The influence of the post-processing method on knoop hardness of photosensitive resins for 3D SLA printer used in Dentistry

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ABSTRACT | *Objectives*: The aim of this study is to compare the mechanical characteristics of resins for 3D printers with the acrylic resins that have been used in Dentistry, according to the post-processing method. *Materials and Methods*: Using an SLA 3D printer (Form 2 – Formlabs, Massachusetts, USA), samples (discs) were produced with the printer's resins, Dental SG®, Dental LT®, Clear®. Samples made of thermopolimerized and auto polymerized acrylic resins were produced as well (Gold Standart parameters). The Knoop Hardness (KH) tests were performed using microdurometer HMV-2 (Shimadzu, Kyoto, Japan). *Results*: The results showed the Dental SG resin presented the highest KH, compared with thermopolimerized acrylic resin, the Clear and Dental LT resins KH were compared with auto polymerized acrylic resin, and the non-post cured Dental LT resin showed the lowest KH. *Conclusions*: Considering the hardness, the printer's resins are comparable with the acrylic resins established, when the post-processing method is thoroughly followed. The absence of material's post-processing reduce significantly the material's hardness. *Clinical relevance*: Regarding the use of 3D printing in Dentistry, the development of materials adequate for the equipment, biocompatible for intraoral uses, and compatible mechanical proprieties are essential.

DESCRIPTORS | Digital Dentistry; Polymers; Hardness Knoop; CAD/CAM; Additive Manufacturing; Dental Resin.

RESUMO | **Influência do método de pós-processamento na dureza Knoop de resinas fotossensíveis para impressoras 3D SLA usadas na Odontologia** • Objetivos: O objetivo deste estudo é comparar as características mecânicas das resinas para impressoras 3D com as resinas acrílicas utilizadas em Odontologia, de acordo com o método de pós-processamento. Materiais e Métodos: Utilizando uma impressora SLA 3D (Form2 – Formlabs, Massachusetts, EUA), amostras (discos) foram produzidas com as resinas da impressora, Dental SG®, Dental LT®, Clear®. Também foram produzidas amostras feitas de resinas acrílicas termopolimerizadas e autopolimerizadas (parâmetros Gold Standart). Os testes de dureza Knoop (KH) foram realizados usando o microdurômetro HMV-2 (Shimadzu, Kyoto, Japão). Resultados: Os resultados mostraram que a resina Dental SG apresentou o KH mais alto, em comparação com a resina acrílica termopolimerizada, as resinas Clear e Dental LT KH foram comparadas com a resina acrílica autopolimerizada e a resina sem pós-cura Dental LT apresentou o menor KH. Conclusões: Considerando a dureza, as resinas da impressora são comparáveis às resinas acrílicas, quando o método de pós-processamento é completamente seguido. A ausência do pós-processamento do material reduz significativamente a dureza do material. Relevância clínica: No que diz respeito ao uso da impressão 3D em Odontologia, o desenvolvimento de materiais adequados ao equipamento, biocompatíveis para usos intraorais e propriedades mecânicas compatíveis é essencial.

DESCRITORES | Odontologia Digital; Polímeros; Dureza Knoop; CAD-CAM; Manufatura Aditiva; Resina Dental.

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INTRODUCTION

The advent of three-dimensional printers with the stereolithography additive manufacture (SLA) technique and the possibility of its use in the healthcare field led to the development of specific photosensitive and biocompatible resins (3DR), particularly for Dentistry.[1]

The advantages of 3D printing include the possibility of producing customized appliances, in an easier and faster process, high accuracy, and the possibility of reproducing the same object multiple times, if necessary.[2]

The professionals must understand the development of the new material and its indications and characteristics to obtain the best and safest treatment results, considering the increasing number of studies about materials for CAD/CAM use in Dentistry.[3,4]

The acrylic resins (AR) have been used in Dentistry for a long time to produce dental restorations, prosthesis, and models, and its characteristics, proprieties, and indications are well known; they are considered the gold-standart materials.[5]

Despite the material's components of 3DR being similar to AR (Table 1), there are differences regarding the components of 3DR and the photoinitiators and the different degree of material conversion that could lead to different mechanical proprieties.[6, 7, 8, 9]

TABLE 1 | Resins' Composition.

