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Influence of different processing techniques for prosthetic acrylic resins in the surface roughness parameters: a research article



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Abstract

Background Different processing techniques are employed to obtain poly (methyl methacrylate) (PMMA) with consistent surface quality in terms of topography and tribological function. The purpose of this research is to evaluate its influence on the surface height distribution.

Methods In this research, samples of conventional and CAD/CAM acrylic resins were prepared. The following surface roughness parameters were extracted from the profilometric readings: arithmetic mean roughness (Pa), skewness (Psk) and kurtosis (Pku). Profilometric profiles were additionally obtained.

Results The average roughness (Pa) with the conventional technique was significantly higher compared to CAD/ CAM (t=4.595; P<0.001). Heat-cured resins presented the highest mean Pa (F=6.975; P=0.06). Heat-cured and milled resins show lower coefficient variation (CV) values, indicating more consistent surface finishing. The surface profiles revealed distinct characteristics in terms of skewness and kurtosis.

Conclusions The surface processing method, chemical composition and resin type significantly influence the surface finishing of the resin. The CAD/CAM resins exhibited superior results in terms of surface arithmetic mean roughness (Pa). However, heat-cured resin revealed to present the better surface consistency.

Keywords Polymers, Polymethyl methacrylate, Surface properties

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Background

In accordance with Specification No. 12 of the American Dental Association (ADA) [1], polymers for prosthetic bases are classified into several types, depending on the polymerization reaction and their composition [2–5]. However, poly (methyl methacrylate) (PMMA) remains the most frequently used [4, 6, 7] due to its favourable characteristics, including processing and pigmentation, reduced toxicity and satisfactory mechanical properties [2].

Conventional PMMA is mainly accessible in the form of a powder-liquid system. The powder incorporates the polymer PMMA with the addition of additives, as

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pigments or acrylic synthetic fibers to mimic the aesthetics of oral tissues and to calibrate the physical properties [4, 6]. The liquid part contains a monomer of methyl methacrylate (MMA) in addition to cross-linking agents and inhibitors [4]. PMMA is derived from a polymerization reaction wherein the conversion of MMA into PMMA occurs during a curing process, activated either by chemical products, light or heat [5, 7].

Computer-aided design and computer-aided manufacturing (CAD/CAM) have been introduced as a method for producing PMMA for prosthetic bases [4]. A notable advantage appears to be the controlled temperature and pressure polymerization of prefabricated blanks of PMMA. Consequently, these materials are commonly referred to as high-performance polymers (HPPs) [3–5, 8].

Numerous researchers conducted comparisons of the properties between conventionally and CAD/CAM manufactured PMMA [3–6, 8]. The chemistry of CAD/ CAM PMMA is similar to that of conventional heat cured PMMA [4, 9]. However, CAD/CAM PMMA exhibits advantages, including surface properties, flexural strength, and flexural modulus [3, 4, 6].

Different processing techniques are employed to obtain PMMA with the specified dimensional tolerances and surface quality consistency, to achieve the desired shapes [10, 11]. This must be examined from two perspectives: process control and tribological functionality [10, 12]. The functional properties are related to the 2D and 3D surface roughness, waviness and surface texture [13]. The surface topography is a random structure composed of microscopic peaks and valleys formed during the manufacturing process. As a result, macro roughness and micro roughness can occur [6, 11, 13].

The challenge arises to the necessity of selecting appropriate surface parameters to monitor whether the desired functional surface properties are achieved. The most common metric used to analyze surface roughness is Ra (arithmetical mean roughness). This parameter summarizes height variations; however, it lacks into surface shape and does not offer details regarding the frequency or regularity of occurrence [14].

Most surfaces exhibit a degree of randomness that may follow a Gaussian (normal) or non-Gaussian distribution. The specific characteristics of a surface's height distribution are influenced by the method used to develop the surface. The Gaussian distribution has become a fundamental tool for classifying surface properties [15]. Surface parameters, such as skewness and kurtosis of the height distribution, are frequently used to characterize Gaussian topographies [16, 17]. Various authors have described the potential occurrence of identical Ra value for surfaces with different shapes and frequencies [15, 17].

