Original paper

Mechanical, optical and surface properties of 3D-printed and conventionally processed polyamide 12

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Abstract

Background. Polyamide-based materials are suitable for three-dimensional (3D) printing.

Objectives. The aim of the study is to examine the impact of aging on the mechanical, surface and optical properties of polyamide 12.

Material and methods. A total of 116 specimens were examined, comprising 58 conventionally processed polyamide 12 (PA12_C) specimens and 58 3D-printed polyamide 12 (PA12_3D) specimens. The modulus of elasticity was determined before and after mechanical and thermal aging with 1,000, 3,000, 9,000, and 1,000, 3,000 and 7,000 cycles, respectively. The surface roughness (Ra), Ra change (ΔRa) and color change (ΔE) were examined before and after chemical aging (1, 12 and 36 days, with artificial saliva, coffee and red wine) using surface profilometry and color spectroscopy. The Kruskal–Wallis test, Mann–Whitney *U* test and Bonferroni–Holm correction were employed, with a significance level of $p < 0.05$.

Results. Before and after mechanical aging, the modulus of elasticity for PA12_3D showed significantly higher values (761 MPa and 747 MPa, respectively) in comparison to PA12_C (515 MPa and 455 MPa, respectively; adjusted $p < 0.001$). Additionally, before and after thermal aging, the modulus of elasticity for PA12_3D exhibited significantly higher values (833 MPa and 705 MPa, respectively) compared to PA12_C (516 MPa and 458 MPa, respectively; adjusted $p < 0.001$). The Ra of PA12_3D was higher than that of PA12_C at the baseline (0.41 μm compared to 0.31 μm, respectively), and remained higher during the aging process. The ΔRa values were small for both groups. The ΔE was significantly higher for PA12_3D compared to PA12_C after 12 days (6.2 (PA12_3D) compared to 4.8 (PA12_C), adjusted $p = 0.003$) and 36 days of storage in red wine (8.2 (PA12_3D) compared to 6.8 (PA12_C), adjusted $p = 0.003$). After 36 days of coffee storage, the observed changes were found to be statistically significant (8.6 (PA12_3D) compared to 6.7 (PA12_C), adjusted $p < 0.001$).

Conclusions. The 3D-printed polyamide 12 demonstrated higher rigidity, Ra and discoloration compared to the conventionally processed polyamide 12. However, not all of the observed parameter differences were significant or clinically relevant. These differences may impact clasp retention, biofilm formation and aesthetic appearance. Nevertheless, the clinical efficacy of 3D printing may be significant.

Keywords: 3D printing, nylon, polyamide 12, dental clasps, removable denture

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Introduction

Nowadays, missing teeth can be replaced with removable partial dentures (RPDs).[1,2] They can be used either temporarily, as interim dentures, or permanently, depending on the design and material.[1] Removable partial dentures can be constructed using metal-based or polymer-based frameworks.[1] Polymethyl methacrylate (PMMA) is a widely used polymer for RPDs, although it has certain limitations. These include residual monomer (methyl methacrylate) leakage, making it unsuitable for patients who are allergic to these components.[3] The use of metal-based frameworks with metal clasps is recommended for the fabrication of definitive RPDs.[1] Despite many advantages, applying this technique may compromise aesthetics.[1] To address these concerns, non-metal clasp dentures (NMCDs) were introduced, utilizing clasps made from thermoplastic resins.[1,4] Non-metal clasp dentures are available in 2 variations: rigid, with a metal framework including occlusal rests; and flexible, without a metal framework.[4] Flexible NMCDs have limited indications, one of which is their use as interim dentures (temporary RPDs).[4]

Flexible NMCDs without a metal framework made of polyamide 12 are of interest to researchers due to their aesthetic qualities, biocompatibility and good patient acceptance.[5] In comparison to PMMA and metals, they have a reduced weight and higher flexibility.[3] Thus, they can be easily inserted into small oral cavities (e.g., in pediatric patients, individuals with microstomia, or those with ectodermal dysplasia).[6] Because of the high flexibility and a lower modulus of elasticity, polyamide 12 dentures are resistant to fractures.[3] Therefore, they are considered a potential alternative for selected indications and patients allergic to methyl methacrylate.[3,5–7] However, despite these advantages, they are difficult to reline and polish, especially in a dental office.[6] Flexible NMCDs made of polyamide 12 have also shown potential to traumatize supporting tissue and increase bone resorption.[4,5] However, finite element analysis demonstrated a reduction in stress for the clasps and for abutment teeth when polyamide 12 clasps were used.[8] The absence of longitudinal studies has resulted in a lack of consensus regarding wider indications and extended wearing duration.[4,5] Compared to conventional temporary dentures, such as RPDs made from PMMA, the processing costs of NMCDs are higher. Consequently, cost-effective and efficient technologies are of interest.[5]

Polyamide 12 can be processed using either conventional thermoforming or through three-dimensional (3D) printing. The conventional method is both time-consuming and complex.[9] Three-dimensional printing is a type of additive manufacturing methods. Recently, these methods have gained increased attention and have become popular in the field of dentistry.[10] 3D-printed NMCDs made of polyamide 12 offer an attractive manufacturing technique. Fused filament fabrication (FFF) printing is a relatively simple, cost-effective and time-efficient method.[11,12] However, it is not frequently used in the field of dentistry due to its longer printing times and lower resolution compared to other 3D printing methods.[10] However, in terms of the fabrication of medical components, FFF printing is the most prevalent technique worldwide for thermoplastic polymers, such as polyamides.[12] Currently, it is the only commercially available 3D printing method for polyamide 12.