Resin	Composition
Thermo polymerized[6]	powder: pre-polymerized methyl spheres (methyl methacrylate), benzoyl peroxide (initiator) Liquid: unpolymerized methyl methacrylate, hydroquinone (inhibitor).
Auto polymerized[6]	powder: poly (methyl methacrylate), benzoyl peroxide (initiator) Liquid: unpolymerized methyl methacrylate, hydroquinone (inhibitor) and tertiary amine.
Dental SG[7]	Methacrylate oligomers; Phosphine oxides
Dental LT[8]	Methacrylic oligomer; Glycol Methacrylate; Phosphine oxide; Pentamethyl-piperidy sebacate
Clear[9]	Methacrylate oligomers; Methacrylate monomers: Photoinitiator(s)

One of the important mechanical proprieties of the resins is their hardness, which elucidates its capacity to resist to wear and deformation. The Knoop hardness test is a test of mechanical microhardness of the materials, in which an indentation is made on the tested material surface pressing (loading) a diamond in a pyramidal form over it. The geometry of the indentation is measured using a microscope, and the data are analyzed using the Knoop Hardness formula.[10,11]

Considering some of the resins for 3D SLA printers (3DR) available in the Dentistry field, the aim of this study was to evaluate the Knoop Hardness of the new resins and compare it with the thermo and autopolymerized acrylic resins.

MATERIALS AND METHODS

SAMPLE MANUFACTURE

Using an SLA 3D printer, Form2 (Formlabs, Massachusetts, USA), discs (n=3) of the resins Dental SG, Clear and Dental LT were manufactured; the printing layer thickness was 0.1 mm and the disc dimensions were 30 mm diameter x 2.5 mm thickness. After the printing process, the discs were post-processed (cleaned and cured) according to the manufacturer guidelines (Table 2), except for the samples of the Dental LT resin that presents one group of cured and non-cured samples. Samples (n=3) of the thermopolymerized and autopolymerized acrylic resins were manufactured in a laboratory.

TABLE 2 | 3D Resins post-processing protocols, following the manufacturer recommendations.

RESIN	WASHING PROCESS	CURING PROCESS
Dental SG	Rinse in isopropyl alcohol (IPA, 96 percent or higher) for 5 minutes.	Exposure for 30 minutes to 108 watts each of Blue UV-A (315 nm-400 nm) and UV-B (400 nm-550 nm) light, in a heated environment at 60 °C.
Dental LT	Rinse in isopropyl alcohol (IPA, 96 percent or higher) for 5 minutes. Do not leave parts in alcohol for more than 10 minutes	Exposure for 20 minutes to 108 watts each of Blue UV-A (315 nm-400 nm) and UV-B (400 nm-550 nm) light, in a heated environment at 80 °C.
Clear	Rinse in isopropyl alcohol (IPA, 96 percent or higher) for 10 minutes	Exposure for 30 minutes to 108 watts each of Blue UV-A (315 nm-400 nm) and UV-B (400 nm-550 nm) light, in a heated environment at 60 °C.

KNOOP HARDNESS (KH) TEST

The discs were polished in a polishing machine (Buehler Automet 250 – Buehler, Coventry, Great Britain) to prepare the samples for the KH test, using silicon carbide sandpapers with the granulations 220, 320, 500, 1200 during 2 minutes each and finalizing with granulation 2000 during 2.5 minutes, the applied force was 20N, there was water irrigation during all the polishing process.

After polishing the discs, they were submerged in distilled water during 24h to hydrate the samples, simulating the materials' intraoral conditions.

The hydrated discs were tested in the microdurometer HMV-2 (Shimadzu, Kyoto, Japan) using CAMPS program, which was calibrated to load the surface of the samples with 25 grams for 10 seconds. Five indentations were performed in each sample (500 µm distant from each other and from specimen's boards). The indentations were analyzed using an optical microscopy and 10 magnification lens and measured following the Knoop hardness formula: $HK = 14{,}229\ X(P/L^2)$ (where P is the load and L is the length of the long axis of the indentation).[10]

STATISTICAL ANALYSIS

For multiple comparisons between the resins, we used the ANOVA test, followed by Tukey's test. The significance level was set at 5%.

RESULTS

Table 3 shows the values found during the KH test:

Data statistical analysis was performed using the website http://vassarstats.net/anova1u.html. Significance was verified in the variation of the average values of the Knoop hardness through the ANOVA statistical test followed by the Tukey's test.

TABLE 3 | KH values per sample (n=5) in the different resins tested.

CLEAR		DENTAL SG (CURED)		DENTAL LT (NOT CURED)	
	KH		KH		KH
1	12.8	1	18.8	1	5.6
	12.8		18.5		5.4
	13.4		18.7		5.5
	13.1		18.2		5.0
	13.9		18.3		5.7
2	12.3	2	18.8	2	5.0
	12.6		18.1		5.6
	12.2		18.0		4.9

continues...