Name	Commercial brand	Country of origin
Probase [®] cold	Ivoclar Vivadent	Liechtenstein
Probase® hot	Ivoclar Vivadent	Liechtenstein
iflex™	tcs®	USA
CediTEC DB	VOCO® GmbH	Germany
V-Print dentbase	VOCO® GmbH	Germany



Fig. 1 Silicone molds with predefined dimensions (20×20×3 mm)

This preliminary research intends to evaluate the influence of different processing techniques for prosthetic acrylic resins on the surface roughness parameters.

Methods

Five denture base acrylic resins were selected as shown in Table 1. Five quadrangular-shaped specimens $(20 \times 20 \times 3 \text{ mm})$ were manufactured according to the instructions and specific standards [18].

For the specimens using conventional resin (self-cured, heat-cured and injected molded) (Table 2), silicone molds were prepared with the predefined dimensions (Fig. 1).

According to the manufacturer's instructions, presented in Table 2, the self-cured denture base acrylic resin Probase[°] Cold and the heat-cured denture base acrylic resin Probase[°] Hot were obtained by a conventional flasking technique (Fig. 1). Both polymerization reactions were carried out in a pressure device for 30 min at 23 °C and for 45 min at 100 °C, respectively.

The resin tube iFlex[™] was placed on tcs[®] Digital Furnace (tcs[®] Dental Inc., California) and injected with tcs[®] Handheld JP90 (tcs[®] Dental Inc., California) (Fig. 2). The polymerization occurred inside the muffle at 23±2 °C.

For the milled samples, the virtual design of the specimen was obtained with CAD software SolidWorks[®], which was converted to a standard tessellation language (STL) file. Then, it was sent to a DWX-52D milling

Material	Composition		Ratio	Curing method
Probase [®] Cold	P :	Li:	P/Li	Self – curing: 23 °C for 30 min
	PMMA	MMA	20.5/10 (g/ml)	(Conventional)
	Dibenzoyl peroxide		-	
Probase® Hot	P :	Li:	P/Li	Heat – curing: 100 °C for 45 min
	PMMA	MMA	22,5/10 (g/ml)	(Conventional)
	Dibenzoyl peroxide	1–4 butanediol dimethacrylate		
iFlex™	Polyolefin			Injected molded
				(Conventional)
Ceditec DB	PMMA		99%	Milling
				(CAD/CAM)
V-Print dentbase	Li:		50-100%	Digital light processing method (DLP)
	UDMA		25-50%	(CAD/CAM)
	Bis – EMA		5-10%	
	TEGDMA			

Table 2 Characteristics of the resins

P – Powder; Li – Liquid; PMMA– Poly Methyl Methacrylate; UDMA– Urethane Dimethacrylate; Bis – EMA – Bisphenol-A-Ethoxylate Dimethacrylate; HEMA – Hydroxyethyl



Fig. 2 Injection technique on the predefined silicone molds

machine (DWX Series, Spain). A PPMA pre-polymerized block (*CediTEC DB*, VOCO^{\circ}, GmbH, Germany) with 98, 5×30 mm dimensions was placed on the appropriate support for the size. A milling bur used at a 90^{\circ} angle

relative to the block position. The milling process was applied dry.

The 3D printed samples were virtually designed with CAD Asiga Composer (Asiga Composer, ASIGA, Germany), which was converted to an STL file. It was sent to an Asiga Max UV 3D printer (ASIGA, Germany). The specimens were obtained through the digital light processing method (DLP). After printing, the specimens were submitted to an ultrasonic bath with isopropyl alcohol for 2 min, and the post–processing procedure was executed with an Otoflash G171 flashing unit (NK-Optik GmbH, Germany): 10 flashes/second with a wavelength of 385 nm.