There is a lack of data regarding the material properties of 3D-printed polyamide 12 for use as flexible, temporary NMCDs. In this study, we will use clinically relevant material parameters to examine whether this innovative method has the potential to replace conventional procedures.

The aim of the present study is to determine the difference in material properties between conventionally processed and 3D-printed polyamide 12 in response to mechanical, thermal or chemical aging. The null hypothesis states that there are no differences between the 2 materials with respect to the modulus of elasticity, surface roughness change (ΔRa) and color change (ΔE).

Material and methods

Figure 1 shows an overview of the study design.

Specimen preparation

A total of 116 polyamide 12 specimens were conventionally processed (n = 58) (PA12_C, control; Johannes Weithas GmbH & Co. KG, Lütjenburg, Germany) or 3D-printed (n = 58) (PA12_3D, r.Pod Dual Extruder; Arfona, New York, USA). Polyamide 12 granules (conventional process) or filaments (3D printing) were used. In both cases, the base material was of the same chemical composition (Valplast® International Corp., New York, USA). All specimens were manufactured with dimensions of 40 mm × 10 mm × 2 mm.

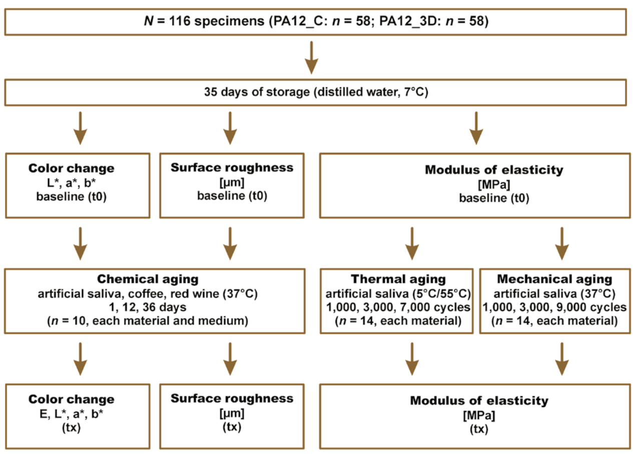

Fig. 1. Study design

PA12_C – conventionally processed polyamide 12; PA12_3D – 3D-printed polyamide; L* – brightness; a* – hue, saturation of the red-green axis; b* – hue, saturation of the yellow-blue axis.

The specimens in the PA12_3D group were produced using FFF printing. The string-shaped polyamide 12 material was subjected to thermoplastic processing in the form of a filament. The material was heated to 220°C through an extrusion nozzle and deposited layer by layer on a build platform in the defined X-Y direction (i.e., along the longitudinal axis of the component). No support material was used during the fabrication of the specimens. The printing path followed a diagonal trajectory at a 45° angle to the X-axis. With a nozzle diameter of 0.4 mm, material layers of 0.3 mm in height were printed with a 100% infill density.

To achieve the optimal surface quality, finishing and polishing were carried out in accordance with the manufacturer's instructions.

The specimens in the PA12_C group (control) were conventionally processed using the thermopress method, utilizing thermoplastic injected polyamide 12 granules. In this process, the granule cartridges in the injection molding machine were heated to approx. 290°C and subsequently injected into the mold at a pressure of approx. 6.5 bar. Post-processing and polishing were carried out following the manufacturer's instructions.

All specimens were stored for 35 days in distilled water at a temperature of 7 ±1°C immediately after production (Med. Kühlgerät MRL 150; Electrolux, Luxembourg City, Luxebourg) to achieve water saturation before testing. The storage temperature was selected to minimize microbial growth during the storage period.

Mechanical aging

The mechanical aging of the PA12_C (n = 14) and PA12_3D specimens (n = 14) was conducted through cyclic compressive loading (Universal Testing Machine Inspekt-Micro LC100N; Hegewald & Peschke, Meß- und Prüftechnik GmbH, Nossen, Germany). The test setup resembled a cyclic three-point bending test in artificial, temperature-controlled saliva at 37°C (UKD saliva solution; University Pharmacy, Dresden, Germany), with a central point load applied to the specimen. The bending cycles were performed at a frequency of 1 Hz, with a displacement of 2 mm, a loading speed of 1 mm/s, and a preload of 1 N. A total of 1,000, 3,000 and 9,000 cycles were performed, which roughly correspond to 1, 3 and 9 years of wear for polyamide NMCDs, respectively.