TABLE 3 | Continuation

CLEAR		DENTAL SG (CURED)		DENTAL LT (NOT CURED)	
	11.2		18.9		5.3
	12.3		18.5		5.4
3	13.4	3	19.9	3	5.0
	13.2		18.7		5.7
	13,6		18.5		5.1
	13.9		19.2		5.2
	13.4		19.5		5.5
Minimum	11.2	Minimum	18.0	Minimum	4.9
Maximum	13.9	Maximum	19.9	Maximum	5.7
Mean	12.94	Mean	18.707	Mean	5.327
SD	0.735	SD	0.519	SD	0.276
DENTAL LT (CURED)		AUTOPOLYMERIZED		THERMO POLYMERIZED	
	KH		KH		KH
1	12.8	1	9.0	1	13.6
	14.8		8.4		13.4
	13.7		9.2		14.1
	10.4		8.5		14.4
	10.3		8.9		14.4
2	10.6	2	11.0	2	19.0
	12.8		12.0		17.9
	12.3		11.4		19.2
	10.6		12.6		19.8
	10.7		11.7		19.5
3	12.0	3	11.5	3	15.8
	11.5		11.4		17.2
	12,2		12.5		16.0
	11.6		12.2		16.9
	11.6		11.5		17.4
Minimum	10.3	Minimum	12.6	Minimum	13.4
Maximum	14.8	Maximum	8.4	Maximum	19.8
Mean	11.86	Mean	10.787	Mean	16.573
SD	1,295	SD	1.524	SD	2.238

RESINS FOR INTRAORAL USE

Table 4 shows the comparative analysis summary, considering the resins used with intraoral propose and those to manufacture dental appliances (Thermo polymerized, Autopolymerized, Dental SG, Dental LT) and the Clear resin; Table 5 shows the data of the ANOVA test and Table 6 the result of the Tukey's test for the same resins. Graph 1 shows the KH mean value of each resin.

TABLE 4 | Summary Statistical Analysis of the intraoral uses' resins.

	Thermo polymerized M1	Autopolymerized M2	Dental SG M3	Dental LT (cured) M4	Clear M5	Total
N	15	15	15	15	15	75
∑x	248.6	161.8	208.6	177.9	194.1	1063
Mean	16.5733	10.7867	18.7067	11.86	12.94	14.1733
∑x2	4190.24	1777.82	5252.86	2133.37	2519.21	15873.5
Variance	5.0078	2.3241	0.2692	1.6769	0.5397	10.9087
Std. Dev	2.2378	1.5245	0.5189	1.2949	0.7347	3.3028
Std. Err.	0.5778	0.3936	0.134	0.3344	0.1897	0.3814

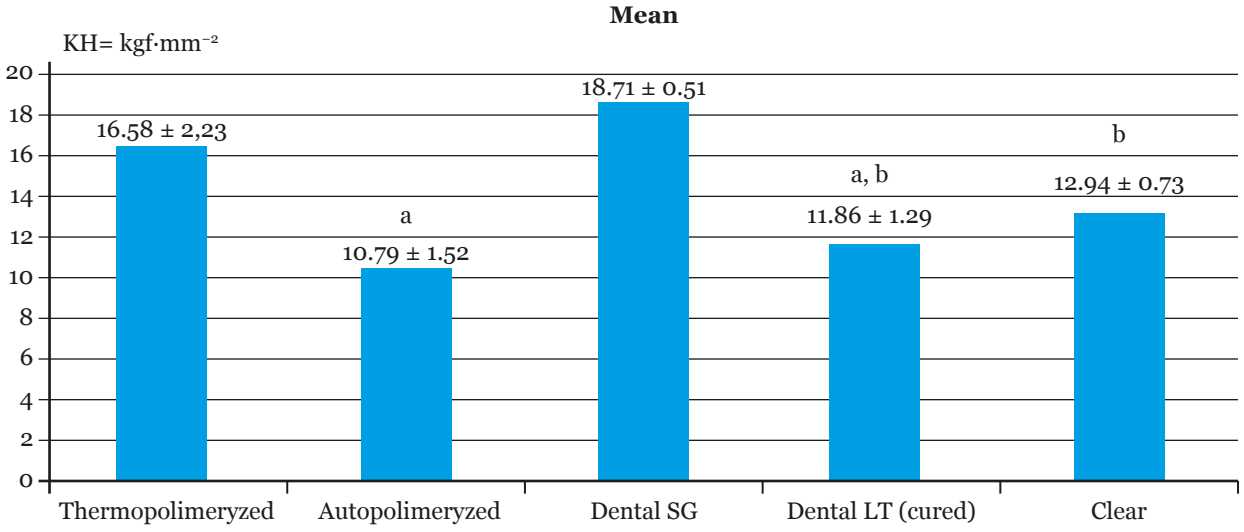
TABLE 5 | Data Summary for ANOVA test of intraoral resins.

