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A Spectrophotometry Evaluation of Clear Aligners Transparency: Comparison of 3D-Printers and Thermoforming Disks in Different Combinations

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Abstract: (1) Background: the aim of this study was to investigate the transmittance levels of aligners in relation to different thermoforming disks and printers after 14 days of in vitro aging. (2) Methods: the transmittance level of 18 aligners was investigated. Three printers were used to create the aligner: Carbon L1, Prodways LD20 and RapidShape D100+. Each printer produced 6 aligners: three were made of Zendura FLX material and three of Scheu Ca Pro+. Each sample was subjected to spectrophotometry analysis of its transmittance levels, for a total of 54 measurements at T0. Then, all samples were aged in vitro at a constant temperature in artificial saliva supplemented with food coloring for 14 days each. The spectrophotometry protocol was repeated, and the same 54 measurements were collected at T1 (after aging). The resulting data were analyzed and compared by means of ANOVA ($p < 0.05$). (3) Results: all tested aligners revealed lower transmittance values after aging. Scheu CA Pro+ aligners showed higher transparency at T0, but a significant worsening of its aesthetic at T1. On the other hand, Zendura FLX aligners presented slightly reduced transmittance levels before aging, which, however, remained more stable after 14 days, showing no significant difference. In the specific, aligners produced by Prodways LD20 printers showed better optical properties than the others, both at T0 and T1. (4) Conclusions: Differences in pre-and-post-aging optical properties of aligners are influenced by the manufacturing process. Both the thermoplastic disks and the printers, thanks to new technologies, played a positive role in the final transparency of the product, which improved in all values compared to previous studies.

Citation: Cremonini, F.; Vianello, M.; Bianchi, A.; Lombardo, L. A Spectrophotometry Evaluation of Clear Aligners Transparency: Comparison of 3D-Printers and Thermoforming Disks in Different Combinations. *Appl. Sci.* **2022**, *12*, 11964. <https://doi.org/10.3390/app122311964>

Academic Editors: Andrea Deregibus, Gabriele Rossini and Simone Parrini

Received: 8 November 2022
Accepted: 21 November 2022
Published: 23 November 2022

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Keywords: orthodontic aligners; transparency; spectrophotometry; materials; 3D

1. Introduction

3D printing technologies are currently increasing their importance in dentistry, both for clinical and research purposes [1,2].

In the field of orthodontics, 3D printers play an essential role in the manufacturing of aligners, which are becoming increasingly popular as the answer to aesthetic demand and the need for comfort [3].

Since thermoplastic aligners can be accurately 3D printed directly from a digital image of teeth, the extra steps of creating a physical model may be eliminated. Furthermore, 3D printing may help decrease the cost as well as increase treatment performance and improve patient comfort [4,5].

Several 3D printing processes may be used for the direct printing of clear aligners, such as fused deposition modelling, selective laser sintering, selective laser melting, direct pellets fused deposition, stereolithography, multi-jet photo-cured polymer process, or continuous liquid interface production technology.

Photo-polymerization from clear resin is nowadays the most suitable 3D printing method [6].

To further minimize these errors, a clear biocompatible aligner can be 3D printed for direct patient usage [7,8]. During this manufacturing process not only is the chosen printer influencing the fitting and aesthetics of the aligner, but also the thermoforming disks [9] Ryu et al. demonstrated that thermoforming increases water absorption and solubility and reduces the transparency levels of thicker materials and, together with the surface hardness of tested materials [10].

The optical properties of the materials are determined by the way they react to light in terms of absorbance and transmittance. The greater the transmittance the more transparent the material; Conversely, the greater the absorbance, the less transparent the material. Transparency is the key to the aligner's success. Transmittance is the fraction of incident light at a settled wavelength, that passes through the material [11].

3D print quality has influenced transparency by two parameters: resolution and accuracy. The former is the minimum size that the device manages to print onto a specific spatial plane. The latter is the ability of a printer to produce items as identical as possible to their 3D original files. The higher the resolution of the printer, the thinner the individual layers that make up the cast on which the aligner will then be thermoprinted on. A recent study compared different 3D technologies, considering several variables such as precision, authenticity, and accuracy, and concluded that there were statistically significant differences between printers using different technologies. Thanks to the evolution of digital technology, new methods of 3d printing have been developed.