Thermal aging

The thermal aging was simulated using a thermocycler (THE-1200; SD Mechatronik GmbH, Feldkirchen-Westerham, Germany). The specimens (PA12_C, PA12_3D, n = 14 each) were cyclically exposed to temperature-controlled artificial saliva solution (5°C/55°C, UKD saliva solution; University Pharmacy). Each cycle lasted 77 s, with 27 s in each liquid container and 9 s of drip time. A total of 1,000, 3,000 and 7,000 cycles were performed to simulate 1, 3 and 8 months of use, respectively.

Chemical aging

The PA12_C and PA12_3D specimens were stored for 1, 12 and 36 days at 37°C in artificial saliva (UKD saliva solution; University Pharmacy), coffee (65 g/L water, NESCAFÉ® GOLD; Nestlé Deutschland AG, Frankfurt am Main, Germany) or red wine (pH 3.3, König Arthur Republik Moldau; Andreas Oster Weinkellerei, Cochem, Germany) in a heat chamber (kelvitron® t; Heraeus Instruments, Hanau, Germany). Ten specimens of each material were stored in each medium. A total of 1, 12 and 36 days of storage in the colorants were performed to simulate the intake of beverages over a period of 1 month, 1 year and 3 years, respectively.

Modulus of elasticity

Polyamide 12 was evaluated in accordance with the ISO 20795-1:2013 standard and classified as a denture base polymer, falling under classification type 3: "Thermoplastic molded forms or granules".[13] The modulus of elasticity was determined using a three-point bending test (TIRAtest 2720; TIRA GmbH, Schalkau, Germany). The specimens were subjected to axial loading at a 90° angle across the entire specimen width using a conical indenter (2-mm radius) and a constant test speed of 1 mm/min (preload: 1 N, test endpoint criterion: 10 N). The modulus of elasticity was calculated using the following formula (Equation 1):

$$E = L^2m/4bd^2 \quad (1)$$

where:

E – modulus of elasticity [N/mm^2];

L – support span [mm];

m – gradient of the initial strength-line portion of the load deflection curve [N/mm];

b – width of the specimen [mm];

d – thickness of the specimen [mm].

Surface roughness

The surface roughness was measured with the use of a contact profilometer (Hommel-Etamic W20; JENOPTIK Industrial Metrology Germany GmbH, Villingen-Schwenningen, Germany) and the stylus method. For each specimen, 4 measuring distances were recorded, comprising 2 longitudinal measurements and 2 transverse measurements, each positioned perpendicular to the other. The angle of measurement for the diagonal printing path was 45°. The measurement was conducted with a stylus tip radius of 2 µm and a tip angle of 90°. The feed mechanism moved horizontally along the surface at a constant speed of 0.5 mm/s and a measuring force of approx. 0.8 mN. The measuring length was 4.8 mm, with a cut-off wavelength of 0.8 mm, and a measurement path of 4.0 m. Subsequently, for each specimen at each measurement time point within the artificial aging process, the arithmetic mean roughness value (Ra) was determined from the 4 measuring distances.

Color change

The color change was determined in accordance with the ISO/TR 28642:2016 standard.[14] For the determination of color stability, the Lab* color system spectrophotometer (Gretag SPM 100; Gretag, Regensdorf, Switzerland) was used. The CIE L*a*b* color space is an approximately uniform color space with coordinates for brightness (L* axis, where L* = 0 represents black and L* = 100 represents white), as well as for hue and saturation (red-green axis (a*), where +a* represents red and –a* represents green; yellow-blue axis (b*), where +b* represents yellow and –b* represents blue). The changes in brightness (ΔL*) and hue (Δa* and Δb*) were defined as differences and were determined for the respective immersion periods and storage media. The individual color parameter differences (ΔL*, Δa* and Δb*) were assessed by subtracting the parameter variables at 2 time points: the measurement time point at baseline (t0) as a specified reference; and after the aging process (tx). The resulting overall ΔE was determined using the following CIE formula (Equation 2):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{2}$$

The color measurements were conducted using a standardized CIE Illuminant D65, which corresponded to natural daylight. The observer angle was set at 2° and was derived from the area of optimal color vision in the human eye. To obtain an average, the measurements were taken at 4 defined points for each specimen. The precise repositioning of the specimens for measuring the L*, a* and b* values at the 4 defined measuring points was ensured through the use of a fixed placement aid on the spectrophotometer. Prior to each measurement, the specimens were thoroughly rinsed with running water and allowed to dry, in order to prevent light reflection.

Statistical analysis

The statistical analysis was conducted using the IBM SPSS Statistics for Windows software, v. 24.0 (IBM Corp., Armonk, USA). The normality of the data was assessed using the Kolmogorov–Smirnov test and the Shapiro–Wilk test. Descriptive statistics were used to summarize the data. For the modulus of elasticity and ΔE, explorative inference statistics were calculated using the Kruskal–Wallis test, given that the data was not normally distributed. A non-parametric Mann–Whitney *U* test was performed to examine differences between the groups. To account for multiple tests, the Bonferroni–Holm correction method was applied to adjust the *p*-values. The alpha level was set at 5%.