ANOVA Summary					
Source	SS	df	MS	F	P
Treatment (between groups)	669.7987	4	167.4497	85.28	<.0001
Error	137.448	70	1.9635		
Total	807.2472	74			

TABLE 6 | Tukey's test results of intraoral resin.

Tukey's HSD test	
HSD[.05] = 1.43; HSD [.01] = 1.73	
M1vs M2	P <.01
M1 vs M3	P <.01
M1 vs M4	P <.01
M1 vs M5	P <.01
M2 vs M3	P <.01
M2 vs M4	nonsignificant
M2 vs M5	P <.01
M3 vs M4	P <.01
M3 vs M5	P <.01
M4 vs M5	nonsignificant
M1 = Thermo polymerized; M2 = Autopolymerized; M3 = Dental LT (cured); M4 = Dental LT (not cured); M5 = Clear	
HSD = The absolute [unsigned] difference between any two sample means required for significance at the designed level. HSD[.05] for the .05 level; HSD[.01] for the .01 level.	

GRAPH 1 | KH Mean values of the resins for intraoral uses, standard deviation and significance (groups identified by the same letter there was nonsignificant: (a) – autopolimerized and dental LT (cured) and (b) – dental LT (cured) and Clear)



The results of the Knoop hardness among the resins for intraoral use showed the mean value of the Thermo polymerized, Autopolymerized, Dental SG and Dental LT are [16.58], [10.79], [18.71], [11.86], respectively. Despite the Clear resin not being used for intraoral use, considering the Knoop Hardness, its mean value [12.94] is comparable with the resins used intraorally, with its KH being significantly higher than the autopolymerized resin.

The SG resin mean value is the highest, being significantly different than all others. On the other hand, the lowest mean value is in the autopolymerized resins' samples.

RESINS DIFFERENCE RELATED TO THE CURE

Considering the resin recommended for intraoral long-term use, Dental LT, the Knoop hardness difference of post-processing light curing was evaluated. There was a non-post-cured and a post-cured group. They were compared with the thermo and autopolymerized resins. Table 7 shows the comparative analysis summary; Table 8 shows the data of the ANOVA test, and Table 9 the result of the Tukey's test for the same resins. Graph 2 shows the Knoop hardness mean value of each.

TABLE 7 | Summary Statistical Analysis of the resins – Cure Type.

	Thermo polymerized M1	Autopolymerized M2	Dental LT (cured) M3	Dental LT (non-cured) M4	TOTAL
N	15	15	15	15	60
∑x	248.6	161.8	177.9	79.0	668.2
Mean	16.5733	10.7867	11.86	5.3267	11.1367
∑x2	4190.24	1777.82	2133.37	426.67	8528.1
Variance	5.0078	2.3241	1.6769	0.0764	18.4166
Std. Dev	2.2378	1.5245	1.2949	0.2764	4.2915
Std. Err.	0.5778	0.3936	0.3344	0.0714	0.554

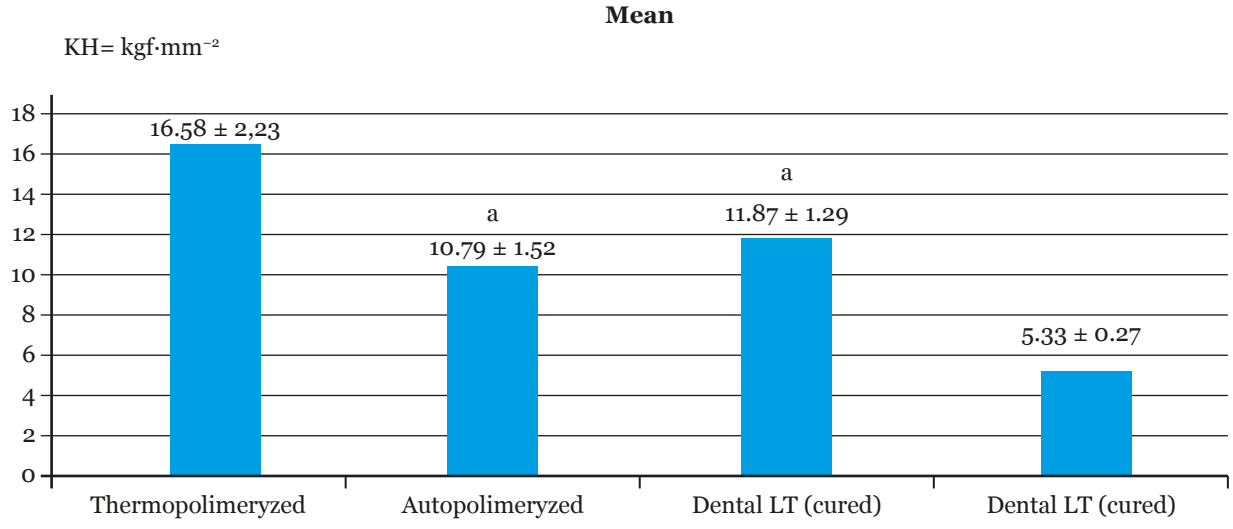
TABLE 8 | ANOVA's test Data Summary of the resins, considering its cure type.