The photopolymer printer (PPP) works similarly to an inkjet printer, with the exception of a component in which UV light cures the material, while it is dispensed from the nozzles. The object is cured layer by layer, starting from bottom to top, which determines a better quality of printing. Once the liquid resin is sprayed onto the platform, the UV light connected to the printer head simultaneously cures the material as it is printed.

One technology is represented by Stereolithography (SLA), which consists of a photosensitive resin and an ultraviolet (UV) light acting on the resin positioned on the platform. The laser keeps on tracing and forming each layer of the previous one, starting from the bottom until the final result is achieved. The UV light cures every layer; as the layer is processed, the tray deforms to add more liquid resin. Instead, digital light processing (DLP) has a projector that cures the entire layer each time. Another approach to the DLP printer is represented by a continuous digital light printer (cDLP), which allows the light to cure the polymers with no interruption. Previous investigations on the precision of 3D printed models indicated significant differences among 3D printing technologies [12]. The procedural characteristics mentioned can affect the aesthetics of an aligner in a positive or negative way.

The aligners currently on the market are distinguished according to the thermoforming materials, some of those used are polypropylene (PP), polycarbonate (PC), thermoplastic polyurethanes, and copolyester, the most used being polyethylene terephthalate glycol (PETG), and many others. Aligner thickness tends to vary between 0.50 to 1.50 mm.

Like with their manufacturing material, this can impact their chemical properties, and, therefore, their optical characteristics, already affected by masticatory stress, salivary enzymes, and food coloring during their 14 consecutive days of wear [13–15]. From an aesthetic point of view, since each template should last two weeks, the transparency of the aligner should be maintained during this period to ensure that the patient has a palatable option [16,17].

The optical properties of the aligner are determined by spectrophotometric transmittance. It is usually expressed as percentage transmittance (%T) and is defined as the percentage of light that can be transmitted from the other side of the surface, so the greater the transmittance the more transparent the material [11].

The first study conducted in 2009 with the aim of investigating aligner aesthetics at this term is limited to only taking the absorbance values of a single brand into consideration [15]. In 2015 Lombardo et al. analyzed for the first time the different levels of transmittance and absorbance of various models of clear aligners, selected from three different

manufacturers: All in (Micerium, Avegno, GE, Italy), Invisalign (Align Technology, Santa Clara, CA, USA), and F22 (Sweden and Martina, Due Carrare; PD, Italy). Of those analyzed, F22 was significantly more transparent, before and after aging. It emerged that around 80% of light goes through the F22 aligner, compared to 70% for Invisalign aligners and 55% for All in [18].

In 2022 Lombardo et al. examined the transmittance and absorbance of 21 clear aligners from six different manufacturers: All in (Micerium, Avegni, GE, Italy), Air Nivel (NIVOL SRL, Navacchio Cascina; PI, Italy), Arc Angel (Dextra Group Srl, Modena, MO, Italy), Invisalign (Align Technology, Santa Clara, Ca, USA), F22, F22 EvoFlex (Sweden & Martina, Due Carrare, PD, Italy), and Nuvola (G.E.O. UK, European Orthodontic Ltd.). F22 and F22 EVOFlex resulted significantly in better absorbance and transmittance than the others [19].

Electromagnetic radiation in the range of visible light has wavelengths from 400 to 700 nm, but the human eye evaluates the intensity corresponding to the various wavelength to different extents. In fact, the higher wavelengths (near 700 nm) are poorly absorbed by the visual pigments; the lower wavelengths (near 400 nm) can be absorbed by the visual pigments of the eye, but do not reach the retina because they are absorbed by the cornea and lens. The peak of the highest human spectral sensitivity measured is at about 560 nm, the yellow-green color region.

Currently, literature studies correlating how the type of 3D printer and different thermoforming disks could influence aligner aesthetics are insufficient. The aim of this study is to appraise how transparency is affected by printers and thermoforming disks. Hence, we set out to compare the optical properties of 18 aligners, produced with three different printers while using two different materials.

2. Material and Methods

Three 3D printers were used to carry out this study: Carbon (L1 3D printer; Carbon Global HQ, London, UK), RapidShape (D100+ 3D printer, RapidShape GmbH, Heimsheim, Germany), and Prodways (LD20 Prodways Tech R&D-Technologies & Headquarters, Montigny-le-Bretonneux, France). Starting from the same prototyped resin model of the superior arch each of these printers was used to make three identical aligners through two different types of materials: Zendura FLX and Scheu CA Pro+. A total of 18 aligners were compared and analyzed. (Figure 1) As for previous studies [18,19], measurements were taken at each model's central incisor (1.1).