Results

Modulus of elasticity after thermal and mechanical aging

Table 1 presents the descriptive data for the modulus of elasticity values following thermocycling and mechanical aging. In both aging methods, the modulus of elasticity for PA12_C showed significantly lower values compared to PA12_3D at all measured time points (raw and adjusted $p < 0.001$). Following thermal (7,000 cycles) and mechanical aging (9,000 cycles), the modulus of elasticity decreased in both PA12_C and PA12_3D compared to the baseline.

Table 1. Descriptive data for the modulus of elasticity before and after thermocycling and mechanical aging

Cycles, *n*	Aging	Material	Modulus of elasticity [MPa]			
			median	*IQR*	min	max
0 (baseline)	TC	PA12_C^{Aa}	516	489–537	446	551
		PA12_3D^{Aa}	833	782–897	754	1,000
1,000		PA12_C^{Bb}	522	484–561	458	571
		PA12_3D^{Bb}	824	782–873	778	909
3,000		PA12_C^{Cc}	525	525–541	467	556
		PA12_3D^{Cc}	792	770–867	737	898
7,000		PA12_C^{Dd}	458	442–478	426	498
		PA12_3D^{Dd}	705	678–747	664	794
0 (baseline)	MA	PA12_C^{Ee}	515	468–539	443	565
		PA12_3D^{Ee}	761	734–791	676	887
1,000		PA12_C^{Ff}	464	454–487	422	566
		PA12_3D^{Ff}	775	754–817	713	877
3,000		PA12_C^{Gg}	493	473–505	426	541
		PA12_3D^{Gg}	779	735–818	701	847
9,000		PA12_C^{Hh}	455	442–470	399	528
		PA12_3D^{Hh}	747	738–794	709	864

IQR – interquartile range; min – minimum; max – maximum; TC – thermocycling; MA – mechanical aging; PA12_C – conventionally processed polyamide 12 (control); PA12_3D – 3D-printed polyamide 12. Lowercase superscript letters indicate significant differences when compared to the respective control (raw *p*-value ≤0.05, Mann–Whitney *U* test). Uppercase superscript letters indicate significant differences in comparison to the respective control (adjusted *p*-value ≤0.05, Mann–Whitney *U* test).

Roughness after chemical aging

The Ra values at the baseline for PA12_3D were observed to be high, reaching up to 0.49 μm (interquartile range (*IQR*): 0.37–0.56 μm). The median Ra value for the control group (PA12_C) was 0.31 μm (*IQR*: 0.26–0.36 μm). Table 2 shows the descriptive data for each tested group. In both groups, none of the Ra values fell below the threshold of 0.2 μm, which is the recommended maximum.[15,16]

Table 3 presents the ΔRa after aging. Overall, only minor changes in Ra were observed.

Color change after chemical aging

Figures 2 and 3 show the specimens before and after 36 days of immersion in coffee. A perceptible ΔE could be observed. Figure 4 depicts the specimens following a 36-day storage period in red wine.

Table 4 presents the descriptive data for color change. After 1 day of storage in coffee or wine, the color change was small and below or equal to 1.9.

Table 2. Descriptive data for the roughness (Ra) before and after chemical aging

Storage time [days]	Medium	Material	Ra [μm]			
			median	*IQR*	min	max
0 (baseline)	artificial saliva	PA12_C	0.29	0.23–0.35	0.20	0.37
		PA12_3D	0.45	0.34–0.82	0.31	1.22
	coffee	PA12_C	0.34	0.28–0.41	0.22	0.50
		PA12_3D	0.35	0.33–0.55	0.28	0.59
	wine	PA12_C	0.31	0.26–0.35	0.22	0.67
		PA12_3D	0.49	0.37–0.56	0.32	0.80
1	artificial saliva	PA12_C	0.32	0.24–0.36	0.22	0.42
		PA12_3D	0.43	0.37–0.77	0.32	1.03
	coffee	PA12_C	0.34	0.29–0.42	0.24	0.47
		PA12_3D	0.37	0.34–0.56	0.32	0.62
	wine	PA12_C	0.30	0.29–0.44	0.26	0.61
		PA12_3D	0.49	0.34–0.61	0.33	0.71
12	artificial saliva	PA12_C	0.33	0.23–0.36	0.20	0.38
		PA12_3D	0.52	0.34–0.76	0.33	1.17
	coffee	PA12_C	0.32	0.27–0.41	0.20	0.45
		PA12_3D	0.36	0.28–0.39	0.20	0.70
	wine	PA12_C	0.28	0.25–0.35	0.23	0.74
		PA12_3D	0.47	0.30–0.71	0.27	0.79
36	artificial saliva	PA12_C	0.28	0.22–0.34	0.20	0.47
		PA12_3D	0.51	0.37–0.51	0.31	1.27
	coffee	PA12_C	0.27	0.23–0.42	0.20	0.49
		PA12_3D	0.39	0.34–0.49	0.27	0.72
	wine	PA12_C	0.28	0.24–0.40	0.21	0.59
		PA12_3D	0.47	0.32–0.65	0.31	0.80