ANOVA Summary					
Source	SS	df	MS	F	P
Treatment (between groups)	959.3873	3	319.7958	140.8	<.0001
Error	127.192	56	2.2713		
Total	1086.5793	59			

TABLE 9 | Tukey´s test results, considering resin´s cure type.

Tukey's HSD test	
HSD[.05] = 1.46; HSD [.01] = 1.8	
M1vs M2	P<.01
M1 vs M3	P<.01
M1 vs M4	P<.01
M2 vs M3	nonsignificant
M2 vs M4	P<.01
M3 vs M4	P<.01
M1 = Thermo polymerized; M2 = Auto polymerized; M3= Dental LT (cured); M4= Dental LT (not cured)	
HSD = the absolute [unsigned] difference between any two sample means required for significance at the designed level. HSD[.05] for the .05 level; HSD[.01] for the .01 level.	

GRAPH 2 | KH mean values of the resins, considering its cure type, standard deviation and significance (groups identified by the same letter there was nonsignificant: (a) – autopolimerized and dental LT (cured) and (b) – dental LT (cured) and Clear).



The results of the Knoop hardness when comparing the resins, considering the post-processing cure, showed the mean value of the Thermopolymerized, Autopolymerized, Dental LT (cured) and Dental LT (not cured) are [16.58], [10.79], [11.86], and [5.3267], respectively. Significant differences were found between the types of resin, except between autopolymerized and Dental LT (cured) resin. The absence of the post-curing process reduced by more than 55% of the Knoop Hardness of the material. Proper resin post-curing is highly recommended by the manufacturer.

DISCUSSION

The hardness of the materials is important data for clinicians to understand its intraoral behavior. Thermopolymerized resins have been considered the gold standard of the acrylic resins since they, when correctly handled, present high material cure and high KH values. Clinically, they can be interpreted as a stable and wear resistant material, the autopolymerized resin usually has a lower KH value due to the different cure degree efficiency and the possibility of porosities during the manipulation of the material, even so, its KH value is pretty acceptable for manufacturing intraoral appliances.[12]

Based on the KH results of this research, when considering the new material, the SG resin showed higher KH than thermopolymerized resin, being the hardest material of these samples, the SG resin indication is to manufacture surgical guide appliances and the material hardness must keep the accuracy and reliability for the guidance.[13]

The Dental LT and Clear resin presents hardness lower than Dental SG and thermopolymerized resins, but Clear resin has a significant higher KH value than autopolymerized resin, and the Dental LT KH value is similar to the autopolymerized resin, showing that all resins tested are potentially compatible with the intraoral use, considering the hardness aspect. Despite the manufacturer indications of intraoral long-term use for the Dental LT resin, no studies have been published yet about the resin, except for our investigation study.

To follow the correct protocol for resin manufacture is indispensable,[14,15,16] as shown in the different results of the Dental LT post cured and non-post-cured resin. The values of the non-post-cured resins are much lower than the post-cured ones and all other resins, which could be interpreted as not recommended for intraoral use.

CONCLUSION

In conclusion, considering the hardness characteristics, printer resins are comparable with the established acrylic resins, when handled according to the manufacturer's recommendations. The absence of material post-processing reduce significantly the hardness of the material.

As their hardness is compatible for intraoral use, the clinical indications and other mechanical characteristics must be considered when choosing the best resin for each case.

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COMPLIANCE WITH ETHICAL STANDARDS

Conflict of Interest: All the authors declare no conflict of interest.

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Ethical approval: This article does not contain any studies with human participants or animals performed by any of the authors.

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