Eclipse Resin System: Eclipse Base Plate and Eclipse Contour Resins (Dentsply-DeguDent) were analyzed, in saliva and dry environment. Ten samples were immersed in saliva with low microbial content and neutral pH, at 37°C for 30 days. The other ten samples were kept dry for 30 days. Saliva was collected from clinically healthy subjects and tested for germs with Vivacare line CRT bacteria 2 in one test kit. The test results showed level two of four possible contaminations and so the saliva was considered not severely contaminated. Its pH, determined with an indicator strip, was normal, with an average value of six, as shown in **Figure 2**. In order to determine the water percentage content, the samples were initially weighed and further weighed after 48, 144, 312 and 720 h.

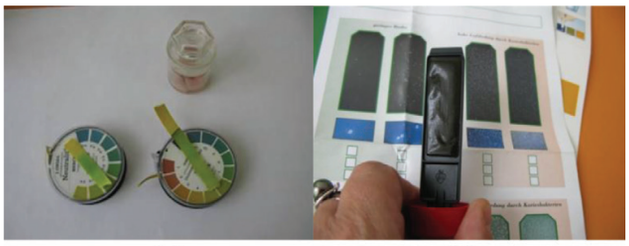

Figure 2. (a) pH index and (b) quantitative evaluation of Streptococci and Lactobacilli microorganisms.

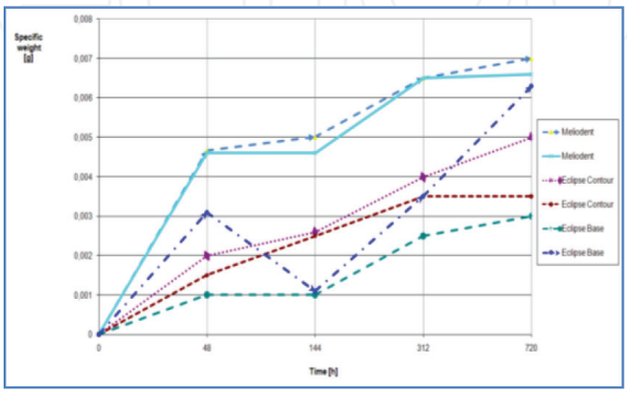

Figure 3. Correlation between specific weight and time for the tested polymers (specific weight = measured weight – initial weight).

Meliodent (Heraeus-Kulzer) was proven to have the highest water absorption capacity, followed by Eclipse Contour Resin and Eclipse Base Plate (Dentsply-DeguDent) (**Figure 3**).

The diagram showing correlation between the three types of resins and the percentage humidity content reveals that the heat-curing resin absorbs more water than the light-curing resins. The diagram indicates the maximal and minimal values for each material (**Figure 4**).

Zwick Roell extensometer (Zwick GmbH & Co.) was used to determine the moment of sample breaking or fracture point and its elongation. TestXpert software was used to standardize the applications (**Figure 5**).

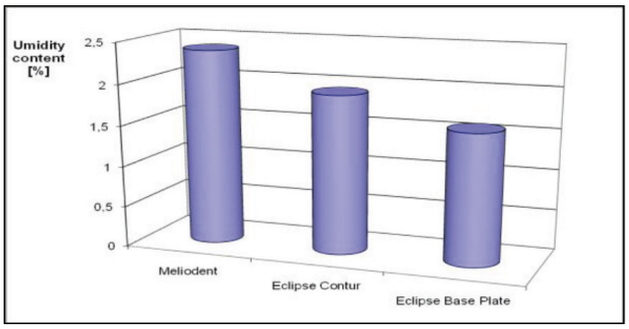

Figure 4. The determination of percentage humidity content of polymer.

Figure 5. The determination of tensile mechanical resistance using the Zwick Roel extensometer.

Materials	Normal conditions		Humid conditions (1 month)	
	E [MPa]	R_m [MPa]	*E* [MPa]	R_m [MPa]
Meliodent	1615.60	52.77	1168.50	48.51
Eclipse base	2527.60	94.46	1921.50	66.76
Eclipse contour	1955.00	40.53	1577.00	25.39

Table 2. The mechanical properties of the studied materials kept in dry and in humid conditions for 1 month.

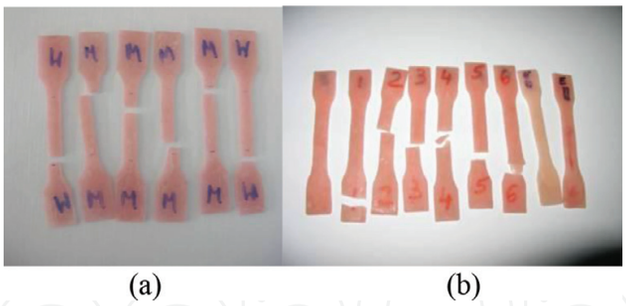

Figure 6. (a) Meliodent samples broken after stretching and (b) broken Eclipse samples.

Results showed that the humid samples (kept in saliva) had significant lower values than the dry samples, realized from the same material. The Young's elasticity modulus (E) and ultimate tensile strength (R_m) were taken into consideration. The average values after the sample analysis are shown in **Table 2**.

There is an evident difference among the tested materials. The heat-curing resin has a lower value of the elasticity modulus than the urethane-based resins. The values decrease distinctly in humid environment, especially in the case of Eclipse Base resin. The mechanical strength also shows decreased values for the humid samples, for all three resins tested in the present work. Generally, the results indicate a higher decrease of mechanical strength values for urethane-based light-curing resins (Eclipse) when compared to heat-curing acrylate (Meliodent) resins. The heat-curing acrylate shows a higher decrease in elasticity than the light-curing resins (**Figure 6**). The differences noticed between humid and dry environmental conditions indicate that there is clear evident role of the saliva in the biodegradation of the denture base polymers [8].