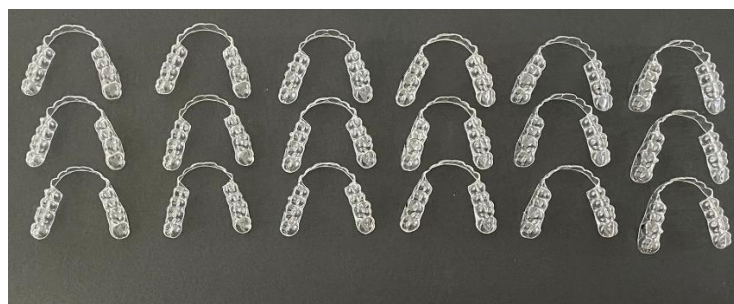


Figure 1. The 18 aligners before aging.

Each aligner's transmittance was analyzed through a spectrophotometer (T0) (Jasco UV-vis V630PC, Tokyo, Japan) that has the following specifications: deuterium light source for UV range, and halogen lamp for visible range, double beam, single monochromator. To obtain all the transmitted light, the sensor is positioned 1 cm behind the detection window.

The spectrophotometer was calibrated before each measurement through the use of the white light spectrum. The tongue area of all the aligners was removed from canine to canine by means of a rotating bur, leaving only the buccal surface to be exposed to the

light source. Each aligner was then rinsed in distilled water, dried with an air jet, and positioned inside the spectrophotometer on a 35 mm-high stand with the vestibular surface of the upper central incisor placed vertically, in contact with the detection window. The wavelengths considered included a range from 400 to 700 nm, considering only the wavelengths in the spectrum of visible light were selected, and the transmittance (%T) was automatically recorded by the spectrophotometer.

Every sample was measured three times consecutively, while slightly changing the inclination of the surface with reference to the light beam. The nine total spectrophotometer reading curves resulting from the analysis of the three aligners of each model were processed via Spectra Manager II software (Jasco, Tokyo, Japan) allowing for the achievement of the numerical values of the average curve and the standard deviation.

Each one of the 18 aligners was then submerged for 14 days in a glass box (40 cm × 20 cm × 15 cm), which contained 500 mL of artificial saliva, diluted with 2 L of water and integrated with brown food coloring at a ratio of 1:1 (*v/v*). A heating item was also immersed in the solution, connected to a temperature controller set at 37 °C ± 1 °C, to keep the bath at a constant temperature. (Figure 2)

After 14 days of aging, every aligner was washed with distilled water, dried with an air jet, and analyzed under spectrophotometry (T1) with the same procedures described above. (Figure 3) Finally, a total of 54 transmittance measurements were achieved before and 54 after aging.



Figure 2. Saliva bath used to age the samples.



Figure 3. The 18 aligner after aging.

3. Statistical Analyses

The Graph Pad Prism 9 software (Graphpad, San Diego, CA, USA) was used to carry out the statistical analysis.

The transmittance curves referring to the before-and-after aging periods for each aligner type were compared through a t-test with Welch's correction (to not assume equal SDs). The analysis of variance (ANOVA) was performed to settle the difference between groups of aligners (3D printers and materials) using multiple comparisons and Tukey's post-test. p -values < 0.05 were considered to be significant. p -values < 0.01 were considered to be significant and $p < 0.001$ high significant.

4. Results

The transmittance data, before and after aging, recorded at 400 nm and 700 nm by the spectrophotometer (Table 1) (chosen as the limits of the measurement range) were used to create average curves for each aligner produced with the three 3D printers and the two thermoforming disks considered in this study (Figures 4 and 5).

