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Original article

In-house 3D-printed aligners: effect of *in vivo* ageing on mechanical properties

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Summary

Objective: To investigate alterations in the mechanical properties of in-house three-dimensional (3D) printed orthodontic aligners after intraoral ageing.
Materials and methods: Sixteen 3D-printed aligners (TC-85DAC resin, Graphy, Seoul, Korea) were used for the purpose of the study, which were divided into 10 control (not used) aligners and 6 materials retrieved from 4 patients after 1-week service (retrieved group). Samples from the control group were analysed by attenuated total reflectance-Fourier-transform infrared (ATR-FTIR) spectroscopy. Samples from control/retrieved groups were embedded resin and subjected to instrumented indentation testing (IIT) to record force–indentation depth curves, calculating the following (as per ISO 14577-1, 2002 standard): Martens hardness (HM), indentation modulus (E_{IT}), and elastic index (η_{IT}), and the indentation relaxation index (R_{IT}). Differences between control and retrieved 3D-printed aligners were checked with Mann–Whitney/*t*-tests at an alpha = 5%.
Results: ATR-FTIR analysis showed that aligners were made of a vinyl ester–urethane material. The results of the IIT testing were: HM (control: median 91.5 N/mm^2, interquartile range [IQR] 88.0–93.0/as-retrieved: median 90.5 N/mm^2, IQR 89.0–93.0); E_{IT} (control, mean 2616.3 MPa, standard deviation [SD] 107.0 MPa/retrieved, mean 2673.2 MPa, SD 149.4 MPa); η_{IT} (control: median 28.6%, IQR 28.2–30.9%/as-retrieved: median 29.0%, IQR 28.7–29.2%); and R_{IT} (control: median 45.5%, IQR 43.0–47.0%/as-retrieved: median 45.1%, IQR 45.0–45.3%). No differences between as-retrieved and control aligners were found for any of the mechanical properties tested ($P > 0.05$ in all instances).
Conclusion: The mechanical properties of the in-house 3D-printed aligners tested were not affected after 1 week in service period.

Introduction

Aligners present a highly aesthetic orthodontic treatment modality and sometimes the first preference for many adult patients (1–3) regardless about their objective performance (4). Despite the high demand however for this modality, aligners are still a rather costly and complicated third-party controlled treatment option, due to the necessary involvement of aligner manufacturers or laboratories in the manufacturing process, which incurs fees and delays the appliance delivery. To overcome these obstacles, dental practitioners have adopted in-house three-dimensional (3D) printing technology as a cost-effective 'Do It Yourself' (5–7) in-office method. Such techniques are propagated to be able to offer same-day appliance delivery, at a much lower cost compared with traditional fixed appliances, while providing at the same time a simplified workflow fully controlled by the operator (8).

Despite the practical advantages, 3D printing and in general in-house fabrication of orthodontic appliances is coupled with concerns related to uncertainties around the physical and mechanical properties, ageing pattern, chemical stability, and broader biological profile of the materials used, as well as technical aspects of the printing process itself (7, 9, 10). As a rapid emerging technology, scientific data in the published literature about fundamental parameters of these 3D Printed In-House (3DPIN) aligners are very limited. In contrast to long-established manufacturers like Invisalign®, information on the mechanical properties, chemical composition, biocompatibility, and force exertion of forces of 3DPIN aligners is lacking or severely limited. A study (11) has reported that conventional (thermoformed) aligners present different deformation status (plastic versus elastic) when compared with the 3DPIN aligners. In addition, the stress relaxation phenomenon due to ageing under intraoral conditions poses another hindrance affecting the stability of initial force magnitude during treatment (12, 13). This is a process already described in polyurethane or polyethylene terephthalate glycol (PETG)-based aligners (14) and may have clinical implications, as the rapid reduction of force at early stages of force initiation may result in an insufficient application of forces. It becomes clear that as tempting as it may appear to be, this 3DPIN aligner trend is rather unsubstantiated, requiring a thorough characterization of the end-product, which could also vary depend on the raw materials used, the printing/sintering process, and printer-output-related variables.