2.2. Fracture behaviour after elongation of two heat-curing acrylic resins

The same type of samples (plates: 2 mm in thickness, 30 mm in length and 5 mm in width) made of Meliodent (Heraeus-Kulzer) and Royaldent Plus (Palatinal Kft.) heat-curing acrylic resins were tested to compare the fracture behaviour after elongation. Both longitudinal and transversal surfaces of the samples, after breaking, were analyzed using the Olympus type SZX7 stereomicroscope equipped with an image processing system QuickphotoMicro 2.2. soft (**Figure 7**).

The two acrylic resins have different fracture behaviour. In the case of Meliodent resin, the elongation before fracture was lower compared to that of Royaldent resin, indicating a ductile fracture behaviour.

The following data were obtained by testing the two resins using Zwick Roell extensometer (Zwick GmbH & Co.). Meliodent: Ultimate tensile strength (R_m): 54–75 MPa, Young's elasticity modulus (E): 1383–1688 MPa and elongation: 1–3.5%. Royaldent: Ultimate tensile strength (R_m): 69–90 MPa, Young's elasticity modulus (E): 1282–1937 MPa and elongation: 2–5%.

In the longitudinal section, Meliodent samples do not show elongation. The final fracture being sudden compared to the Royaldent samples, which had a significant elongation before fracture. In the transversal section, one may remark that dark reinforcement fibres from Meliodent

Figure 7. Stereomicroscope Olympus type SZX7.

(**Figure 8a**) do not break together with its polymeric matrix, whereas both matrix and fibres are broken at the same time in the case of Royaldent sample (**Figure 8b**). The different fracture behaviour of the two acrylic resins may be explained by the differences between mechanical characteristics of reinforced fibres and the polymeric matrix. The mechanical characteristics of fibres are better than those of the matrix in the case of Meliodent samples, whereas Royaldent samples showed the similar characteristics for fibres and matrix. Therefore, Royaldent samples show a better behaviour to fracture than Meliodent samples as well as ductile behaviour.

Stereomicroscopic analyses of two acrylic resins showed that the entire sample has a brittle fracture having a quasi-crystalline aspect in the transversal section.

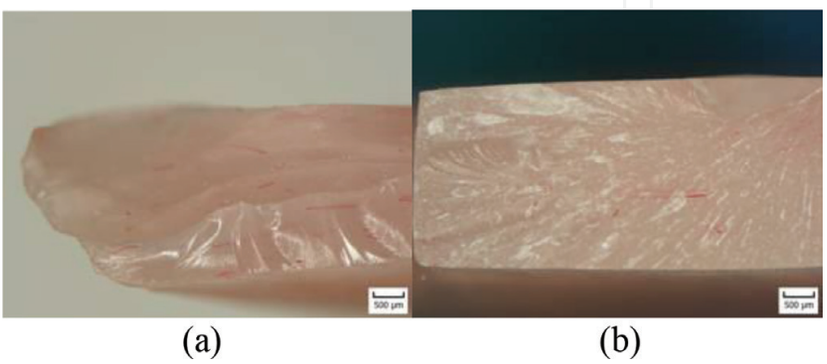

Figure 8. The stereo microstructural aspect of the samples: (a) Meliodent and (b) Royaldent.

2.3. Fracture toughness evaluation

Being long-term prosthetic pieces, complete dentures need a warranty regarding their mechanical resistance and lifetime. The fracture toughness, which reflects its resistance to fracture and represents the energy required for a crack to propagate through a material to its complete fracture, was evaluated in complete denture technology.

Samples without initial cracks were considered for testing so that the value of the stress intensity factor (K_{IC}) depends only on sample's dimension and critical load value.

Two different heat-curing acrylics were selected. Meliodent (Heraeus Kulzer) and Royaldent Plus (Palatinal Kft.), and a light-curing urethane-based resin-Eclipse Resin System (Dentsply-DeguDent) were taken into consideration. The samples were disk-shaped with a circular hole in the centre. Five different samples with the following dimensions were taken for the test:

Sample 1: R_{out} = 42 mm, R_{in} = 4.2 mm, R_{in}/R_{out} = 0.1 and h = 2 mm.

Sample 2: R_{out} = 45 mm, R_{in} = 6.75 mm; R_{in}/R_{out} = 0.15 and h=2 mm.

Sample 3: R_{out} = 48 mm, R_{in} = 9.6 mm; R_{in}/R_{out} = 0.2 and h = 2 mm.

Sample 4: R_{out} = 50 mm, R_{in} = 12.5 mm; R_{in}/R_{out} = 0.25 and h = 2 mm.

Sample 5: R_{out} = 53 mm, R_{in} = 15.9 mm; R_{in}/R_{out} = 0.3 and h = 2 mm.

where R_{in} = hole radius, R_{out} = disk radius and h = disk thickness.

Five samples were made of each material (**Figure 9**).

The compression tests were performed with the same static loading machine (**Figure 6a**), model Zwick Roell of 5 kN (Zwick GmbH & Co.), connected to a computer (TestXpert specific soft.). The samples were compressed until breaking (**Figure 10**).