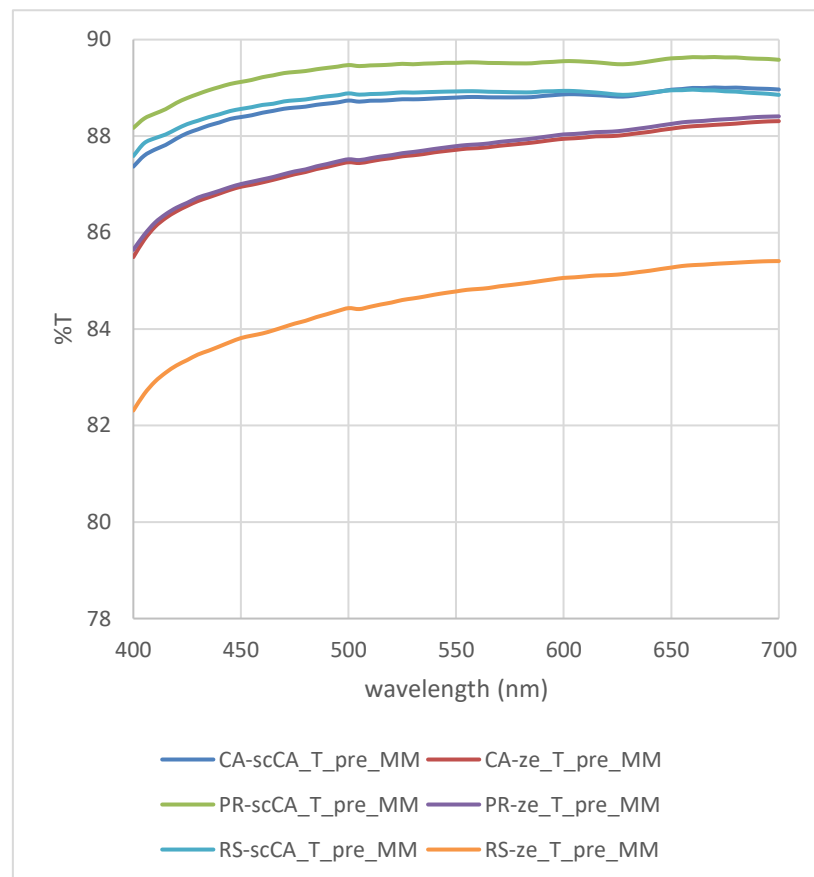


Figure 4. Transmittance curves of all aligners at T0 without SD for better visual clarity.

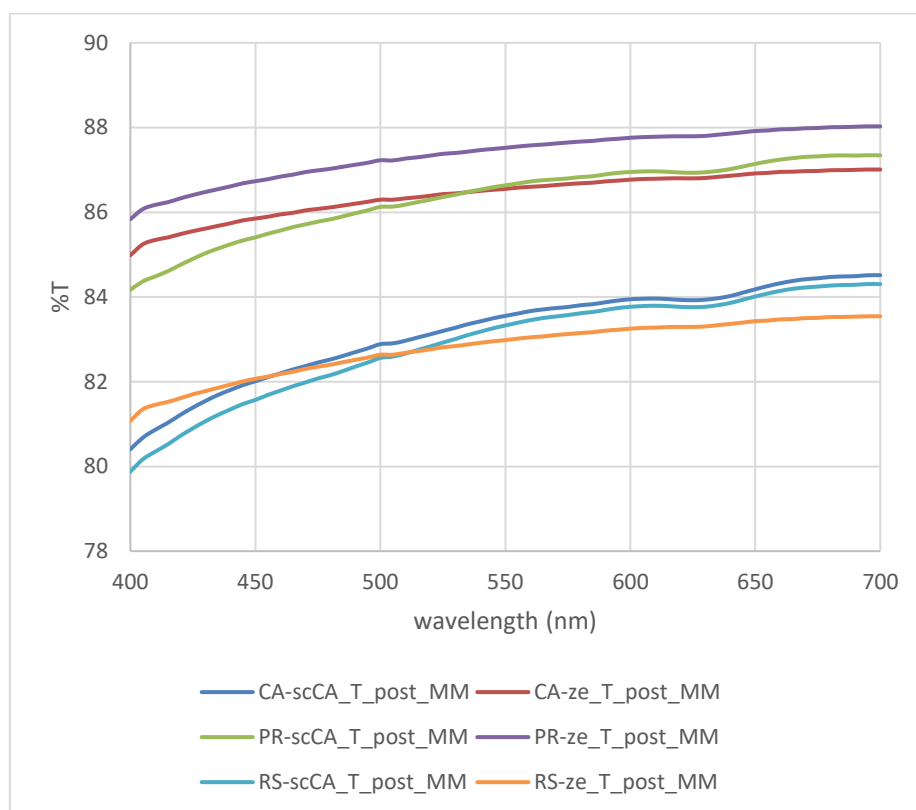


Figure 5. Transmittance curves of all aligners at T1 without SD for better visual clarity.