Therefore, the aim of this study was to examine if the mechanical properties of 3DPIN aligners show inferior mechanical properties after intraoral exposure. The null hypothesis was that there is no difference in the *in vitro* mechanical properties of unused 3DPIN aligners and 3DPIN aligners used for 1 week.

Materials and methods

Sample collection

Six 3DPIN aligners were retrieved from a single dental practice (NP) after 1 week intraoral placement on four patients and this group was named as RET. The aligners in this sample were constructed with a 0.25 mm planned movement. A second group of 10 orthodontic appliances prepared by the same conditions and 3D-printing device was used as control (CON). All patients signed an informed consent and the relevant national Dental Association approved the study designed, which dealt with anonymized collection of retrieved materials, placed during routine treatment of patients and, which after the term of their service would had been otherwise discarded (Reference 210209 NP).

All aligners were 3D printed employing the Moonray S100 printer (Srintray, Los Angeles, CA, USA). The tank was filled with the TC-85DAC resin (Graphy, Seoul, Korea) indicated for manufacturing of clear aligners. The aligners were printed in successive layers of 100 μm nominal size employing a 405 nm blue-violet light and digital light processing technology. Then the aligners were post cured for 5 minutes from cervical and incisal side in a post curing unit (Cure M, Graphy, Seoul, Korea). Treatment with aligners included no attachments and overall a similar degree of arch variability (mainly anterior crowding). For the prescribed 7-day application, directions were given and compliance was checked at the end of the week through a questionnaire addressing compliance.

Chemical composition

Five samples from the central incisor region from each group were cut with a lancet. The buccal surface of the sample was placed against the diamond reflective element of a single-reflection attenuated total reflection (ATR) accessory equipped with Zn–Se lenses (Golden Gate, Specac, Kent, UK). A firm contact was achieved by pressing the sample to the sapphire anvil of the accessory. Spectra were obtained from each sample employing a Fourier-transform infrared spectroscopy (FTIR) spectrometer (Spectrum GX, Perkin-Elmer Corp, Bacon, UK) operated under the following conditions: 4000–650 cm^{-1} range, 4 cm^{-1} resolution, and 20 scan co-addition. The depth of analysis was estimated as to ~2 μm at 1000 cm^{-1}. All spectra were subjected to ATR and baseline corrections. The extent of the C=O intermolecular bonding in the material (Ri) was determined from the net peak area ratio of hydrogen bonded ester to the freely vibrating ester groups, after Gaussian curve fitting of the complex ester peak at the 1800–1600 cm^{-1} band range.

Mechanical properties

The mandibular first molars from each group were cut off from the appliances and the specimens were embedded in acrylic resin (Verso Cit-2, Struers, Ballerup, Denmark), with their occlusal surfaces parallel to the horizontal plane, ground up to 4000 grit-size SiC papers under water cooling, polished with a water-based diamond suspension (NapR1 DiaPro, Struers, Ballerup, Denmark) of 1 μm particle size in a grinding/polishing machine (Dap-V, Struers, Ballerup, Denmark), and subjected to instrumented indentation testing (IIT). The mechanical properties determined were: Martens hardness (HM), indentation modulus (E_{IT}), elastic index (η_{IT}), and indentation relaxation (R_{IT}). Testing was conducted in a universal hardness testing machine (ZHU0.2/Z2.5, Zwick Roell, Ulm, Germany) with a Vickers indenter, applying two different loading regimes. The HM, E_{IT}, and η_{IT} were acquired from force–indentation depth curves applying a maximum load of 4.9N for a 2-second contact time. For R_{IT}, a tetragonal force pulse with a constant indentation depth was applied for 60 seconds and the R_{IT} value was measured by monitoring the decrease in force between the start and the end of the constant indentation depth period. Three measurements were taken from each of the 10 control and 6 retrieved specimens and the average value was used as representative of the specimen. All mechanical properties were calculated according to formulas provided by the international standard ISO14577-1, 2002 (15) using a Poisson's ratio 0.357 (16).