Each sample was loaded by a pair of point forces, which acted along the diameter. The distribution of the load across the thickness of the disk was uniform. When the force was applied, the micro-cracks situated in the proximity of the force line, at the edge of the inner hole, started to grow, and at a certain value of the force gave rise to a macro-crack. Other

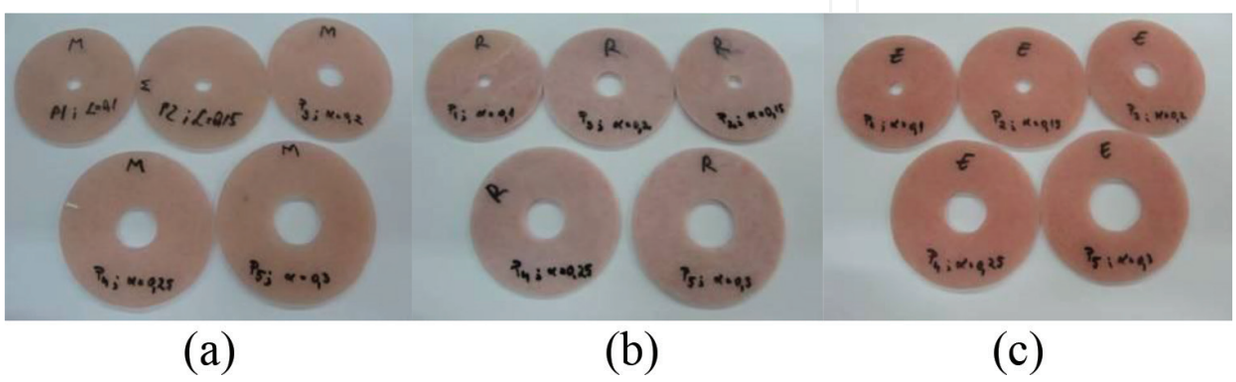

Figure 9. (a) Meliodent samples, (b) Royaldent samples and (c) Eclipse samples.

Figure 10. Meliodent sample during compression experiment.

pre-existing cracks within the specimen did not grow. Here, the central hole, playing the role of the defect, initiated the fracture. As expected, in general the crack developed symmetrically, beginning from the inner hole as shown in **Figure 11**.

The fracture toughness (K_{IC}) was calculated, depending only on the sample's dimensions and critical value of the load. As the brittle materials have high relative compression values and low tension values, the failure begins at the point of inner boundary. In general, the fracture direction was perpendicular to the loading direction. The following values for fracture toughness were obtained: K_{IC} = 2.4 MPa√m for Meliodent, K_{IC} = 2.65 MPa√m for Royaldent and K_{IC} = 3.35 MPa√m for Eclipse (**Figure 12**).

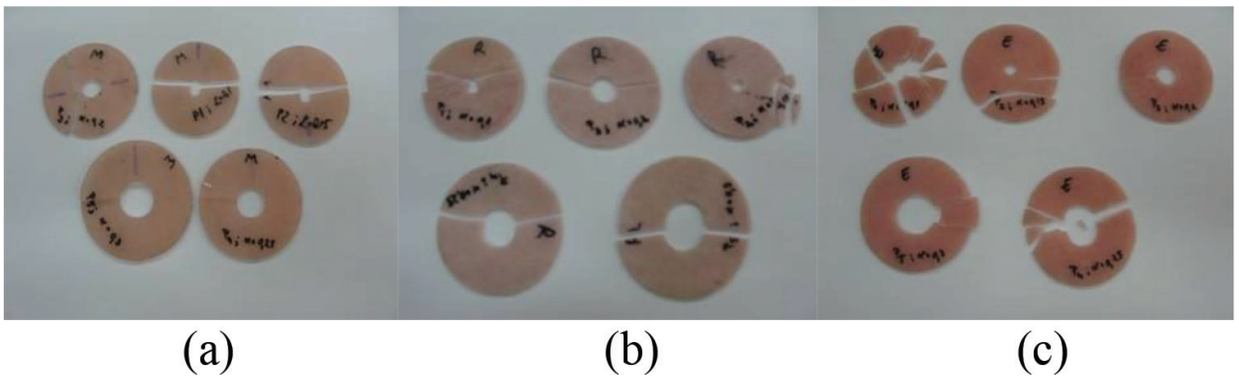

Figure 11. Aspects of the samples after the compression experiment: (a) Meliodent, (b) Royaldent and (c) Eclipse.

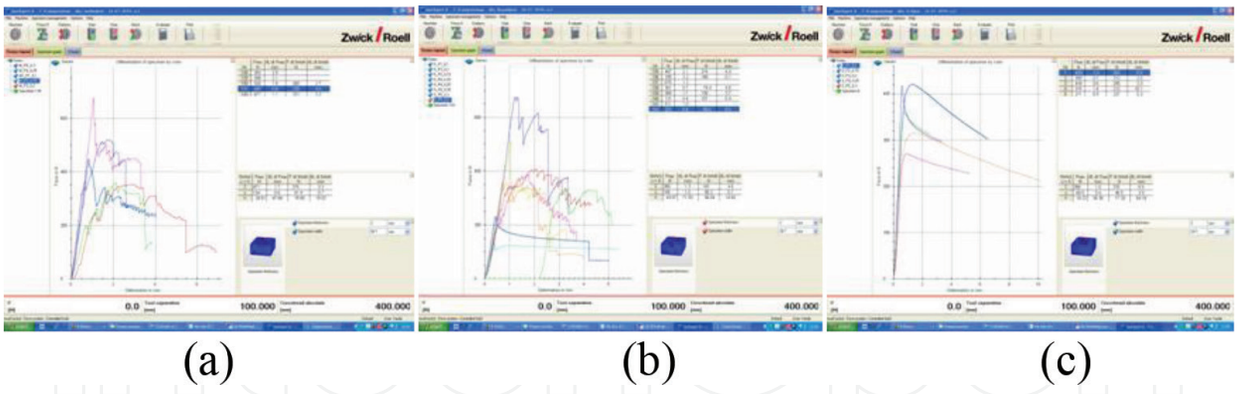

Figure 12. Force-displacement diagrams resulted after caring out compression test: (a) Meliodent, (b) Royaldent and (c) Eclipse.

The results obtained for the three tested resins showed no significant differences, Eclipse resin shows the highest value for fracture toughness [9, 10].

Comparative studies were undertaken with the same materials using different methods, in order to get comparative results. Single-edge-notched beam (SENB) method and indentation strength (IS) method were used. In the case of a single-edge-notched beam (SENB) method, samples were prepared in the form of plates with dimensions of 50 × 50 × 2 mm from which rectangular beams with dimensions of 4 × 2 × 25 mm (width/thickness/length) were cut.

