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Original article

Do the mechanical and chemical properties of Invisalign™ appliances change after use? A retrieval analysis

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Summary

Aim: To investigate the mechanical and chemical alterations of Invisalign appliances after intraoral aging.
Materials and methods: Samples of Invisalign appliances (Align Technology, San Jose, California, USA) were collected following routine treatment for a mean period of 44 ± 15 days (group INV), whereas unused aligners of the same brand were used as reference (group REF). A small sample from the central incisors region was cut from each appliance and the buccal surface was analysed by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy ($n = 5$). Then the appliances were cut ($n = 25$) and embedded in acrylic resin, ground/polished in a grinding polishing machine, and the prepared surfaces were subjected to Instrumented Indentation Testing under 4.9 N load. Force-indentation depth curves were recorded for each group and the following parameters were calculated according to ISO 14577-1; 2002 specification: indentation modulus (E_{IT}), elastic to total work ratio also known as elastic index (η_{IT}), Martens Hardness (HM), and indentation creep (C_{IT})The mean values of the mechanical properties were statistically analysed by unpaired *t*-test ($a = 0.05$).
Results: ATR-FTIR analysis confirmed the urethane based structure of the appliances, without important chemical differences attributed to the aging process. INV group showed significantly lower E_{IT} (REF: 2466 ± 20, INV: 2216 ± 168 MPa), HM (REF: 119 ± 1, INV: 110 ± 6 N mm^{-2}) and higher η_{IT} (REF: 40.0 ± 0.3, INV: 41.5 ± 1.2%), and C_{IT} (REF: 3.7 ± 0.2 INV: 4.0 ± 0.1%). The increase in η_{IT} indicates that INV is a more brittle than REF, whereas the increase in C_{IT}, a decrease in creep resistance.
Conclusion: Despite the lack of detectable chemical changes, intraoral aging adversely affected the mechanical properties of the Invisalign appliance.

Introduction

Contemporary orthodontics has seen an increase in patient demands for aesthetic orthodontic appliances, such as ceramic brackets, lingual orthodontics, and clear aligner therapy (1, 2). Aesthetics play a significant role in patient's decisions to receive orthodontic treatment: a recent survey found that 33 per cent of young adults would be unwilling to wear visible braces if needed (3). Another study found that while traditional metal brackets were aesthetically acceptable to only 55 per cent of adults, clear aligners were acceptable to over 90 per cent (2). Clear aligner preference extends to adolescents as well

(4). This demand will likely continue to increase, despite the limitations with certain types of tooth movements. A systematic review published in 2010 (4) including two longitudinal trials (5) and many case reports concluded that there was lack of evidence to support or not the use of these appliances.

Treatment efficacy with clear aligners has been reported to be 41–59 per cent (6, 7). Great force variation has been claimed during clear aligner therapy, as an aligner with high initial force may be followed by an aligner with a low force, resulting in tooth movement that is not constant (8). Additionally, as the order of sequential aligners increase, aligner strains relating to force delivery increase (9). Orthodontic force produced by a thermoplastic material is strongly correlated with its initial mechanical properties and especially stiffness. Therefore, any significant changes among different systems or over time in the mouth may have an impact on what aligner system the practitioner chooses to use (10). Clements *et al.* (11) found that material properties may effect treatment outcomes, with a stiffer aligner material for a 2-week activation time showing the best results in defined measurements of occlusal and alignment improvement. Beyond the initial mechanical properties, intraoral aging during mechanotherapy through biofilm modifications and oral environmental conditions might have an adverse effect on materials properties over the treatment time, compromising the force delivery capacity and treatment efficacy.

Previous studies (12, 13) found substantial morphological variations in intraorally aged aligners, relative to as-received specimens, involving abrasion at the cusp tips and localized calcification at saliva stagnation sites. Although a clearer understanding of the material properties and aging process may lead to better sequencing of tooth movement, the aforementioned findings are associated only to surface morphological and compositional modifications. Even though there are concerns that intraoral aging may affect also bulk properties, which dominate the force delivery capacity (14), there is currently lack of relevant information. Therefore, the aim of this study was the mechanical and chemical characterization of retrieved thermoplastic aligner appliances. The null hypothesis tested was that intraoral aging of the appliances does not adversely affect their chemical and mechanical properties.

Materials and methods

The institutional ethical board approved the protocol and an inform consent was obtained from patients enrolled in the study. Clinically used Invisalign (Align Technology, San Jose, California, USA) appliances for a mean period of 44 ± 15 days were collected from a patient. Small specimens (5 × 5 mm) were cut from visibly intact areas of the buccal surface of central incisor regions of the intraorally aged specimens (INV). As-received aligners, with no history of intraoral exposure, were used as reference (REF).