Table 3. Descriptive data for the roughness change (ΔRa) after chemical aging

Storage time [days]	Medium	Material	ΔRa [μm]			
			median	*IQR*	min	max
1	artificial saliva	PA12_C	0.01	−0.02–0.04	−0.07	0.14
		PA12_3D	0.00	−0.04–0.02	−0.19	0.08
	coffee	PA12_C	0.00	−0.05–0.04	−0.09	0.09
		PA12_3D	0.02	0.00–0.04	−0.20	0.11
	wine	PA12_C	0.03	−0.01–0.06	−0.20	0.26
		PA12_3D	0.00	−0.05–0.02	−0.09	0.08
12	artificial saliva	PA12_C	0.00	−0.01–0.02	−0.02	0.05
		PA12_3D	0.01	−0.06–0.06	−0.08	0.12
	coffee	PA12_C	−0.01	−0.05–0.02	−0.09	0.04
		PA12_3D	−0.05	−0.09–0.00	−0.20	0.11
	wine	PA12_C	0.00	−0.03–0.04	−0.11	0.08
		PA12_3D	−0.02	−0.08–0.06	−0.11	0.22
36	artificial saliva	PA12_C	−0.02	−0.03–0.01	−0.05	0.13
		PA12_3D	0.02	−0.02–0.07	−0.27	0.28
	coffee	PA12_C	−0.05	−0.10–0.02	−0.15	0.09
		PA12_3D	0.02	−0.01–0.04	−0.13	0.13
	wine	PA12_C	−0.02	−0.06–0.03	−0.11	0.18
		PA12_3D	−0.01	−0.06–0.03	−0.07	0.16

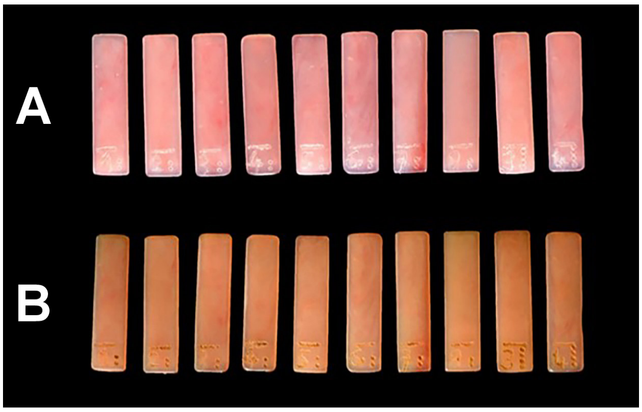

Fig. 2. Conventionally processed polyamide 12 specimens before (A) and after (B) 36 days of storage in coffee

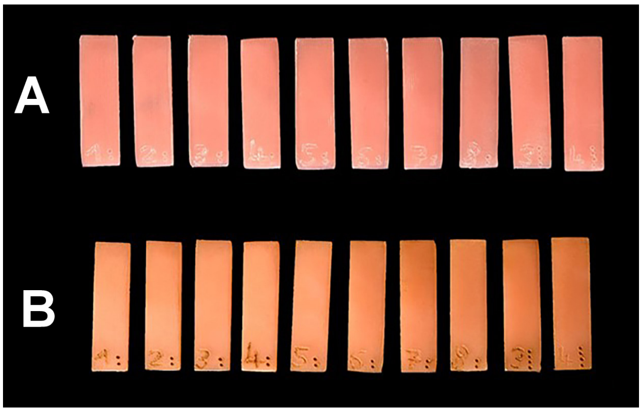

Fig. 3. 3D-printed polyamide 12 specimens before (A) and after (B) 36 days of storage in coffee

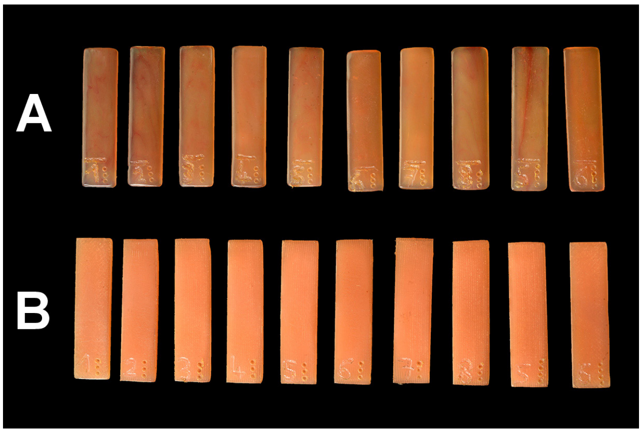

Fig. 4. Conventionally processed (A) and 3D-printed (B) polyamide 12 specimens after 36 days of storage in red wine