The bending tests were carried out on a Zwick-Roell 5 kN testing machine (Zwick GmbH & Co.) (**Figure 6a**). The two halves of the broken samples were used for the measurement of the notch depth c. The toughness and the experimental values for *K*ic, obtained using SENB method were 2.26 MPa√m for Meliodent and 3.18 MPa√m for Eclipse resins.

Indentation strength (IS) method uses a Vickers pyramid to determine the fracture toughness by analyzing the stress field at a crack tip. The indentations of the samples were made using a Vickers hardness tester, model HMO 10, in the middle of the tensile surface of the beams at a load of 98 N, for 15 s, magnitude which prevented radial cracks (**Figure 13**).

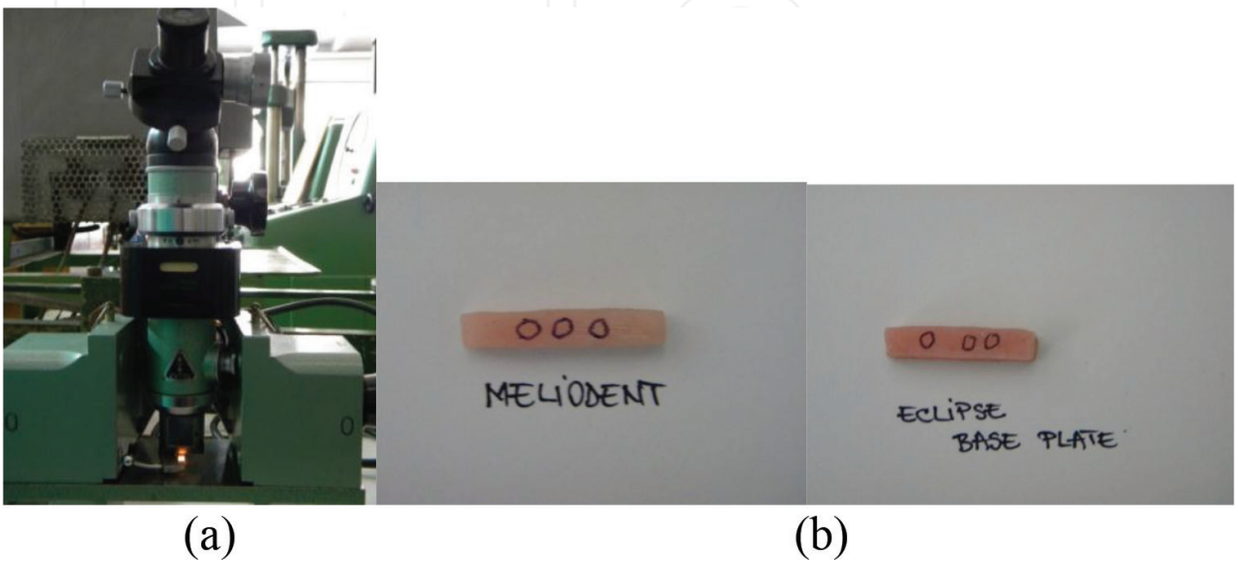

Figure 13. (a) The Vickers pyramid and (b) the samples.

Material	Hardness (H) [MPa]	Fracture toughness (K_{IC}) [MPa√m] SENB	Fracture toughness (K_{IC}) [MPa√m] IS
Meliodent	29.54	2.26	2.31 (v = 0.05 mm/min)
Eclipse	25.35	3.18	3.26 (v = 0.05 mm/min)

Table 3. Measurement results for Meliodent and Eclipse.

The measurements of the fracture toughness (K_{IC}) were found to be 2.31 MPa√m for Meliodent and 3.26 MPa√m for Eclipse resins.

Results obtained by the strength indentation (IS) method are comparable to those obtained by the SENB method at low loading rates (~0.05 mm/min), as shown in **Table 3**.

3. Studies concerning biocompatibility of acrylic resins

Acrylates are well known for their potential allergies. To evaluate the allergy potential of acrylic resins, we used *in vivo* and *in vitro* tests. For *in vivo* testing, we have used the patch test and the tumour necrosis alpha-factor (TNF) test, which is eloquent for cytotoxic detection and can detect early signs of allergy and inflammation by measuring endotoxins in patient serum. Acrylate toxicity is mainly due to the residual monomer. Therefore, we have also carried out tests to determine the amount of residual monomer present in the resin by the volatile-component-content method and bromine index methods [11, 12].

3.1. *In vivo* testing

3.1.1. Patch test

Patch testing involves applying patches dipped in supposedly antigenic substance on a free-rash segment and off the rash periods and maintaining them in contact with the skin for 48 h. The area for testing is the mid-upper back, anterior sides of forearms and upper external region of the arms, as shown in **Figure 14** [13].

IQ Ultra Chambers Box (Chemotechnique Diagnostics) tests were used, with methyl methacrylate as an allergen. All 10 subjects showed tenderness (sensibility) to methyl methacrylate [14].