The changes in the chemical composition of the appliances (INV versus REF groups) were studied by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy. The specimens (n = 5 from each group) were placed with the buccal surface against the diamond reflective element of a single-reflection ATR accessory equipped with ZnSe lenses (Golden Gate, Specac, Smyrna, Georgia, USA) and pressed with a sapphire anvil to obtain firm contact with the diamond crystal. Spectra were acquired employing an 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 scans condition. The depth of analysis was estimated as to 2 μm at 1000 cm^{-1}. All spectra were subjected to ATR and baseline corrections.

Specimens from the appliances (n = 25 per group) were then embedded in an acrylic resin (Verso Cit-2, Struers, Ballerup, Denmark) ground with SiC papers up to 4000 grit and polished) employing a grinding/polishing machine (Dap-V, Struers) under water-coolant. The specimens were then subjected to instrumented indentation testing (IIT), in order to evaluate the following mechanical properties: The indentation modulus (E_{IT}), the elastic index (η_{IT}) defined as the elastic to total work ratio, the Martens Hardness (HM), and the indentation creep (C_{IT}). A universal hardness testing machine (ZHU0.2/Z2.5, Zwick Roell, Ulm, Germany) was used with a Vickers indenter. Force-indentation depth curves were obtained for each group under 4.9 N load and 2 seconds (for E_{IT}, η_{IT}, HM) or 120 seconds (for C_{IT}) contact period. All properties were measured according to the international standard specification ISO14577-1, 2002 (15) as follows:

1. The E_{IT} was calculated from the equation:

$$E_{\mathrm{IT}} = \frac{1-(\nu_{\mathrm{s}})^2}{\dfrac{1}{E_{\mathrm{r}}} - \dfrac{1-(\nu_{\mathrm{i}})^2}{E_i}}$$

where, ν_{s} (0.43) and υ_{i} (0.07) the Poisson's ratios of sample and indenter, respectively, E_{i} the modulus of the indenter (1140 GPa), and E_{r} the reduced modulus given by the formula:

$$E_r = \frac{\sqrt{\pi}}{2C\sqrt{A_p}}$$

where, C denotes the compliance of the contact and is determined by the slope of dh/dF at maximum test force and A_{p} is the projected contact area defined according to ISO 14577-1 (15).

2. The η_{IT} is given by the equation: $\eta_{\mathrm{IT}} = (W_{\mathrm{elast}}/W_{\mathrm{total}}) \times 100\%$, where, W_{elast} is the area under the unloading curve, W_{plast} the area between the loading and unloading curves and W_{total} the sum of elastic and plastic work as determined by the total area below the loading curve.
3. For HM using a Vickers indenter, the following formula applies: $\mathrm{HM} = F/(26.43 \times h^2)$

where, F stands for the test force and h for the indentation depth under exerted test force.

4. The indentation creep (C_{IT}) was measured by recording the increase in indentation depth between the start and the end of the constant force period. The C_{IT} was determined applying the equation: $C_{\mathrm{IT}} = (h_2 - h_1)/h_1 \times 100$, where, h_1 and h_2 are the indentation depths at the time t_1 = 8 seconds and t_2 = 128 seconds, respectively.

A pilot study demonstrated a wide variation of the results of the variables tested potentially assigned to the extreme variation of the level of oral hygiene and plaque accumulation of appliances. From the initial pool of patients tested, the profile of the patients with good oral hygiene was isolated and the aligners of a patient corresponding to this group were processed for analysis to isolate the varying effect of plaque accumulation on the results.

The results of E_{IT}, η_{IT}, HM, and C_{IT} were statistically analysed by unpaired t-test at 95 per cent confidence level (α = 0.05).

Results

Figure 1 demonstrates representative ATR-FTIR spectra from the intraorally aged (INV) and as received (REF) groups. Both groups revealed characteristic bands of OH (3380 cm^{-1}), NH (3313 cm^{-1}), aromatic C–H (3047, 1605, 1597, 812, 766 cm^{-1}), CH (2928, 2853, 1413,915 cm^{-1}), C=O (1728, 1308 cm^{-1}), amide I (C=O of NCO, 1698 cm^{-1}), amide II (NH and C=O of NCO, 1518 cm^{-1}), C–O (1214 and 1205 cm^{-1}), and C–O–C (1100–1060 cm^{-1}). The similarity in reference and intraorally aged spectra denotes that the aged material did not change in chemical composition.