The pre- and post-aging transmittance curves show that more constant transparency was maintained with Zendura FLX material than with Scheu Ca Pro + material, for all three printers compared.

At T0, Scheu CA Pro+ aligners printed with Prodways LD20 have a higher transmittance (T%) than the other analyzed, with values of 88.169 ± 0.65 and 89.581 ± 0.91 , at 400 and 700 nm, respectively.

At T1, the same material and printer showed a high-significance change ($p < 0.001$) with transmittance values of 84.171 ± 0.29 and 87.345 ± 0.80 , at the respective wavelengths. (Figure 6)

Transparency decreased after aging even with Carbon L1 and RapidShape D100+ printers and Scheu CA Pro+ material. (Figures 7 and 8).

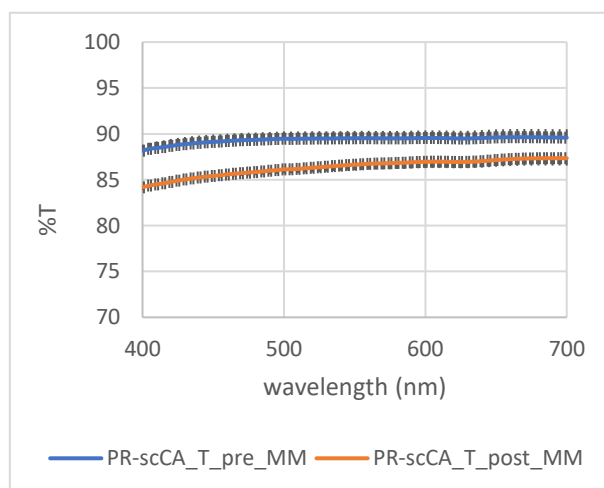


Figure 6. Comparison of transmittance values of the Scheu CA Pro + with Prodways LD20 printer before and after aging. The curves are the average of nine spectrophotometry measurements \pm SD.

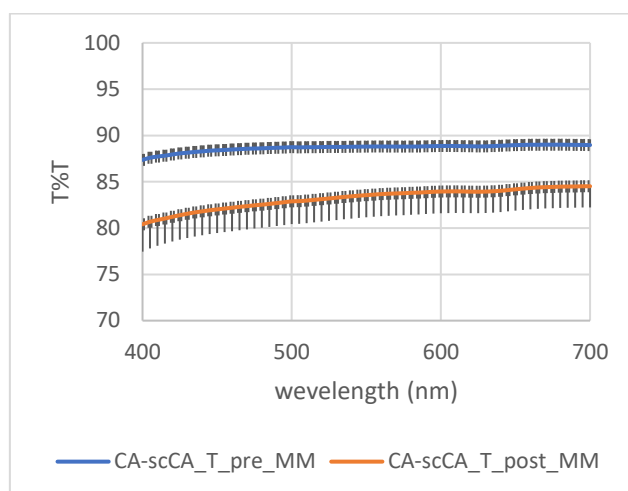


Figure 7. Comparison of transmittance values of the Scheu CA Pro + with Carbon L1 printer before and after aging. The curves are the average of nine spectrophotometry measurements \pm SD.

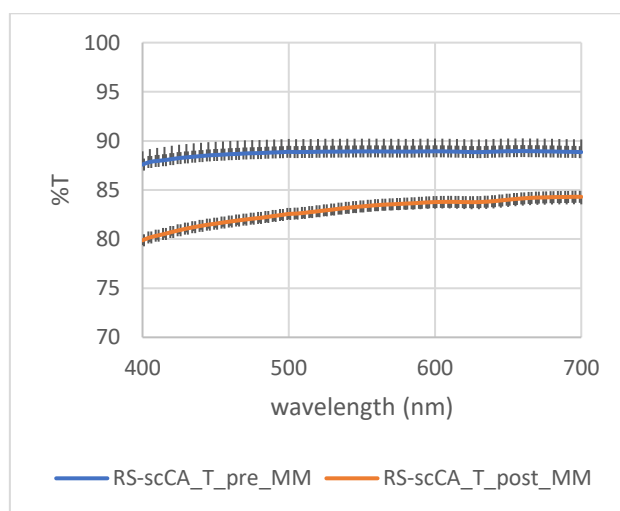


Figure 8. Comparison of transmittance values of the Scheu CA Pro+ with RapidShape D100+ printer before and after aging. The curves are the average of nine spectrophotometry measurements \pm SD.