3.1.2. TNF alpha test

TNF alpha (tumour necrosis alpha-factor) test which is eloquent for cytotoxicity detection was used in three cases of mucosal reactions in patients wearing acrylic dentures. The enzyme-linked immunosorbent assay (ELIZA) method was applied to the patient's serum [15]. Five hundred microliters were harvested from each patient (having a duplicate sample) in order to determine the TNF alpha concentration. Quantikine Human TNF alpha immunoassay which

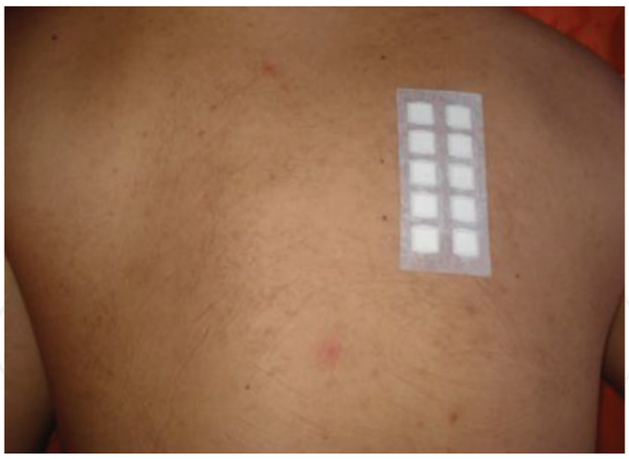

Figure 14. Patch test.

allows the quantitatively determination of cytokines on patient serum was used. The substrate solution was obtained by mixing equal volumes of A and B reagents from the kit, maximum 15 min before usage. The supply solution (the undiluted standard) was prepared by reconstructing the cytokine standard using calibrator thinner RD6-21. For standard preparation, 500 μL of calibrator thinner RD6-21 was used. After pipetting 500 μL of solution in the first tube, the mixing concentration was calculated. The solution was well stirred and 500 μL was transferred into the next tube. The concentration is once again calculated. Standards for different concentrations are prepared in the same way (500, 125, 62.5, 31.2, 15.6 pg/mL). The supply solution was used as high standard (1000 pg/mL) and the calibrating thinner RD6-21 was used as zero standard (0 pg/mL). Note that 100 μL of thinner RD1-51 was pipetted in each hole of the plate and 100 μL of each standard was pipetted in the first strip in the following order: 0, 15.6, 31.2, 62.5, 125, 250, 500 and 1000 pg/mL. Starting with the second strip, 100 μL was pipetted. The plate was covered with an adhesive film and incubated for 2 h at room temperature. After that, the plate was washed automatically four times with 400 μL of washing solution and placed on an absorbent paper to clean the samples without damage. Note that 200 μL of cytokine conjugate was added in each hole and the plate was covered with an adhesive film and incubated for 2 h at room temperature. After the incubation period, the adhesive film was removed and the plate washed in the same way. Note that 200 μL of substrate solution was then added to each hole of the plate, the plate was covered again with an adhesive film and incubated for 30 min at room temperature, in darkness. After incubation time was over, 50 μL of stopping solution was added in each hole of the plate. When the reaction stops, the colour turns from blue to yellow. If the colour is green or does not modify uniformly, the plate will be slightly stirred for complete homogenization. The optical densities are determined 30 min after the reaction was stopped using an automatic reader at a wavelength of 450 nm, with a reference filter of 540 or 570 nm (for correction) (**Figure 15**). In the case of samples that are read only at 450 nm without correction, the accuracy may be influenced. Results are obtained depending on the logarithmic calibration curve of each cytokine, build on absorption and standard concentration (0–1000 pg/mL). The results are shown as optical density units auto-

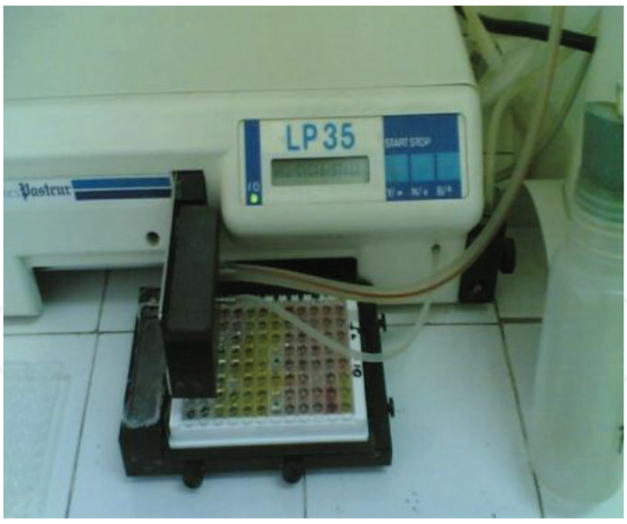

Figure 15. Results reading for TNF alpha test.

matically converted into pg/mL for each of the sample tested. Determination of TNF-alpha concentration in the first case revealed slightly increased values of this cytokine (50.48–50.7 pg/mL). In the second case, the values were higher (90.3–90.9 pg/mL) and in the third case the values were the highest (100.4–107 pg/mL), which indicate certain inflammation. The results obtained with TNF-alpha test are eloquent for cytotoxic detection of early signs of allergy and inflammation by measuring the endotoxins from the patient serum. It is always recommended to associate multiple types of clinical tests and these should always be histologically confirmed [16].

3.2. *In vitro* testing

3.2.1. Volatile-component content method

Three acrylic resin samples were used, each one being harvested from a different full denture base. The samples were preconditioned at 80°C for 2 h for removing moist. The weight of the samples is S1: 0.7863, S2: 0.05638 and S3: 0.8421 g. A Petri box is sterilized at 150°C for 1 h and then weighed in the analytical scale with high precision. The samples are positioned in the Petri box and weighed again very accurately. They are kept in the oven for 10 h at 150°C, and weighed again, very precisely. The weight difference is given by the amount of existing residual monomer: S1: 0.7864 g, S2: 0.5640 g, S3: 0.8422 g. In all these three cases, no significant weight loss was noticed. These results conclude that almost no residual monomer was found in the three full dentures [14].

3.2.2. Bromine index method

In order to verify the above results, we have used the bromine index method which determines the percentage of monomer in the sample, based on the amount of bromine added to the double bond (C=C) links. All the three samples were found to be free from the residual

monomer. We have concluded that in the three PMMA samples, there is no residual monomer in the acrylic resin samples. But, there is less than a 0.0000 g order which is not detectable. This shows that a very accurate manufacturing method was adopted in the case of the three considered full acrylic denture bases [17].