Table 4. Descriptive data for color change (ΔE) after chemical aging

Storage time [days]	Medium	Material	ΔE			
			median	*IQR*	min	max
1	artificial saliva	PA12_C	2.7^{Aa}	1.9–3.3	0.8	3.4
		PA12_3D	0.6^{Aa}	0.4–1.1	0.3	5.4
	coffee	PA12_C	1.5	1.3–2.1	1.2	2.6
		PA12_3D	1.6	1.1–2.0	0.7	3.0
	wine	PA12_C	1.7^{Bb}	1.6–1.8	1.4	2.0
		PA12-3D	1.9^{Bb}	1.8–2.1	1.7	4.5
12	artificial saliva	PA12_C	1.3	0.5–2.2	0.2	3.7
		PA12_3D	1.1	0.7–1.5	0.5	1.8
	coffee	PA12_C	3.1	1.3–2.1	1.2	2.6
		PA12_3D	3.5	3.1–4.0	3.0	4.6
	wine	PA12_C	4.8^{Cc}	4.5–4.8	4.1	5.3
		PA12-3D	6.2^{Cc}	5.6–6.3	4.8	6.4
36	artificial saliva	PA12_C	1.7	1.3–2.2	0.4	2.5
		PA12_3D	1.3	0.7–1.5	0.5	1.8
	coffee	PA12_C	6.7^{Dd}	6.3–6.9	6.0	7.2
		PA12_3D	8.6^{Dd}	7.9–9.0	7.7	10.0
	wine	PA12_C	6.8^{Ee}	6.6–7.0	5.9	7.5
		PA12_3D	8.2^{Ee}	7.8–8.9	6.9	9.7

Lowercase superscript letters indicate significant differences when compared to the respective control (raw p-value ≤0.05, Mann–Whitney U test). Uppercase superscript letters indicate significant differences in comparison to the respective control (adjusted p-value ≤0.05, Mann–Whitney U test).

After 12 and 36 days of storage in coffee or wine, the highest recorded value for color change was 8.6. A significant increase in ΔE was observed for PA12_3D in comparison to PA12_C after 12 and 36 days of storage in wine (raw p = 0.001, adjusted p = 0.003). Significant differences were observed for PA12_3D after 36 days in coffee (raw and adjusted p < 0.001). In contrast, when immersed in artificial saliva, all median values remained below or were equal to 2.7.

Discussion

The study aimed to detect differences in the material properties of conventionally processed and 3D-printed polyamide 12 following exposure to mechanical, thermal and chemical aging at various time points. The popularity of additive manufacturing has increased in the field of dentistry. Given the differences between conventional and additive manufacturing methods, it is possible that the material properties of the end products differ, even with the same chemical composition. Additionally, the additive manufacturing of polymers is still a developing field.[17] Thus, the evaluation of the properties of these materials is of high importance for the clinician.

The results of this study implied that PA12_3D had a higher modulus of elasticity and, thus, higher rigidity and Ra when compared to PA12_C. Furthermore, PA12_3D showed a higher degree of discoloration after storage in wine and coffee for 12 and 36 days.

During the mechanical and thermal aging tests in the laboratory, it was important to simulate clinical conditions over time. It is essential to investigate the potential for material fatigue induced by repetitive clasp deflection when removing RPDs for cleaning, as this could lead to loss of retention and damage of clasps. The repair of polyamide 12 dentures is a challenging process.[7] In our study, we simulated a scenario of 1, 3 and 9 years of wearing polyamide NMCDs for the removal and insertion of the denture. These periods were calculated on the assumption that patients would remove their dentures twice a day. It can be assumed that 3,000 and 9,000 cycles represent the upper limits of durability for temporary dentures. However, in real life, prolonged use should be taken into consideration. To simulate the physiological intraoral conditions during thermal aging, an approximate temperature change of 20 to 50 thermal cycles per day was assumed. Hence, 10,000 thermal cycles corresponded to a wearing time of 1 year.[18,19] In our experiments, thermal cycling corresponds to an approximate wearing time of 1, 3 and 8 months, which is typical for temporary dentures.

The staining of dentures may cause significant aesthetic drawbacks and is attributed to the consumption of food and beverages.[19,20] Consequently, in vitro staining simulations are crucial in anticipating potential color changes during daily use. The storage of dentures in wine and coffee for periods of 1, 12 and 36 days may roughly simulate the consumption of these products over 1 month, 1 year and 3 years, respectively.[21]

Coffee and wine are often used to simulate discoloration.[21–23] Coffee contains tannic acid and yellow colorants that are responsible for color changes.[22] It also has a higher discoloration potential than tea.[22] For red wine, the low pH and ethyl alcohol content may be responsible for discoloration.[22] As previously mentioned, denture use may be prolonged, therefore, simulating 3 years of use aims at a worst-case scenario.