No surface treatment was applied to any of the samples after processing, and sterilized compartments were used to avoid any interference or contamination. Then, the specimens were subjected to a profilometer (Hommelwerke LV-50 with linear unit and T800 controller, Hommelwerke, Germany) reading. The surface of the specimens was measured by a stylus probe with a diamond tip (length of 4.8 mm) at a constant speed of 0.5 m/s. The surface roughness parameters were directly obtained from the primary profile (Profile P). The use of Profile P is clinically relevant since it represents the curve formed when the actual surface of the material is cross-sectioned, without the use of a Gaussian filter [14].

The data were analysed using IBM[°] SPSS[°] Statistics for Macintosh, version 27 (IBM Corporation, USA). Pa roughness values are represented using the mean and standard deviation. A descriptive analysis was used to analyze skewness (Psk), and kurtosis (Pku). High kurtosis values indicate a sharp amplitude distribution with large peaks and valleys. A negative skewness suggests a concentration of the material near the top of the profile and a plateau-like surface. In addition, the percent variation coefficient (CV), defined as the ratio between the standard deviation and the average value was utilized.

Overall Pa (μm), mean ± SD					Inter-group comparison statistics
Conventional		CAD/CAM			
11.35±4.68		2.26±1.29			t=4.595; P<0.001
Resin-specific	: Pa (µm), mean \pm SD			Inter-group c	omparison statistics
Self-cured	Injected molded	Heat-cured	3D printed	Milled	
11.77±5.26	8.19±3.20	14.10±4.80ª. ^b	3.00 ± 1.48^{b}	1.51±0.56ª	F=6.975; P=0.06

 Table 3
 Roughness data for different processing methods and resin types

a, b: significant differences in pairs of resins using Bonferroni post-hoc correction at P<0.05

 Table 4
 Measures of roughness dispersion for polishing techniques and resin types

Resin types and polishing techniques	Variation coefficient (CV)	Skewness (Psk)	Kurtosis (Pku)
Conventional			
Self-cured	0.447	-0.453	0.462
Injected molded	0.391	0.872	1.068
Heat-cured	0.341	0.339	0.267
CAD/CAM			
3D printed	0.493	0.201	1.578
Milled	0.371	-0.135	0.138

Two-way Analysis of Variance (ANOVA) with the Bonferroni post-hoc correction for a small sample size and predicted data not normally distributed was used to compare the distribution of surface arithmetic mean roughness (Pa) between different resin types. In order to test the means between two groups, Student's t test was employed to assess differences in the distribution of Pa between pairs of resins.

Results

Table 3 compares roughness data for different processing techniques and resin types. The overall mean roughness (Pa) for conventional techniques is $11.35\pm4.68 \mu m$, significantly higher than CAD/CAM techniques at $2.26\pm1.29 \mu m$ (t=4.595; P<0.001), indicating that CAD/CAM yields lower overall Pa among resin types, heat-cured resins stand out with the highest mean Pa at $14.10\pm4.80 \mu m$, showing significant differences in intergroup comparison statistics (F=6.975; P=0.06). Post-hoc tests highlight significant differences, with heat-cured resins differing from 3D printed (P=0.034) and milled resins (P=0.015).

Table 4 provides an analysis to the surface roughness measurements for dental acrylic resins and the corresponding processing techniques. The variation coefficient (CV) indicates variability in roughness. 3D printed and self-cured resins have higher CV values (3D printed: CV=0.493, self-cured: CV=0.447), suggesting greater variability. In contrast, heat-cured (0.341) and milled resins show lower CV values (0.371). Surface profiles also reveal distinct characteristics. Self-cured (-0.453) and milled (-0.135) resins have a plateau-like surface with negative skewness, while injected molded resins show sharp variations with positive skewness (0.872) and substantial kurtosis (1.068).

Surface profiles also reveal distinct characteristics (Fig. 3).

Self-cured (-0.453) and milled (-0.135) resins have a plateau-like surface with negative skewness, while injected molded resins show sharp variations with positive skewness (0.872) and substantial kurtosis (1.068) (Table 4).