The highest percentage variation was reported by the RapidShape D100+ printer with Sheu CA Pro+ of -8.8 and -5.1 , respectively, recording a significant loss of transparency.

This printer with this material had mean values of 87.587 ± 1.34 and 88.853 ± 1.29 before aging and 79.878 ± 0.49 and 84.304 ± 0.76 after aging.

On the other hand, non-significant variation ($p > 0.01$) is found with the Zendura FLX material for the three printers considered in the study. Prodways LD20 printer with this second material presented transmittance values, at 400 nm and 700 nm, of 85.643 ± 1.90 and 88.408 ± 1.67 at T0 and 85.837 ± 1.12 and 88.029 ± 1.20 at T1.

When it comes to comparing the same printer with the two different materials, it is clear that the transmittance curves are more constant with Zendura FLX. This result is an indication of how aesthetics are preserved between T0 and T1. (Figure 9)

The percentage change, at two wavelengths of 400 nm and 700 nm is 0.2 and -0.4 , respectively, showing a transparency stability by the material and printer. This consistency of transparency is also found for the other two printers used, Carbon L1 and Rapidshape D100+, with the Zendura FLX material. (Figures 10 and 11)

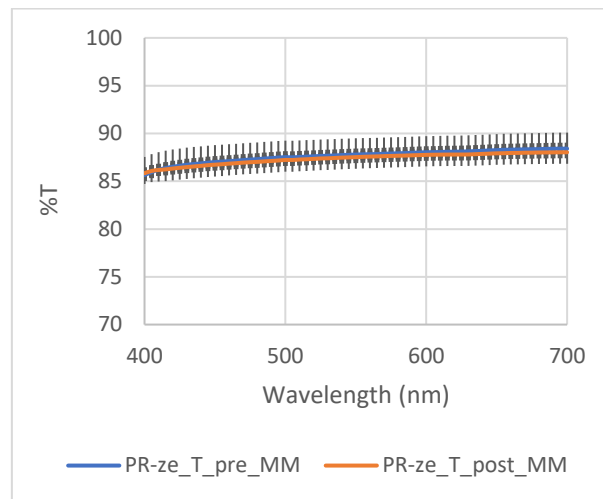


Figure 9. Transmittance values of the Zendura FLX with Prodways LD20 printer analyzed before and after aging. The curves are the average of nine spectrophotometry values \pm SD.

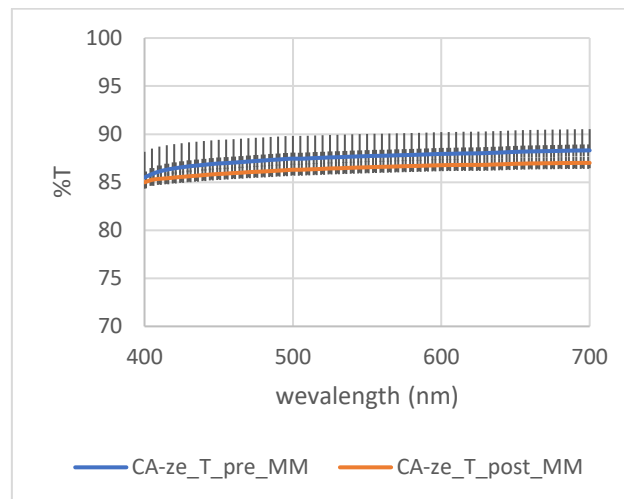


Figure 10. Transmittance values of the Zendura FLX with Carbon L1 printer analyzed before and after aging. The curves are the average of nine spectrophotometry values \pm SD.

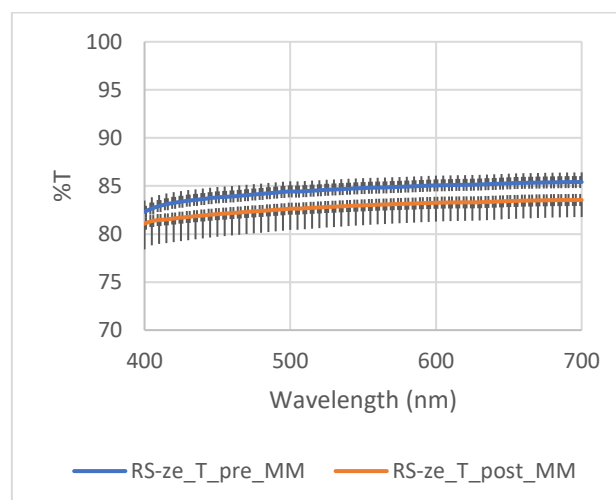


Figure 11. Transmittance values of the Zendura FLX with RapidShape D100+ printer analyzed before and after aging. The curves are the average of nine spectrophotometry values \pm SD.