The modulus of elasticity was tested during mechanical and thermal aging as an indicator of clasp longevity. The null hypothesis was rejected, as the results demonstrated significant differences between both processing methods at all tested time points. The significant difference between the 2 methods remained consistent throughout the course of both aging processes. With regard to the maximum number of cycles tested for both aging methods, the modulus of elasticity decreased slightly in comparison to the baseline.

In this study, the modulus of elasticity for PA12_C was found to be approx. 300 MPa lower than that of PA12_3D. Additionally, it was 500 MPa lower than the values reported in prior studies for conventionally processed material.[22,24,25] For example, Wieckiewicz et al. reported initial values of approx. 1,000 MPa for dry specimens.[22] This discrepancy can be attributed to the water storage and sorption of conventionally processed polyamide 12 (Valplast® International Corp.). This results in a reduction in the flexural strength and modulus of elasticity.[25] It is evident that water molecules permeate the polymer structure, acting as plasticizers that enhance the mobility of polymer chains.[25] The impact of water storage, ranging from 2 days (50 ±2 h) to 30 days at 37°C, resulted in a one-third reduction in the modulus of elasticity.[24,25] The changes in the modulus of elasticity after water sorption have clinical relevance to the retention force.[25] To simulate the clinical use and obtain more accurate results, it was crucial to store the specimens in water before conducting the tests. Moreover, additional differences in experimental design among the referenced studies result in varying experimental conditions. This discrepancy may affect the comparability of the obtained results.

The modulus of elasticity is a critical parameter in the evaluation of dental materials used in clasp manufacturing. Materials with a high modulus of elasticity (>2,000 MPa), such as cobalt–chromium (CoCr) alloys, are recommended for clasp and RPD framework designs.[26] Polyamide 12, on the other hand, has a substantially lower modulus of elasticity. Thus, clasps manufactured from polyamide 12 are more flexible and may use larger undercuts on abutment teeth for retention, which would have been leveled for metal clasps.[24] Flexible clasps facilitate less stressful denture insertion for abutment teeth and reduce stress in the retentive arm of the clasp compared to metal clasps.[8] However, the flexibility of the denture base is a concern, as it can potentially lead to uneven stress distribution on the mucosa and alveolar bone, particularly in the mandible.[4,27]

Our study showed that PA12_C had a significantly lower modulus of elasticity compared to PA12_3D. This discrepancy may be attributed to the different manufacturing methods employed and may be a potential advantage for printed polyamide 12.

Differences could occur using FFF printing. The polyamide 12 filament was melted at a lower temperature compared to conventional processing to ensure dimensional stability. This could result in the emergence of different material properties. The higher rigidity of PA12_3D could be more suitable for use as temporary dentures compared to PA12_C. If the differences in the modulus of elasticity, for example 300 MPa, as observed in our study between conventionally processed and 3D-printed polyamide 12 prove to be clinically significant, further investigation would be warranted.

The higher modulus of elasticity for PA12_3D could have a significant clinical impact, as claps that are too flexible may fail to offer sufficient retention for the RPDs.[28] Furthermore, polyamide 12 clasps require less removal force and exhibit clinically unacceptable retention in small undercuts, when simulated, even with a modulus of elasticity of 1,440 MPa.[8] The lower modulus of elasticity in conventionally processed polyamide 12 clasps can result in inadequate clinical retention. Additionally, contrary to metal clasps, adjusting the retention force after the production of polyamide 12 clasps is not feasible.[4] Nevertheless, Kümbüloğlu et al. observed no significant deformation of conventionally processed polyamide 12 clasps after 36 months of simulated clinical use.[28] Furthermore, a clinical pilot study by Boeckler et al. demonstrated favorable outcomes for clinical use within 6 months.[29] A recent report by Spintzyk et al. showed a clinical application of 3D-printed polyamide non-metal clasp RPDs with acceptable fit and sufficient retention.[30]

In the qualitative assessment of denture base materials, the measurement of the Ra is of particular interest. The Ra value is largely dependent on the preceding polymerization and processing procedures, as well as the subsequent finishing and polishing.[31] To ensure comparable conditions for the Ra measurements, standardized polishing protocols were conducted in accordance with the manufacturers' instructions. The Ra for PA12_3D was consistently higher than that of PA12_C at all measurement time points and for all tested media. This discrepancy is likely attributable to the different manufacturing processes. Fused filament fabrication has a low resolution. The molten filaments are printed layer by layer. Even after the layers have been merged, they can still be identified. Furthermore, grinding and polishing proved ineffective in eliminating the inner layer-wise structure.[30]

Nevertheless, a slight change in Ra values was observed during the chemical aging process, and its clinical relevance remained uncertain. This finding was consistent with other literature results that demonstrated no influence on ΔRa using thermal or chemical aging, even when treated with aggressive chemical agents such as glutaraldehyde or sodium hypochlorite.[4,32]

Regarding Ra, all specimens showed Ra values that were above or equal to the recommended maximal threshold of 0.2 μm.[15,16] The ΔRa between the 2 processing methods was minimal and may be considered clinically irrelevant. Therefore, no interferential statistics were used to compare both processing methods.