Statistical analysis

The data were tested for normality and homoscedasticity by Shapiro–Wilk and equal variance test, respectively. Descriptive statistics included means with standard deviation (SD) for normal and medians with interquartile ranges (IQRs) for non-normal data. Differences in the material properties between the CON and RET samples were tested with independent-samples *t*-test (after checking for variance-equality with the Brown–Forsythe test) or Mann–Whitney, as appropriate. All analyses were done in Stata 14.0 (Stata Corp, College Station, TX, USA) with a two-sided alpha of 5% and an openly provided dataset (17).

Results

Chemical composition

Figure 1 illustrates a representative ATR-FTIR spectrum of the CON group. The spectrum shows the characteristic bands of OH (3380 cm^{-1}), NH (3330 and 1528 cm^{-1}), CH (2937, 2858, 1456, 1369, 924, and 775 cm^{-1}), C=O (1715 and 1695 cm^{-1}), CN (1528 and 1307 cm^{-1}), C(O)OC (1235, 1159, and 1102 cm^{-1}), and COC (1032 cm^{-1}) groups, which comply with a polyester–urethane polymer structure. Gaussian curve fitting of the 1800–1600 cm^{-1} band range revealed the presence of ester groups in hydrogen bonded (amide C=O b, 1690 cm^{-1}) and freely vibrating states (C=O f, 1720 cm^{-1}) along with a small peak of residual C=C (1640 cm^{-1}). The R_{IT} was estimated as to 0.41. No vibrations of aromatic groups were detected, indicating that the polymer is an aliphatic vinyl-functionalized polyester–urethane material. Spectra of the retrieved material indicate identical pattern with absence of any indication of compositional material other than integuments (biofilm) arising from the intraoral exposure of aligners (data not shown).

Mechanical properties

Figure 2 demonstrates representative force–indentation depth curves from CON and RET groups used for calculation of the HM, E_{IT}, and η_{IT}. Figure 3 illustrates the tetragonal force pulse applied (Figure 3a)

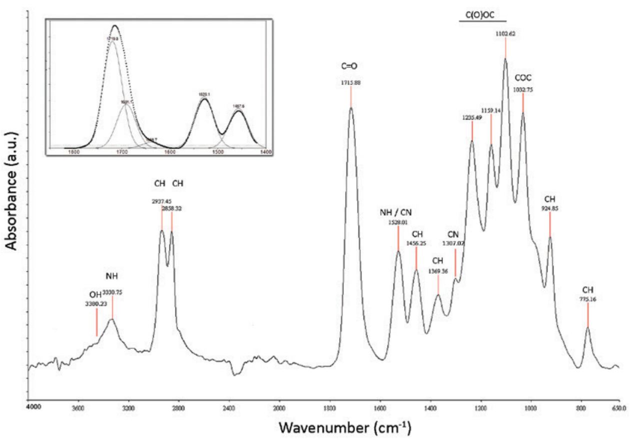

Figure 1. A representative ATR-FTIR spectrum from CON group. The insert demonstrates the Gaussian area peak fitting of the ester group (absorbance scale, r^2 = 0.9995). ATR-FTIR, attenuated total reflectance-Fourier-transform infrared.