The transmittance data showed that before aging, the aligners produced with Scheu CA Pro + material had higher values than Zendura FLX, for all the 3D printers. Following treatment with artificial saliva and brown food coloring, the Scheu CA Pro+ material exhibited a higher percentage variation than Zendura FLX in optical properties (Table 1). After aging the highest transmittance values are recorded with the different printers, respectively. Prodways LD20 and Carbon L1 with Zendura FLX, and Prodways LD20 with Scheu CA Pro+.

In compliance with ANOVA, instead, the multiple comparisons of all the aligners in this study showed different statistical significance either before and after aging or between materials and printers. This difference for example was significant on each printer that used Scheu CA Pro+ materials.

Table 1. Transmittance values of six type of aligners before and after in vitro aging. The data are the average of nine values \pm SD. High significance level ($p < 0.001$).

Aligner	Trasmittance at 400 nm (\pm SD)				Trasmittance at 700 nm (\pm SD)			
	As Received	After Aging	<i>p</i> -Value	% Variation	As Received	After Aging	<i>p</i> -Value	% Variation
CA-ze	85.492 \pm 2.67	84.985 \pm 0.65	0.604.	-0.6	88.309 \pm 2.21	87.009 \pm 0.54	0.119	-1.5
CA-scCA	87.367 \pm 0.63	80.404 \pm 2.95	<0.001	-8.0	88.965 \pm 0.62	84.516 \pm 2.28	0.003	-5.0
PR-ze	85.643 \pm 1.90	85.837 \pm 1.12	0.799.	0.2	88.408 \pm 1.67	88.029 \pm 1.20	0.592.	-0.4
PR-scCA	88.169 \pm 0.65	84.171 \pm 0.29	<0.001	-4.5	89.581 \pm 0.91	87.345 \pm 0.80	<0.001	-2.5
RS-ze	82.312 \pm 1.17	81.075 \pm 2.67	0.238.	-1.5	85.408 \pm 1.00	83.545 \pm 1.77	0.018	-2.2
RS-scCA	87.587 \pm 1.34	79.878 \pm 0.49	<0.001	-8.8	88.853 \pm 1.29	84.304 \pm 0.76	<0.001	-5.1

5. Discussion

The stability of the aesthetic properties of clear aligner materials has not been widely investigated. Indeed, the color stability of dental materials is influenced by various factors, such as ultraviolet irradiation, staining beverages, and mouthwashes. To satisfy the patient's aesthetic request, the color stability and transparency of clear aligners should be stable for the two week orthodontic period of wearing.

The current study compared the transparency of aligners both before and after aging, while trying to analyze how changes in optical properties can be affected by both the thermoforming disk and the printer used. In literature, it has been shown that 3D printed models accurately reproduce the occlusion and are now a very important tool for both diagnosis and treatment planning. However, the manufacturing process of aligners directly from their scanning is still in its initial phase, together with any information related to accuracy and aesthetic properties [20,21].

The printers used in this study carry the most innovative technologies: Rapidshape D100+ and Prodways LD20 use Digital Light Processing (DLP), a technology formed by a platform for building the object, and a projector to cure the resin on the platform and a photosensitive resin. The digital projector has the objective to make a single image of each layer of the 3D object. The light emitted by this type can be UV, if created specifically for the 3D printing process.

DLP printer works through an additive process, a projector works on a single layer, and for each layer that is cured, the tray descends to add a layer to the previous one, in this way the aligner is printed from start to finish.

The Carbon L1 printer instead uses the cDLP approach, which stands for Continuous Digital Light Processing. This new technology works through vertical movement without interruption of the building plate, allowing light a continuous polymerization. Since the projector is a digital screen, the image of each layer is composed of square pixels. This implies the formation of a 3D layer consisting of small rectangular cubes called voxels. In the case of these printers, what determines the resolution of the XY axis is the size of the square pixels. Consequently, the higher the native resolution of the projector, the higher the resolution of each layer. The focal distance between the projector lamp and the

printing area is crucial. This is the reason why DLP printers can have different resolutions corresponding to inversely proportional print areas. The pixels in this case range from 35 to 100 microns. DLP and cDLP technologies have a higher production speed than SLA, as the projector exposes all the dots belonging to the same layer to photopolymerization at the same time.