Discussion

In terms of analysis of the surface properties, the authors proposed a different approach to the assessment using the following parameters: skewness (Psk), kurtosis (Pku) and arithmetic mean roughness (Pa) [14]. The validation of the use of Pa instead of Ra, commonly used, had already been demonstrated [14, 19, 20]. The results published by the authors of the present research were reused for the present analysis [14].

Considering the existing drawbacks between the mechanical and physical properties of conventional PMMA, new processing methodologies were developed [4, 8, 9, 21]. Superior surface properties in comparison to conventional PMMA may be attributed to the unique processing method of the CAD/CAM PMMA in which high temperatures, pressure and lower levels of residual monomer are used to obtain pre-polymerized PMMA, in case of subtractive technique, or a layer by layer polymerization, in case of additive technique [5, 6, 21]. In general, when compared the two processes in relation to surface roughness, a significant difference in mean Pa (t=4.595; p < 0.001) highlights the processing method impact on surface finishing. In the analysis in pairs, heat-cured differs significantly from 3D printed (p=0.0034) and milled resins (p = 0.015).

Considering the chemical composition, several studies reveals that the composition of the CAD/CAM PMMA



Fig. 3 Probability of having a given height of the surface for the specimens according to resin processing type: A (self-cured), B (heat-cured), C (3D printed), D (milled), E (injected molded)

is similar to that of conventional PMMA [4, 9]. In contrast with what is presented in Table 2, also the chemical composition of PMMA polymers reveals influence on the surface roughness. Heat cured resins reveals the highest values of Pa in contrast with the results obtained by Berger et al. [22]. The reaction of polymerization is activated by heat, therefore it is expected that the degree of conversion of MMA monomer occurs almost totally. Additionally, the polymer that constitute has a lower granule size in comparison with self cured resins, for example. A direct effect on the surface roughness by the reaction initiatior can be established as this resins uses benzoyl peroxide and 1–4 butanediol dimethacrylate [6, 22].

When assessing the overall roughness level, surface height distribution symmetry is a crucial aspect related to surface characteristics. As a result, it has the potential to measure the consistency of surface texture [16, 23-25]. Probability density and distribution curves are determined upon the nature of the processing method [15]. The variation coefficient is a measure of dispersion in relation to mean values in this study related to the surface roughness (Pa). The results of CV reveal lower variation on the overall Pa in milled (CV=0.371), heat-cured resins (CV=0.341) which means a higher probability density and a lower dispersion of Pa values in the distribution curve. The opposite appears in the self cured resins (CV=0.447) and 3D printed (CV=0.899). In terms of texture considerations, a lower CV indicates a more homogeneous surface. Heat-cured resin presented the higher Pa values with the lowest CV, indicating a more consistent surface quality, in comparison with milled resin with the lowest values of Pa. The opposite also occurs for hight CV value with a more heterogenous surface.

The correlation skewness (Psk) and kurtosis (Pku) provides valuable insight for analyzing the symmetry of a texture amplitude and to understand whether it contains inordinate high peaks/valleys on the surface and its influence on the bacterial adhesion [10, 15, 26, 27]. A non-Gaussian distribution of the roughness profile is characterized by Psk and is responsive to sporadic deep valleys or high peaks, as it quantifies the symmetry of the profile distribution with respect to its central line [10, 15]. Negative skewness pertains to profiles that are more prevalent in deep valleys, as occurs in self-cured (Psk = -0.453) and milled (Psk = -0.135). Further, non-Gaussian surfaces with relatively flat peaks and valleys are indicated by a Pku value less than 3, presented in all types of resins. Injected molded resins contrast with sharp variations with positive skewness (0.872) and substantial kurtosis (1.068). The higher Pku value indicates that the surface contains extreme peaks or valleys [23].