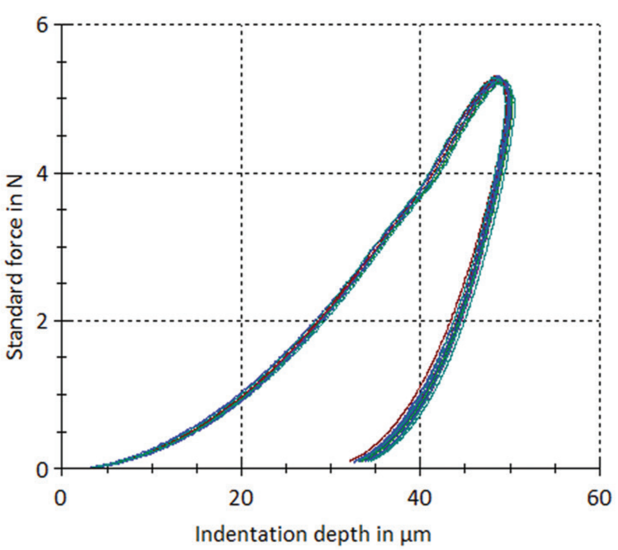

Figure 2. Representative force–indentation depth curves for both groups tested. (overlapping of curves arises from the lack of effects of intraoral ageing which results in coincidental lines).

and representative relaxation curves obtained from the groups tested (Figure 3b). The numerical results for HM, E_{IT}, η_{IT}, and R_{IT} along with the statistical outcome are presented in Table 1. No significant differences were allocated between CON and RET groups for all the properties tested.

Discussion

Based on the experimental results of this study the null hypothesis could not be rejected as no significant differences were identified between the CON and RET groups implying that the mechanical properties of the 3D-printed aligners tested are not deteriorated during the 1-week intraoral exposure period, prior to replacement, as advised by the manufacturer.

The results of the ATR-FTIR spectroscopic analysis indicate that the material is an aliphatic vinyl ester–urethane polymer, possibly with methacrylate functionalization. This material is completely different form the polyurethane-based material used in the production of Invisalign® aligners (18–21) and the PETG compounds used exclusively for the production of thermoformed orthodontic aligners (14, 20).

The HM of CON group was found close to lower values of clear thermoformed aligners made of PETG polymer (CTA, 92–101 N/mm^2) (20) and lower than Invisalign® (118–122 N/mm^2) (20–22). This means that the 3DPIN aligners tested in this study could be more susceptible to intraoral wear compared with conventional thermoformed aligners and Invisalign® aligners. The E_{IT} of CON group was found comparable to Invisalign® (2467–2616 MPa) (20–22), but higher than that reported for conventional thermoformed aligners (2212–2374 MPa) (20). Therefore, the 3DPIN and Invisalign® appliances may provide higher counter forces under the same strain compared with conventional thermoformed aligners. The η_{IT} of the 3DPIN material (29.4%), indicative of the material brittleness, was found much lower than Invisalign® (40.0–40.8%) and conventional thermoformed aligners (34.0–35.9%) (20–22) implying a more ductile behaviour. The relaxation index, though, was found much higher compared with Invisalign® anticipating a higher decay of orthodontic forces.

No statistically significant differences were identified between CON and RET groups, indicating that the mechanical properties of the 3DPIN material tested are not deteriorated during the 1-week period of intraoral service. This is a noteworthy difference with the results of a previous study, where intraoral ageing was found to adversely affect the mechanical properties of Invisalign® aligners for similar exposure times (22). Interestingly, there was no difference between 1- and 2-week exposure to the intraoral environment for Invisalign® aligners, implying that the described effects on the mechanical properties, which most probably are assigned to water attack (23) but can entail also microbial or fungal degradation (24), occur relatively early.

The differences in the structure between the aliphatic vinyl ester–urethane polymer of the 3DPIM material tested and the aromatic urethane polymer of Invisalign® along with the individual manufacturing procedures (light-curing versus stereolithography of a thermoset polymer) may explain the differences found in the corresponding mechanical properties. The stiffness provided by the aromatic groups in the polymer network and the thermoset nature of Invisalign® offer increased hardness at a comparable range of indentation modulus. Remarkably, there is almost 10 times higher relaxation index of the 3DPIN aligners compared with the Invisalign®, which is alarming for the extent of relaxation that 3DPIN aligners