Figure 2 illustrates representative force-indentation depth curves of the groups tested. The curve of the intraorally aged material was shifted towards higher indentation depth, implying lower hardness, whereas the unloading curve of the reference group was steeper than the intraorally aged, indicating higher modulus.

A representative indentation depth–time curve is presented in Figure 3. The indentation depth increased under constant load, reaching the maximum value at approximately 70 seconds after load application.

The results of mechanical properties tested are presented in Table 1. The specimens of the intraorally aged group showed significantly lower values for E_{IT}, HM, and higher for η_{IT}, C_{IT} in comparison with the reference group.

Discussion

This study did not identify significant chemical changes in the appliances after intraoral aging. However, the mechanical properties tested showed significant differences in comparison with the reference material. Therefore, the null hypothesis must be partially rejected in regards of the mechanical properties.

The results of FTIR analysis comply with previous findings confirming that Invisalign is made of a polyurethane-based material (13). However, on contrary to previous studies, where compositional differences were found in the intraorally aged materials associated with the developed biofilm (12, 13), no differences were detected between the reference and the intraorally aged aligners in this study. The retrieved material examined was lacking of organized biofilm precipitations, facilitating thus, the resolving power of the ATR-FTIR surface analysis method in discriminating structural material changes from the intraorally adsorbed species. The relative short period of intraoral aging and the high level of oral care, which was monitored during treatment, certainly contributed to the absence of matured integuments from the surface of the retrieved appliances. Selection of the outer buccal appliance surfaces for analysis was preferred over the inner surfaces facing the teeth, since the former are directly exposed to the oral environment and tensile force trajectories.

The lack of differences among the chemical groups between the two testing conditions (reference/intraorally aged) comply with previous results that confirmed no residual monomers and/or byproducts release in artificial saliva (13). Nevertheless, similar spectra may not imply the same composition in polymers, since the degree of polymerization (i.e. the number of the repeated monomers units in the polymer chain) may vary.

Retrieval analysis obtains critical information as it tests the material in its intended environment (14). However, testing the mechanical properties of intraorally aged Invisalign structures is impossible

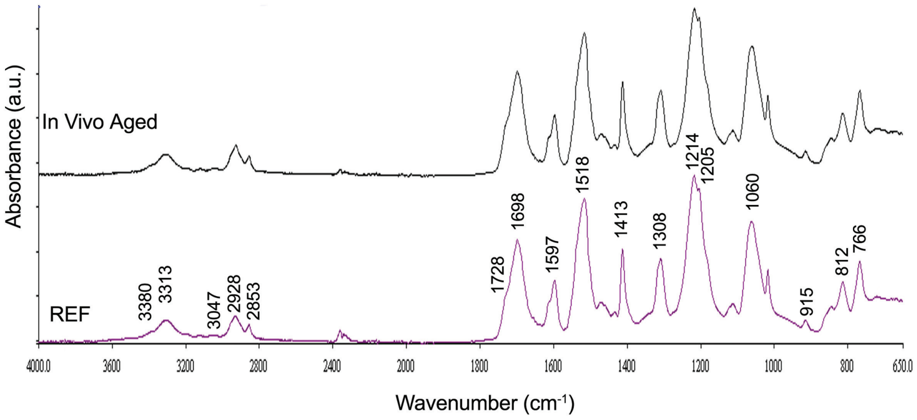

Figure 1. ATR-FTIR spectra of intraorally aged and reference appliances.

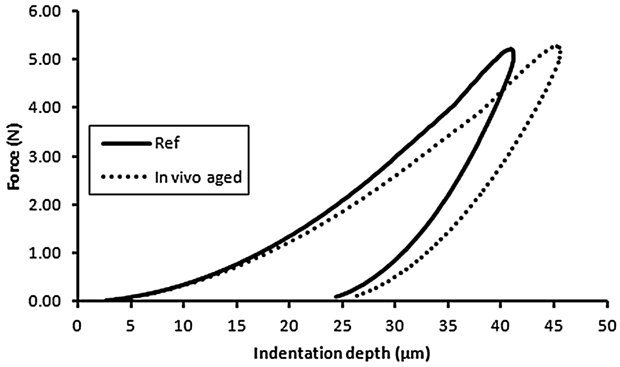

Figure 2. Representative force-indentation depth curves for the reference and intraorally aged groups.