The presence of rough surfaces on clasps and denture base materials promotes the accumulation of plaque and bacterial adhesion.[6] As a clinical consequence, the risk of denture stomatitis or caries at abutment teeth may be elevated.[6] High roughness on retentive clasp surfaces is considered unfavorable, with a smooth surface being the desired target.[33,34] Proteoglycans in human saliva are effective lubricants. Thus, it can be assumed that rough surfaces of denture clasps do not contribute to clasp retention. It is therefore recommended that improvements be made in the production or polishing process.

Regarding color changes, the null hypothesis was found to be partially rejected, showing significant differences between both processing techniques at various time points and in the presence of different chemical aging media.

The specimens derived from both manufacturing processes exhibited a similar tendency towards discoloration. Surprisingly, PA12_C showed the highest ΔE after 1 day when stored in artificial saliva. This discrepancy in color change did not fit the overall data and may be attributed to measurement error. The most significant discoloration was observed following exposure to red wine and coffee, particularly when simulating more than 1 month of use. A color change of 3.7 is regarded as the threshold recommended for gingival shades.[35,36] The color changes observed when simulating 1 year of storage in wine and 3 years in coffee or wine, respectively, exceeded this threshold. Perceptible color changes could pose substantial aesthetic concerns for patients and affect their satisfaction with the treatment.[20,35–38] There is an established association between the color of artificial teeth and the utilization of RPDs.[39] Additionally, it is important to note that an increased dissatisfaction with tooth appearance is related to a dissatisfaction with tooth color and is significantly linked to the desire for treatment.[40] Patients expressing dissatisfaction with tooth color may be susceptible to discoloration of the polyamide clasp color. Furthermore, patients under the age of 65 are more likely to experience aesthetic dissatisfaction.[39] Given that RPDs, especially temporary dentures, are utilized across all patient groups, good color stability is crucial in dental materials, particularly in polyamide clasps.

The results of this study are in line with those previously reported by Wieckiewicz et al. regarding discoloration, indicating a need for material improvement.[22] A potential avenue for improvement entails modifications to the printing process. Another potential solution is the application of a sealant agent. A recent study showed that this treatment could markedly reduce the color change of polyamide 12.[41] Reducing the color change could have a positive impact on the clinical performance of polyamide 12 dentures.

Limitations

One of the limitations of this study was that the same specimens were tested at different time points. If a specimen was damaged at the beginning or during the course of the experiment, the error was carried over all measurement time points. To minimize the potential for damage during the three-point bending test, the end-of-test criterion was carefully selected to ensure that no irreversible material change could have occurred. No tests exceeded the linear section of the curve for the determination of the modulus of elasticity using Hooke's straight line. As previously stated by Hamanaka et al., the proportionality limit of polyamide 12 (Valplast® International Corp.) is reached at a load of 19 N when tested according to ISO 1567 and ISO 1567:1999/Amd 1:2003.[42–44] In our study, the established end-of-test criterion of 10 N corresponded to a specimen deflection of 1.2 mm in the elastic range of polyamide 12. This was below the proportionality limit, and it is unlikely that it had a negative impact on our findings.

A further limitation is the lack of the modulus of elasticity and roughness measurement before saturation with water. Including these data points might facilitate a more comprehensive understanding and interpretation of the data. Additionally, a comparison with other studies could be more straightforward. Nevertheless, the values obtained for dry polyamide 12 have limited clinical implications, as the saturation level simulates the condition in the oral cavity during the wearing period. Only the data obtained from saturated specimens is clinically relevant. The water saturation affects the modulus of elasticity, influencing the rigidity of clasps and denture bases, as well as the retentive force of the clasp.[25] The retention force plays a crucial role in the clinical success of RPDs. This highlights the importance of in vitro conditions that closely resemble clinical scenarios.

Furthermore, since only 2 different manufacturing processes of chemically identical polyamide 12 material were evaluated, the generalizability of the results to different polyamide 12 products is limited. The literature indicates that there are variations in mechanical, physical and surface properties among different polyamide products.[7,25,42] Moreover, the findings are confined to the processing parameters, particularly in the case of 3D-printed polyamide 12, as it has been demonstrated that these can significantly influence the properties of the material.[45] This limitation also restricts the generalizability of the results.

Conclusions

In conclusion, the findings of the present study indicate that there are notable differences in the properties of 3D-printed polyamide 12 compared to those of conventionally processed polyamide 12. The higher roughness and discoloration of the 3D-printed material may prove disadvantageous in clinical applications. Conversely, the higher modulus of elasticity could be advantageous due to the enhanced rigidity. Further studies are required before 3D-printed material can be recommended for clinical use.

Ethics approval and consent to participate

Not applicable.

Data availability

The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

Consent for publication

Not applicable.

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