Despite the fact that the present research presents an "in vitro" design, further studies should proceed with the evaluation of the clinical implication related to the parameters Pa, Psk and Pku. First, in terms of selecting the appropriate polishing protocol for each type of acrylic resin, considering different processing techniques, their chemical composition, and consequently, the implications in terms of surface properties, such as the behaviour of roughness along the profile of a surface. Second, there is a lack of consensus regarding the minimum level for microbial adhesion and could differ according to the acrylic used and the hability of the microorganism to adhere to different surfaces [26, 27]. Studies report that microorganisms appear to have a preference for adhesion on surfaces with scratches and grooves and not necessarily with higher Pa values [26]. Therefore, the surface topography may have a greater influence on the bacterial adhesion than the roughness parameter value itself. A consensus should be establish on microbial adhesion thresholds and explore the interaction between surface topography and bacterial adherence. Two main limitation can be displayed. First, only five commercial brands of acrylic resins for prosthetic bases were tested in terms of composition and processing technique. Second, in relation to the shape of the test specimens, the quadrangularshaped specimens do not resemble the complexity shape of the prosthetic bases at the clinical level.

Conclusions

This research undertook a comprehensive analysis of surface properties in acrylic resins using the parameters Pa, skewness and kurtosis. The surface processing method has a direct influence on the surface behavior. The distribution height curve characterizes the surface topography of manufacturing procedures. CAD/CAM resins exhibited superior results in terms of surface roughness, although, heat-cured resin revealed to present a better surface consistency. A focus on achieving optimal surface properties should extend to the selection of appropriate polishing protocols based on resin's type, processing technique and chemical composition.

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Author contributions

Conceptualization, M.M.Q., A.C., C.F., P.F. and J.M.; Methodology, M.M.Q. and C.F.; Software, C.F.; Validation, M.M.Q. and C.F.; Formal analysis, A.C., P.F. and J.M.; Investigation, M.M.Q. and C.F.; Resources, M.M.Q., C.F. and A.C.; Data curation, M.M.Q.; Writing-original draft preparation, M.M.Q. and C.F.; Writing—review and editing, M.M.Q., C.F., A.C., P.F. and J.M.; Visualization, A.C., P.F., and J.M.; Supervision, A.C., P.F. and J.M.; Project administration, A.C., P.F. and J.M.; Funding acquisition, A.C. and P.F. All authors have read and agreed to the published version of the manuscript.

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Data availability

All data generated or analysed during this study are included in this published article.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare no conflict of interest.

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References

- Swaney AC, Paffenbarger GC, Caul HJ, Sweeney W. American Dental Association specification 12 for denture base resin: second revision. J Am Dent Association. 1953;46(1):54–66.
- Hassan M, Asghar M, Din SU, Zafar MS. Thermoset polymethacrylate-based materials for dental applications. Materials for Biomedical Engineering: Elsevier; 2019. pp. 273–308.
- Raszewski Z, Nowakowska-Toporowska A, Nowakowska D, Więckiewicz W. Update on acrylic resins used in dentistry. Mini Rev Med Chem. 2021;21(15):2130–7.
- Zafar MS. Prosthodontic applications of Polymethyl Methacrylate (PMMA): an update. Polym (Basel). 2020;12(10).
- Engler MLPD, Güth J-F, Keul C, Erdelt K, Edelhoff D, Liebermann A. Residual monomer elution from different conventional and CAD/CAM dental polymers during artificial aging. Clin Oral Invest. 2020;24:277–84.
- Al-Dwairi ZN, Tahboub KY, Baba NZ, Goodacre CJ, Özcan M. A comparison of the surface properties of CAD/CAM and conventional polymethylmethacrylate (PMMA). J Prosthodont. 2019;28(4):452–7.
- Zafar MS, Ahmed N. Nanoindentation and surface roughness profilometry of poly methyl methacrylate denture base materials. Technol Health Care. 2014;22(4):573–81.
- Bidra AS, Taylor TD, Agar JR. Computer-aided technology for fabricating complete dentures: systematic review of historical background, current status, and future perspectives. J Prosthet Dent. 2013;109(6):361–6.
- Srinivasan M, Gjengedal H, Cattani-Lorente M, Moussa M, Durual S, Schimmel M, et al. CAD/CAM milled complete removable dental prostheses: an in vitro evaluation of biocompatibility, mechanical properties, and surface roughness. Dent Mater J. 2018;37(4):526–33.
- 10. Petropoulos GP, Pandazaras CN, Davim JP. Surface texture characterization and evaluation related to machining. Surf Integr Mach. 2010:37–66.
- 11. Oravcová J, Labašová E, editors. The analysis of surface roughness of the samples produced by 3D printing. Journal of Physics: Conference Series; 2022: IOP Publishing.
- 12. Shi R, Wang B, Yan Z, Wang Z, Dong L. Effect of Surface Topography parameters on Friction and wear of Random Rough Surface. Mater (Basel). 2019;12(17).
- Grzesik W. Prediction of the functional performance of machined components based on surface topography: state of the art. J Mater Eng Perform. 2016;25:4460–8.
- Quezada MM, Fernandes C, Montero J, Correia A, Salgado H, Fonseca P. A different Approach to analyzing the Surface Roughness of Prosthetic Dental Acrylic resins. Appl Sci. 2024;14(2):619.

