

Denture Base Polymer Biodegradation: In Vitro Study

Alessandra-Aniela Cerghedi¹, Zita Fazakas², Melinda Székely¹, Carmen Biriş¹, Cristina Molnar-Varlam¹

¹ Faculty of Dental Medicine, "George Emil Palade" University of Medicine, Pharmacy, Science and Technology, Târgu Mureş, Romania

² Faculty of Pharmacy, "George Emil Palade" University of Medicine, Pharmacy, Science and Technology, Târgu Mureş, Romania

CORRESPONDENCE

Alessandra-Aniela Cerghedi

Str. Gheorghe Marinescu nr. 38
540139 Târgu Mureş, Romania
Tel: +40 265 215 551
Email: cerghedianiela@yahoo.com

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ABSTRACT

Introduction: Acrylic resins are the most frequently used materials for the bases of prostheses, and are also used in the re-optimization and the repair of prostheses. The **aim** of our study was to investigate whether direct contact with the resin causes decomposition of methyl methacrylate and formation of ketone bodies in the oral cavity. **Material and methods:** The in vitro study included 12 samples of autopolymerized polymethyl methacrylate and 8 samples of thermopolymerized polymethyl methacrylate. Some of the resin samples were intentionally prepared incorrectly, with modified powder to liquid ratios or thermal regime, to be able to compare them with samples prepared according to the manufacturer's instructions. Some of the samples were immersed in gastric juice or alcohol for 48 h at 37 °C in a thermostatic bath to simulate the environment and temperature of the oral cavity, while others were kept at room temperature. The Legal reaction was used to identify the presence of ketone bodies in the solutions. **Results:** The samples that were prepared incorrectly and were kept at 37 °C were the most affected. The presence of ketone bodies was demonstrated by the formation of a precipitate on the bottom of the test tube and the color change of the solution. Samples that were kept at room temperature were less affected, both from a spectrophotometric and biochemical point of view. **Conclusion:** The quality of polymethyl methacrylate can be improved by respecting the manufacturer's instructions and work protocols, and by avoiding substances that are considered aggressive, such as gastric juice, alcohol, and local factors in the oral cavity.

Keywords: bases of prostheses, unstable compounds, thermostatic bath, Legal reaction

INTRODUCTION

Polymethyl methacrylate (PMM) is a synthetic polymer derived from methyl methacrylate, a monomer that can be obtained through several methods, most frequently from acetone cyanohydrin, produced by the precipitation of acetone and hydrogen cyanide. These dental materials are produced through a free radical polymerization reaction activated by chemicals, heat, or light. N,N-dimethyl-p-toluidine is a chemical activator used for autopolymerizing materials. In the case of heat-polymerizing materials, heat can be provided by a hot water bath or microwave energy, whereas light-polymerizing materials use visible light as an activator. Acrylic-based resins are used in various applications in dental prac-

Zita Fazakas • Str. Gheorghe Marinescu nr. 38,
540139 Târgu Mureş, Romania. Tel: +40 265 215 551,
Email: fazzita@yahoo.com

Melinda Székely • Str. Gheorghe Marinescu nr. 38,
540139 Târgu Mureş, Romania. Tel: +40 265 215 551,
Email: mszekely_2000@yahoo.com

Carmen Biriş • Str. Gheorghe Marinescu nr. 38,
540139 Târgu Mureş, Romania. Tel: +40 265 215 551,
Email: biriscarmen74@yahoo.com

Cristina Molnar-Varlam • Str. Gheorghe Marinescu nr.
38, 540139 Târgu Mureş, Romania. Tel: +40 265 215
551, Email: molnar.stanca@gmail.com

tice, such as denture bases, orthodontic appliances, and temporary crowns.¹

Denture liners improve the fit of denture bases, increasing the retention and stability of removable prostheses. There are different types of denture liners, including hard relined resins and soft lining materials. Soft lining materials can be divided into two categories.²⁻⁵ The first includes materials in which the liquid is composed of a monomer, such as methyl methacrylate, ethyl methacrylate, or butyl methacrylate, as well as plasticizers, such as phthalates, citrates, or sebacates, which increase the flexibility, transparency, durability, and longevity of the material. The second group consists of tissue conditioners, in which the liquid also contains a plasticizer and a mixture of ethyl alcohol.^{6,7}