4. Alternative resins and technologies for denture manufacturing

Our experience in denture manufacturing includes a variety of alternative resins and manufacturing technologies such as self-curing acrylics manufactured by casting, different thermoplastic resins manufactured by injection, light-cured diacrylic and urethane-based resins and poly(ether ether ketone) (PEEK) high-performance polymers manufactured by milling.

4.1. Self-curing acrylics manufactured by casting

Full-denture casting represents one choice to classic heat-curing acrylic dentures. Self-curing acrylic resins suitable for casting belong to type 2, group 2 of acrylic resins (**Table 1**). For polymerization, temperatures below 65°C are used. The acrylic paste was previously prepared in a texture suitable for casting and then poured in a special flask. The mould is made up of either reversible hydrocolloid or silicone (**Figure 16**), compared to the classic plaster mould used for investing heat-cured acrylic dentures. The casting system has the following advantages: the reversible hydrocolloid can be reused and the polymerization time is shorter. There are wide colour ranges (10 colours) of the acrylics and minimal adjustments are required. The most common errors when using this technology are consequence of bubbles forming when pouring the mould. This causes porosity of the mucosal surface and lack of substance due to the fast setting of the resin. Therefore, great skill is required when pouring the mould. Porosity may also occur due to improper preparing of the acrylate [4, 18].

Figure 16. The mould made up of (a) reversible hydrocolloids and (b) silicone, before pouring the acrylic paste.

4.2. Thermoplastic resins manufactured by injection

Compared to classical self- or heat-curing acrylates, thermoplastic resins have a number of advantages as follows: a very good long-term performance, maintaining their size and colour

in time, stability, resistance to deformation, wear and solvents, very good tolerance due to the absence or reduced quantity of residual monomer, responsible for allergies in a lot of patients, no porosity which prevents development of microorganisms and deposits [4].

The advantages of the injecting system lie in the fact that the resin is delivered in a cartridge (**Figure 17a**) which eliminates dosage errors, guaranteeing long-term stability of the shape, reduced contraction, as well as mechanical resistance with ageing. The disadvantages are mainly the consequence of the high cost of the injection device (**Figure 17b**) and of the materials to be used.

The processing technology implies the thermal plasticization of the material, in the absence of any chemical reaction and injection of the plasticized resins into a mould [3].

Advantages of thermoplastic resins include removable partial dentures, preformed clasps, partial denture frameworks, temporary prosthetic restorations, full dentures, orthodontic appliances, anti-snoring devices, mouth guards and splints.

Thermoplastic resins include acetal, polycarbonate (polyesters group), acrylates and polyamides (nylons) [19].

Metal-free removable partial dentures made up of thermoplastic materials represent a modern alternative solution to the classical metal framework dentures. These have the advantages of being lightweight, flexible and much more comfortable to the patient. These are also biocompatible, non-irritant, sure, non-toxic, biologically inert, superior aesthetics and also offer quality static and dynamic stability [5]. The clasps are made up of the same material as the denture base or are readily-made from the same material. Though the mechanical resistance is most important, the first choice for manufacturing the framework is an acetal resin. The removable partial dentures with acetal resin framework are the most laborious to manufacture. The acetal framework was being manufactured first, followed by the acrylic saddles and artificial teeth (**Figure 18**).

These types of partial dentures have thin frameworks, with flexible and aesthetic clasps [20].

Thermoplastic polyamide (nylon) is a versatile material, with high flexibility, physical strength, heat and chemical resistance. The super flexible polyamide is extremely elastic, virtually unbreakable, lightweight and impervious to oral fluids. The medium-low flexibility polyamide is a half-soft material which offers superior comfort, good aesthetics and could be

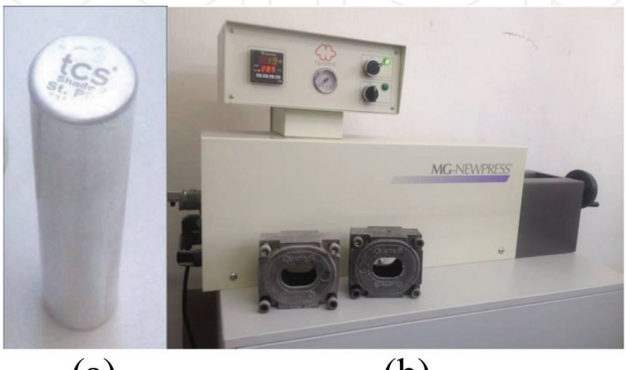

Figure 17. (a) The cartridge of thermoplastic material and (b) the injection unit MG-Newpress (Quattroty).

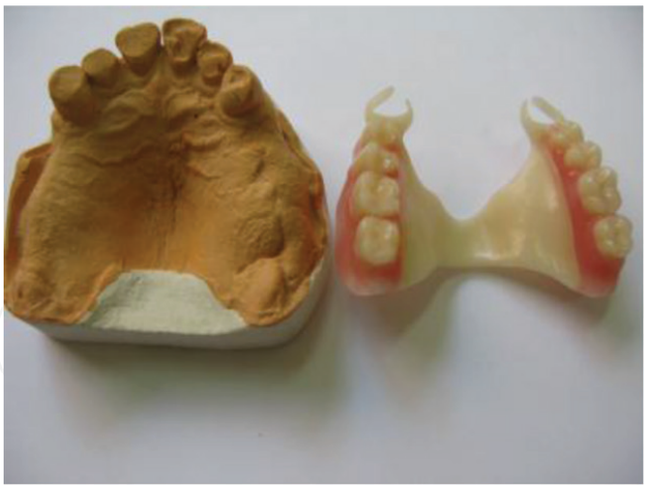

Figure 18. Partial denture with acetal framework, clasps and acrylic saddles.

used for removable partial dentures. Super flexible polyamide is especially useful for retentive dental fields, which would normally create problems with the insertion and disinsertion of the removable partial dentures. The clasps are made up of the same material as the denture base in the case of super flexible polyamide dentures. In the case of medium-low flexibility polyamide dentures, ready-made clasps are an option. Metal clasps may also be used [21] (**Figure 19**).