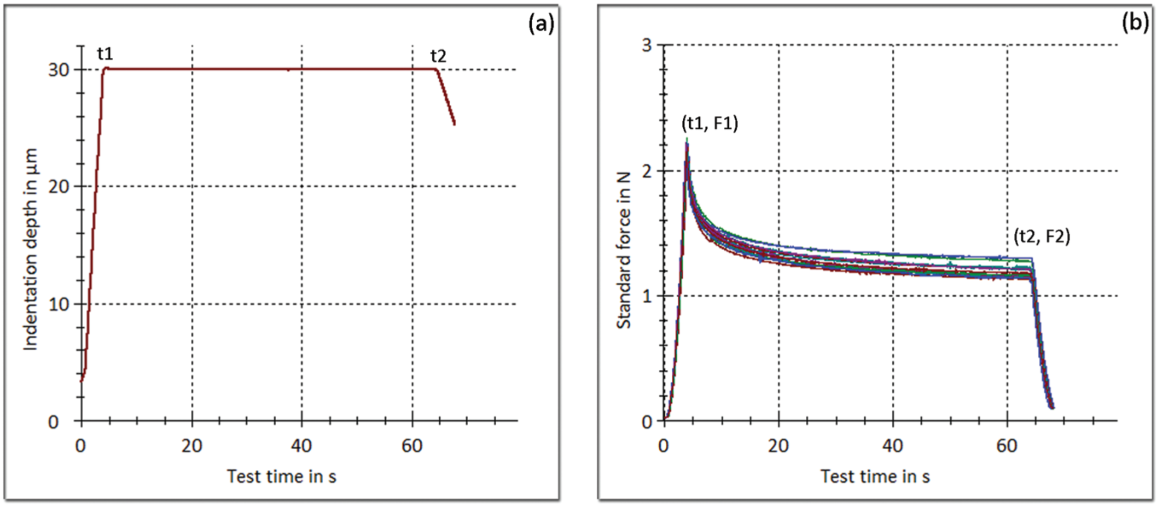

Figure 3. The tetragonal force pulse applied with a constant indentation depth of 30 µm for 60 seconds (a). Representative indentation relaxation curves showing the force decay as a function of the test time. The constant indentation depth results in decreasing force over testing time (b).

Table 1. The results of Martens hardness (HM), indentation modulus (E_{IT}), elastic index (η_{IT}), and indentation relaxation (R_{IT}) for control and retrieved in-house 3D-printed aligners.

Variable	Control (n = 10)	Retrieved (n = 6)	P value
HM (N/mm^2), median (IQR)	91.5 (88.0–93.0)	90.5 (89.0–93.0)	0.74*
E_{IT} (MPa), mean ± SD	2616.3 ± 107.0	2673.2 ± 149.4	0.39**
η_{IT} (%), median (IQR)	28.6 (28.2–30.9)	29.0 (28.7–29.2)	0.96*
R_{IT} (%), median (IQR)	45.5 (43.0–47.0)	45.1 (45.0–45.3)	0.66*

IQR, interquartile range; SD, standard deviation.
*Mann–Whitney test.
**Independent-samples *t*-test.

might undergo in clinical conditions. The R_{IT} of conventional thermoformed aligner materials and Invisalign® (14, 21) was much lower than in the 3DPIN material, suggesting that the latter may be more susceptible to secondary reactions involving the ester moiety, including the hydrolytic degradation.

This first report on chemical and mechanical characterization of unused and retrieved 3DPIN orthodontic aligners cannot be used to characterize the entire spectrum of the various 3D-printing methods (i.e. stereolithography, digital light processing, material jetting, material extrusion, etc.) and resins used for this purpose (25). Despite the absence of a notable effect on the mechanical properties of 3DPIN aligners induced by intraoral service, there are many aspects requiring further investigation, including printing conditions, type of printer, and methods to ensure a quality control of the printed material, before this mode of aligner production is established as an alternative to conventional aligner treatment.

Conclusions

One week of intraoral service does not seem to significantly change the mechanical properties of an in-house 3D-printed orthodontic aligner.

Funding

The study did not receive any funding.

Conflicts of interest

None to declare.

Data availability

The data underlying this article are available in Zenodo at http://doi.org/10.5281/zenodo.4288246.

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