The literature reports significant differences between 3D technologies in the accuracy and precision of 3D printed models.

Owais et al. concluded that these two technologies are the most accurate in making the print. These two technologies were studied in their mechanical aspects, such as accuracy and fidelity to the model. On the other hand, in this study, we investigated their influence on aesthetic appearance [12,22–24].

The three printers selected were used to produce three identical aligners with two different types of materials: Zendura FLX and Scheu CA Pro+. The aligners currently present on the market differ in the material and the most used is polyethylene terephthalate glycol (PETG), followed by polycarbonate (PC), polypropylene (PP), thermoplastic polyurethanes, copolyester, and many others are used to manufacture aligner. Aligner thickness has a value in the range of 0.50 and 1.5 mm [13]. The Zendura FLX is a polyurethane. This material is characterized by the presence of two materials: an elastomeric core that gives flexibility, and a hard coating that characterizes elasticity and firmly grips the teeth [25]. On the other in the Scheu CA Pro+ the flexible elastomer layer ensures high elasticity and break resistance, while reducing initial force and increasing patient comfort. This is three-layer aligner material with a flexible elastomer core in a hard-elastic double shell which is able to maintain a constant force level at a minimal loss of power [26].

The decrease in detected transmittance after aging compared with previous studies indicates that at the clinical level great improvements have been made as technologies have progressed. Indeed, all observed transparency rated both before and after aging appear to be higher if compared to the ones analyzed in previous studies conducted with the same method [18,19].

The materials analyzed and the new printers' technologies show respectively improved optical properties after being aged and better performance compared to previous studies. Indeed, the percentage variation before and after aging is in the range of 0.2–8.8%, whilst, 5 to 11% of deterioration was observed after 14 days of aging in previous studies [18,19].

All the printers tested with Zendura FLX material show a non-statistically significant variation after aging, indicating that the optical properties have been excellently maintained if this thermoforming disk was used. On the other hand, the Scheu CA Pro+ aligners, despite having better pre-aging transmittance values, underwent a significant deterioration, even though smaller variation ranges compared to previous studies are still shown.

These results indicate a good maintenance of transparency levels, a standard that satisfies the growing aesthetic demand of patients, who are increasingly interested in an invisible treatment [27] [28]. The popularity of mass-produced transparent aligners is possible thanks to a growing technological revolution that allows for the creation of increasingly more precise and aesthetic aligners [29].

The perception of transparency and how the degradation is perceived by human eyes was not considered in the previous study. On the other hand, Transmittance (%T) was considered an objective variable that could be quantified pre- and post-aging. This was carried out *in vitro*, therefore it is not certain that oral aging could produce the same effects on optical properties, given that the *in vivo* aligner is normally subjected to further mechanical and chemical stresses. In fact, other studies [14] tell us that the aesthetic of aligners further degrades when they have been worn for the same amount of time inside the mouth. However, the choice of conducting an *in vitro* study is correlated to the need of standardizing the aging process in artificial saliva, ensuring that the transparency level

wouldn't be affected by individual habits, but only by the intrinsic optical properties of the aligner [30].

6. Conclusions

Within the limits of this study, Carbon L1, LD20, and Rapidshape D100+ 3D printers have been shown to produce aligners that suffer less deterioration in optical properties than in previous studies, with both thermoforming disks analyzed. Surely Zendura FLX material is the one that varies the least in transparency both before and after aging and therefore can optimally satisfy the aesthetic need of the patient. Certainly, improvements in technologies can have intimate clinical implications on the aesthetics required by the patient. As *in vitro* testing conditions are unable to accurately reproduce the conditions in the oral environment, further studies will be required to measure the transmittance of aligners after a cycle of wear *in vivo*. Moreover, they should investigate whether these small differences in transparency rates detected at spectrophotometry are actually perceived by the human eye as well.

Author Contributions: Conceptualization, L.L.; Investigation, A.B.; Writing, M.V.; Supervision, L.L.; Data curation, F.C.; Methodology, F.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: All procedures performed in the study were in accordance with the ethical standards of the Institutional and national research committee and with the 1975 Helsinki declaration and its later amendments or comparable ethical standards.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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