Polycarbonate resins are particularly polyester materials. These have good fracture strength and flexibility, a natural translucency, but the wear resistance is lower than acetal resins and are not recommended for partial denture frameworks. The finishing is very good, which makes them suitable for temporary prosthetic restorations.

Thermoplastic acrylate has the highest impact rating of any acrylic, has long-term stability, its surface structure being dense and smooth. This material was developed for manufacturing complete dentures. It is not elastic, but its flexibility makes it practically unbreakable as one can bounce such a denture off the floor without cracking the base. The biocompatibility is very good due to the absence of residual monomer. The denture has very good long-term stability because water retention is limited.

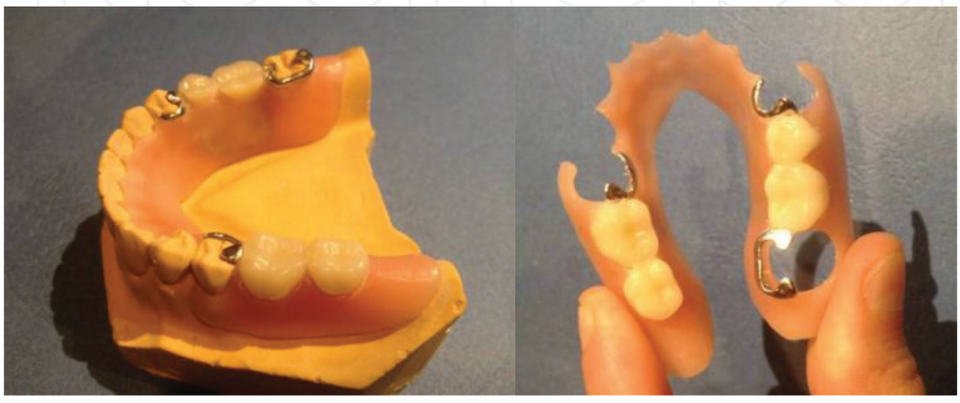

Figure 19. Removable partial denture made up of superflexible polyamide with metal clasps.

4.3. Light-cured diacrylic and urethane-based resins

Diacrylic composite resins are complex materials. Initially elaborated as aesthetic restorative materials, these developed a lot. The advantages of prosthetics are as follows: veneering of metal-polymeric fixed dentures, single-tooth or temporary crowns, inlays, onlays, epitheses, repairing damaged porcelain veneers, artificial teeth, base of removable dentures and repairing removable dentures. Compared to acrylics, these have a lower shrinkage during poly-merization and have superior physico-mechanical and chemical resistance. Diacrylic composite resins can be made using self-, heat or light-curing, in some cases several curing methods being combined. Light-curing diacrylic resins are successfully used in dental laboratories, especially for veneering, having the advantage of prolonged handling time. In addition, these physico-chemically adheres to the metallic framework, have good colour stability in time and a special aesthetic effect, in part due to the wide selection of shades available for veneering. These can be easily repaired after fixing in the oral cavity, if needed [1].

The absence of methyl, ethyl, propyl and butyl groups in urethane-based resin composition does not generate contact allergies. The light-curing Eclipse Resin System (Dentsply-DeguDent) allows a rapid manufacturing of full dentures, eliminating some time-consuming intermediate steps, like investing and heat-curing. The light-curing resins of Eclipse Resin System contain aliphatic urethane dimethacrylate-urethane oligomers (UDMA) as base monomers and acrylic copolymers, an inorganic submicronic silica filling, a light-curing initiating system and additives. The system consists of three types of resins, which can be handled like wax (base plate, set-up and contour resins). The light-curing protocol was made available by the producer in many variants, which correspond to different technical procedures. The system is extremely efficient, a complete denture base may be ready in 30 min, after master model complete setting. The 'wax-up' is practically made on the denture's polymerized base and, after checking it, the rest of the pattern (saddles) was light-cured. Thereafter, the denture was finished [6] (**Figure 20**).

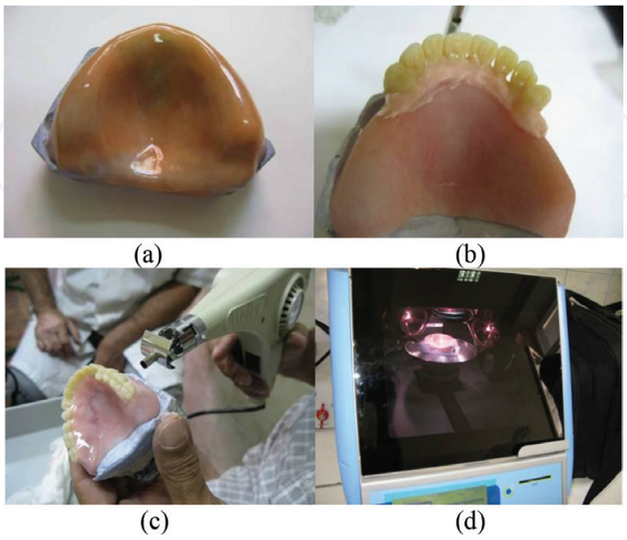

Figure 20. (a) Base plate resin before light-curing, (b) teeth mounting using set-up resin, (c) contour resin processed using the warm air gun and (d) light-curing unit in use.

4.4. High-performance polymers, manufactured by milling

Poly(ether ether ketone) (PEEK) is a high performance polymer used in dentistry since 2002. PEEK is a biocompatible thermoplastic material, with superior properties such as mechanical properties, resistance to wear and fracture and elasticity comparable to bone. PEEK for dental use may be optimized by adding ceramic 0.3–0.5 μm particles. It is resistant to high temperature, good stability, easy to be polished properly, insoluble in water and ideal for allergic patients. The material (grains) may be injected at 400°C or milled (disks) using a CAD/CAM system (**Figure 21a**). It is indicated for crowns and bridges (replacing the metal framework), abutments and removable partial dentures including precision attachments [22, 23].