One of the most important issues related to the clinical use of acrylic resins is biodegradation, defined as a change in their chemical, physical, and mechanical properties due to local factors in the oral cavity.^{8,9} The oral cavity is a complex environment in which dental materials are exposed to both endogenous and exogenous substances. The complex interactions that take place in this environment result in

a general phenomenon of biodegradation that affects the materials present in the oral cavity, including PMM. These changes permanently affect the properties of the material and may endanger its functionality.¹⁰ The aim of our study was to investigate the biodegradation of resins in the presence of aggressive substances.

MATERIAL AND METHODS

The study was divided into two parts: 1) the production of PMM samples; 2) the chemical analysis of the samples made.

For the first part of the study, we needed autopolymerized PMM (PMMA) (Figure 1) and thermopolymerized PMM (PMTT) (Figure 2), as well as a conformer in the form of a cone trunk, plaster, packing table, press, and water bath. The study group included 20 acrylic resin samples divided into two subgroups: PMMA ($n = 12$) and PMMT ($n = 8$). Four PMMA and four PMMT samples were prepared using a modified powder to liquid ratio and thermal regime to compare them with those that were prepared according to the manufacturer's instructions.



FIGURE 1. Preparation of PMM trunk cones



FIGURE 2. The immersion of samples in alcohol and gastric juice



FIGURE 3. The Legal reaction and the presence of ketone bodies

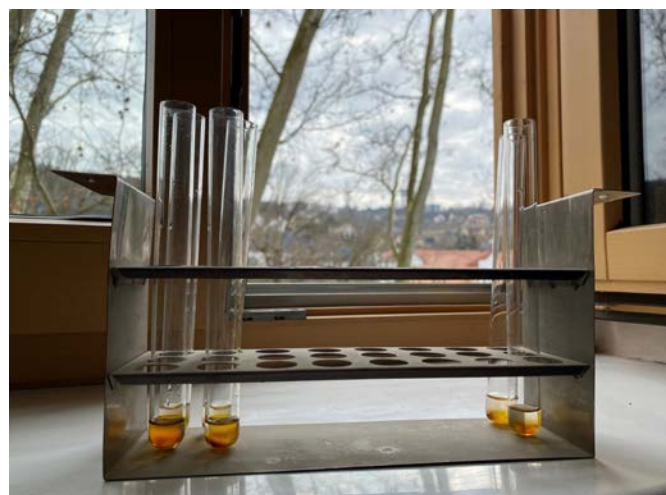


FIGURE 4. The formation of the precipitate at the bottom of the test tube

Considering the wide use of PMM in dentistry, in the second part of the study we analyzed whether different compounds are released from the resin or it retains its chemical integrity after being immersed in different substances considered to be aggressive. We chose an endogenous substance, gastric juice, which has a pH between 1 and 2.5, bitter taste, and no or slightly opalescent color, and an exogenous substance, ethyl alcohol, with a pH of around 4, no color and pungent smell. The gastric juice used in the study had a pH of 1.54, and the alcohol had a pH of 4.07. For both PMMA and PMMT, half of the samples were kept at room temperature (24 °C) for 48h, and the other half were placed 48h in a thermostatic bath to simulate the temperature in the oral cavity (37 °C).

We also performed several biochemical determinations. To identify the presence of ketone bodies, we

used the Legal reaction, adding 2 drops of 10% sodium hydroxide, 3 drops of 10% sodium nitroprusside solution, and 1 mL of glacial acetic acid to the solutions in which the samples were immersed (Figures 3 and 4). The precipitate at the bottom of the test tubes and the color change that occurred after adding the reagents demonstrated the presence of ketone bodies in the solution, the intensity of the color being directly proportional to the amount of ketone bodies. Each solution containing the samples underwent a spectrophotometric analysis at a wavelength of 300 nm to measure the amount of ketone bodies (Figure 5).