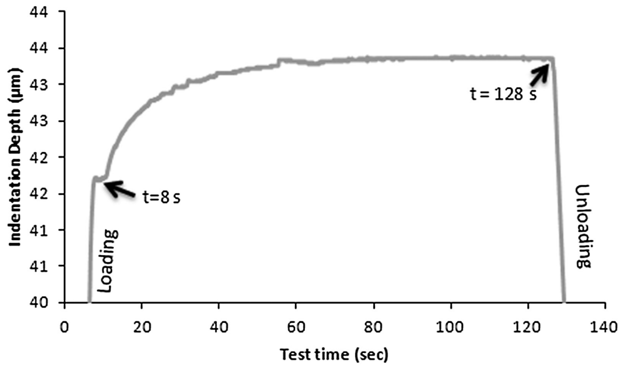

Figure 3. Representative indentation creep curve showing the indentation depth as a function of the test time. The constant load results in increasing indentation depth.

Table 1. Mean values and standard deviations of indentation modulus E_{IT}, elastic index η_{IT} Martens hardness HM, and indentation creep C_{IT} for reference (REF) and intraorally aged (INV) groups. All properties demonstrated statistical significant differences between the two groups ($P < 0.05$).

Group	E_{IT} (MPa)	η_{IT} (%)	HM (N mm^{-2})	C_{IT} (%)
REF	2466 ± 20	40.0 ± 0.3	119 ± 1	3.7 ± 0.2
INV	2216 ± 168	41.5 ± 1.2	110 ± 6	4.0 ± 0.1
P value	**0.008**	**0.025**	**0.005**	**0.028**

Bold values of *P* denote statistical significance.

with the conventional mechanical tests (i.e. tensile, bending, compression, and others) as bulky specimens with predefined dimension are required. This limitation is overwhelmed by IIT, where a simple hardness measurement is used to yield a variety of mechanical properties. This method has been already used to characterize the mechanical properties of thermoplastic orthodontic materials (10).

Based on the experimental outcome of this study, all the mechanical properties tested were adversely affected following intraoral aging. The values of indentation modulus (E_{IT}) were found within the range (1500–3000 MPa) reported for orthodontic thermoplastic aligners (10). From a mechanical standpoint of view, the decrease of modulus implies attenuation of the force delivery capacity by the appliance during intraoral use. The increased elastic index value (η_{IT}) implies that the aged material has been moved towards a more brittle behaviour, while the decrease in HM indicates a less wear resistant material. Martens hardness was selected against traditional Vickers hardness in order to eliminate the material rebound effect around the indentation, as documented with traditional hardness measurements, providing thus values independent of the indentation size effect (16). The results of creep measurements (C_{IT}) clearly showed that under constant forces developed by opposite dentition, the deformation of the intraorally aged material increased, weakening thus the orthodontic forces exerted.

The deterioration in the mechanical properties tested, as documented in the intraorally aged Invisalign appliances, is typical of the polyurethane softening mechanism. This mechanism has been assigned to the two-phase microstructure of thermoplastic polyurethanes, which are characterized as randomly segmented copolymers consisting of hard and soft segments (17). The soft segments create amorphous regions, whereas the hard segments, composed of polar molecules forming hydrogen bonds, tend to aggregate into ordered domains. The softening mechanism has been associated with the orientation of hard domains perpendicularly to the applied stress and for cases of high strains, with fragmentation into smaller pieces to accommodate further strain (17). The ATR-FTIR analysis, though, failed to probe differences in the H-bonding status of the C=O groups (~1728 cm^{-1}), which were identical in the reference and intraorally aged groups.

The degradation of the mechanical properties can be also related to relaxation of residual stresses developed during the manufacturing procedure or leaching of plasticizers during intraoral exposure. However, the later was not confirmed by ATR-FTIR analysis possibly due to the low concentration of the plasticizer.

From a clinical standpoint, the results of this study indicate that the exerted orthodontic forces are decayed during treatment, but there is no evidence yet that the extent of mechanical degradation could have a direct impact on the efficiency of tooth movement. Clinical studies assessing this parameter, during initial and subsequent treatment stages, might provide information about the potential necessity of shortening the time of individual appliance wear, should the decrease in the mechanical properties of the aligners as indicated in this study, is linked to effects on treatment parameters.

The limitations of the study relate to the design which selected the aligners of a good oral hygiene patient for analysis and thus no inference to the bad oral hygiene patients is possible; and the lack of information of actual clinical impact of the reduction in some mechanical properties on the clinical performance of the aligners.

Conclusions

1. Intraoral aging does not change the molecular composition of Invisalign aligners.
2. The mechanical properties of Invisalign appliance deteriorate during orthodontic treatment, however, the actual impact of these changes on the clinical performance of these appliances remains to be demonstrated in clinical trials.

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