A removable partial denture framework made up of Juvora PEEK (Invibio) (including clasps), using the Exocad CAD and Coritec 450i (imes-icore) CAM, weights only 1.36 g (**Figures 21b** and **22a**). The saddles are made of acrylate having the entire denture weights only 3.36 g (**Figure 22b**).

Figure 21. (a) PEEK milling disk and (b) PEEK framework on a weighting scale.

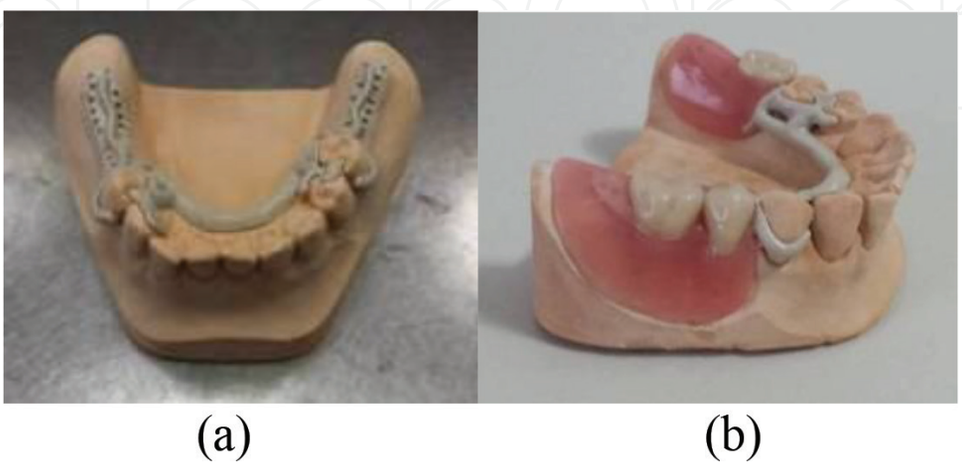

Figure 22. (a) PEEK framework and (b) finished denture.

5. Conclusions

New choices of resins, with better properties compared to acrylics, are now suitable for dental applications. Alternative technologies for processing dental resins, like casting, injection, light-curing and milling are meant to improve their clinical performances.

Long-term deterioration of resin-based dentures in oral environment is still an unsolved problem. This can be improved by bringing innovations in the manufacturing technology, thereby reducing polymer defects and distortions in a warm and humid environment, material's fatigue and ageing. Moreover, we have to consider various possible environmental aggressions such as acids, alcohol, tobacco and thermal fluctuations, the continuous contact with water and salivary enzymes, food remnants, fluctuation of the oral balancing system, the contact with live tissues, bacteria and yeasts. It seems that the enzymes from human saliva are able to produce the softening of the resin surface, probably by hydrolyzing the small oligomers into monomer phases [8].

Choosing the right material for manufacturing partial or full dentures is very important because it has direct effect on their quality and lifetime. Because they are brittle, dentures made up of acrylic resins have a limited life in the mouth. Moreover, following some manufacturing procedures, small defects (holes in the polymer structure) may occur. The continuous mastication stress (repeated movements of low amplitude) and the oral environment have an important role in the degradation of the denture in time [9].

The fracture toughness depends on the type and the nature of the polymer and the reinforcement added components. For example, fracture toughness of a monomethacrylate-based material is lower than that of dimethacrylate-based material. An increase in the fracture toughness can be achieved by adding reinforcement fibres which prevent or slow down the crack growth or by adding rubber-like substances, which increase elasticity [9].

Currently, the selection of dental materials is made particularly in terms of manufacturing technology and aesthetic criteria. These criteria are not sufficient to provide functional, durable and comfortable dentures. In the case of acrylic resins used in dental prosthetics, in addition to aesthetic aspect and strength, elasticity and elongation are also important features. Biomechanical studies of dental resins, implying different technologies, are necessary in order to discover potential causes of failure. These are not only the consequence of material defects and solubility, but can also depend on the technological procedures and processing. Most of the resins distort and fracture at low level of tension dependent on the environmental or loading conditions. In our studies, the values of assessed mechanical properties were lower for the wet samples than for the dry samples, indicating a clear influence of saliva in the biodegradation of the material, with direct consequences biomechanical performances and lifetime for dentures [24, 25].

As far as the allergy potential of acrylic resins is concerned, our results show as follows: *in vivo* tests, both patch test and TNF-alpha showed allergic reactions to acrylate. Both *in vitro* determinations for residual monomer showed a very small and in fact practically undetectable amount in our samples. This led to the conclusion that the manufacturing process was carried out with maximum thoroughness.

Resin-based dental materials have a wide range of applications. But, despite the efforts made to continuously improve their physical, mechanical and aesthetic properties thereby cause side effects regarding their biocompatibility. These situations may lead to local lesions which can prove extremely unpleasant for the patient [16].

In our opinion, the best results in denture manufacturing may be achieved by combining scientific principles with creativity, while the optimal choice of the material and technique has a major importance.

Author details

Lavinia Cosmina Ardelean[1]*, Cristina Maria Bortun[2], Angela Codruta Podariu[3] and Laura Cristina Rusu[1]

*Address all correspondence to: lavinia_ardelean@umft.ro

1 Department of Technology of Materials and Devices in Dental Medicine, "Victor Babes" University of Medicine and Pharmacy, Timisoara, Romania

2 Department of Dentures Technology, "Victor Babes" University of Medicine and Pharmacy, Timisoara, Romania

3 Department for Preventive Dentistry, Community Dentistry and Oral Health, "Victor Babes" University of Medicine and Pharmacy, Timisoara, Romania

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