- 15. Bhushan B. Surface roughness analysis and measurement techniques. Mod-
- ern tribology handbook, two volume set: CRC; 2000. pp. 79–150.
 Sabino TS, Carneiro AC, Carvalho RP, Pires FA. The impact of non-gaussian height distributions on the statistics of isotropic random rough surfaces. Tribol Int. 2022;173:107578.
- Stout K. Surface roughness~ measurement, interpretation and significance of data. Mater Design. 1981;2(5):260–5.
- Iso E. ISO 20795-1:2008 Dentistry Base polymers part 1. International Organization for Standardization; 2008.
- Corsalini M, Carella M, Boccaccio A, Lamberti L, Pappalettere C, Catapano S, et al. An alternative approach to the polishing technique for acrylic resin surfaces. Int J Prosthodont. 2008;21(5):409–12.
- Corsalini M, Boccaccio A, Lamberti L, Pappalettere C, Catapano S, Carossa S. Analysis of the performance of a standardized method for the polishing of methacrylic resins. Open Dent J. 2009;3:233–40.
- Baba NZ, Goodacre BJ, Goodacre CJ, Müller F, Wagner S. CAD/CAM complete denture systems and physical properties: a review of the literature. J Prosthodont. 2021;30(S2):113–24.
- Berger JC, Driscoll CF, Romberg E, Luo Q, Thompson G. Surface roughness of denture base acrylic resins after processing and after polishing. J Prosthodontics: Implant Esthetic Reconstr Dentistry. 2006;15(3):180–6.
- Das J, Linke B. Evaluation and systematic selection of significant multi-scale surface roughness parameters (SRPs) as process monitoring index. J Mater Process Technol. 2017;244:157–65.
- Ba ECT, Dumont MR, Martins PS, Drumond RM, Martins da Cruz MP, Vieira VF. Investigation of the effects of skewness R sk and kurtosis R Ku on tribological behavior in a pin-on-disc test of surfaces machined by conventional milling and turning processes. Mater Res. 2021;24:e20200435.
- Pawlus P, Reizer R, Wieczorowski M, Krolczyk G. Material ratio curve as information on the state of surface topography—A review. Precis Eng. 2020;65:240–58.
- Andreotti AM, De Sousa CA, Goiato MC, da Silva EVF, Duque C, Moreno A, et al. In vitro evaluation of microbial adhesion on the different surface roughness of acrylic resin specific for ocular prosthesis. Eur J Dentistry. 2018;12(02):176–83.
- Meirowitz A, Rahmanov A, Shlomo E, Zelikman H, Dolev E, Sterer N. Effect of denture base fabrication technique on Candida albicans adhesion in vitro. Materials. 2021;14(1):221.

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