RESULTS

The results show that both the PMMA and the PMMT samples kept at 24 °C had insignificant, almost non-existent changes. The samples that were incubated at 37 °C have changed both in terms of pH and spectrophotometrically, demonstrating that with the increase of temperature, decomposition of PMM and formation of ketone bodies takes place. At the same time, the micro-environment of the oral cavity had a demonstrable effect on the samples. Significant changes occurred in samples that were not prepared according to protocol, were immersed in gastric juice or alcohol, and were kept at 37 °C. We found statistically significant differences between the minimum pH values of PMMA samples prepared correctly (pH 2.34) and those prepared incorrectly (pH 4.35), when immersed in alcohol (Table 1). The differences in the pH values of PMMT samples prepared correctly and incorrectly were negligible both in gastric juice and alcohol, with an average difference of <0.5 (Tables 2, 3 and 4). Some of the samples



FIGURE 5. Spectrophotometric analysis

TABLE 1. Modifications observed in PMMA samples after immersion in alcohol and gastric juice

Medium	Temperature	Sample no.	Prepared according to the manufacturer's instructions	Mean pH	pH change	Ketone bodies
Alcohol (initial pH 4.07)	37 °C	3	Yes	2.346	↓	0.516 λ
		4	Yes	3.270	↓	0.514 λ
		6	No	3.700	↓	0.514 λ
	24 °C	3	Yes	3.583	↓	0.503 λ
		4	Yes	4.400	↑	0.507 λ
		6	No	4.356	↑	0.516 λ
Gastric juice (initial pH 1.57)	37 °C	1	Yes	3.976	↑	0.518 λ
		2	Yes	4.293	↑	0.523 λ
		5	No	4.186	↑	0.516 λ
	24 °C	1	Yes	3.630	↑	0.508 λ
		2	Yes	3.813	↑	0.515 λ
		5	No	3.846	↑	0.507 λ

TABLE 2. Modifications observed in PMMT samples after immersion in alcohol and gastric juice

Medium	Temperature	Sample no.	Prepared according to the manufacturer's instructions	Mean pH	pH change	Ketone bodies
Alcohol (initial pH 4.07)	37 °C	2	Yes	3.803	↓	0.476 λ
		4	No	4.513	↑	0.515 λ
	24 °C	2	Yes	3.573	↓	0.520 λ
		4	No	4.100	↑	0.503 λ
Gastric juice (initial pH 1.57)	37 °C	1	Yes	1.180	↓	0.525 λ
		3	No	1.273	↓	0.518 λ
	24 °C	1	Yes	1.290	↓	0.525 λ
		3	No	1.110	↓	0.505 λ

prepared incorrectly, with excess of monomer, could not analyzed due to technical issues (Table 1).

The spectrophotometric analysis revealed that the samples that contained the highest amount of ketone bodies were those that were intentionally prepared incorrectly, as well as those that were incubated in the thermostatic bath, demonstrating that PMM decomposition occurs with the increase of temperature and non-compliance with the manufacturer's instructions regarding the optimal ratio of ingredients. The maximum value obtained was 0.523 λ, and the minimum value was 0.476 λ. The amount of ketone bodies was very similar to pure acetone.

One-sample *t*-tests comparing mean pH values obtained after immersing the samples in gastric juice and alcohol yielded statistically significant differences ($p \leq 0.001$) for the majority of samples (Tables 3 and 4).

DISCUSSION

One of the most important consequences of biodegradation is the release of unbound monomers and additives that can be toxic to the oral cavity. In terms of material stability, biodegradation can cause significant changes in the physical and mechanical properties of a material, which can lead to catastrophic failure. Several studies have highlighted the release of compounds from different types of resins,⁷ dental prostheses,^{11–13} and repairing materials,⁴ as well as orthodontic appliances, restorative materials, and tissue conditioners^{14–17} with different chemical compositions. However, few clinical studies have focused on compound release from acrylic materials. A study evaluated the residual monomer concentration resulting from self-polymerizing resins. One of the consequences of the

TABLE 3. One-sample *t*-test comparing mean pH values of samples immersed in alcohol (pH 4.07)

Resin type	Temperature	Sample no.	pH (mean $\pm$ SD)	Difference between initial pH and pH at 48 h	p value
PMMA	37 °C	3	2.346 $\pm$ 0.484	-1.723	0.025
		4	3.270 $\pm$ 0.095	-0.800	0.005
		6	3.700 $\pm$ 0.088	-0.370	0.019
	24 °C	3	3.583 $\pm$ 0.344	-0.486	0.134*
		4	4.400 $\pm$ 0.125	0.330	0.045
		6	4.356 $\pm$ 0.032	0.286	0.004
PMMT	37 °C	2	3.803 $\pm$ 0.065	-0.266	0.019
		4	4.513 $\pm$ 0.049	0.443	0.004
		2	3.573 $\pm$ 0.051	-0.496	0.004
	24 °C	4	4.100 $\pm$ 0.017	0.030	0.095

TABLE 4. One-sample *t*-test comparing mean pH values of samples immersed in gastric juice (pH 1.57)

Resin type	Temperature	Sample no.	pH (mean $\pm$ SD)	Difference between initial pH and pH at 48 h	p value
PMMA	37 °C	1	3.976 $\pm$ 0.015	2.406	0.000
		2	4.293 $\pm$ 0.025	2.723	0.000
		5	4.186 $\pm$ 0.021	2.616	0.000
	24 °C	1	3.630 $\pm$ 0.17	2.243	0.001
		2	3.813 $\pm$ 0.049	2.276	0.001
		5	3.846 $\pm$ 0.037	-0.360	0.013
PMMT	37 °C	1	1.180 $\pm$ 0.000	-0.296	0.008
		3	1.273 $\pm$ 0.045	2.060	0.001
		1	1.290 $\pm$ 0.072	-0.453	0.001
	24 °C	3	1.110 $\pm$ 0.000	-0.460	0.008

biodegradation of materials, highlighted by several studies, is the elution of unbound components such as methyl polymethacrylate, benzoyl peroxide,¹⁸ and phthalate esters. According to studies, most of the residual monomer is released in the first 24 h after immersion, after which the release rate decreases.^{17,19–21} Some of these studies reported changes in pH as a result of biodegradation. Low pH increases the concentration of monomers, which affects the properties of acrylic resins used for denture bases.^{19–21}

Ketone bodies are an important sign of chemical degradation of the prosthesis. Acrylic resins become porous as a consequence of degradation, and the risk of fracturing due to porosity increases considerably.²² With time, poor hygiene of the prosthesis will affect the stability of the color of acrylic resins, and due to microporosity, a permanent microbial infiltrate will appear, which will lead to stomatitis and inflammation accompanied by discomfort.²³

The toxicity of methyl methacrylate can be attributed to free radicals released during the polymerization reaction, due to oxidative stress; moreover, residual methyl meth-

acrylate can also exhibit toxicity.¹⁸ In a study in which glutathione was used to analyze the effect of methyl methacrylate regarding the expression of oxidizing enzymes, cell cultures have highlighted the toxicity of residual methyl methacrylate from resin-based materials, causing genotoxicity and changes in cellular cytokine factor expression.¹⁷

CONCLUSION

To improve the chemical stability of resins, it is mandatory to follow the protocol provided by the manufacturer and to instruct the patient on how to maintain and properly use his dental prosthesis. The quality of PMMA and PMMT is conditioned by respecting the work protocol and by local factors related to the oral cavity, digestive factors (gastric juice), and food-related factors (alcohol).

CONFLICT OF INTEREST

Nothing to declare.

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