Evaluation of In-Vivo Aging of 3D printed Orthodontic Aligners

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***Abstract*—Clear aligner therapy has revolutionized orthodontics, offering aesthetic and patient-friendly treatment options. While traditional vacuum thermoforming methods are widely used, direct 3D printing offers a promising alternative. This study proposes a novel, integrated measurement approach to evaluate the chemical stability of 3D-printed aligners fabricated using Tera Harz TC-85 resin after exposure to the oral environment. Combining Raman spectroscopy, X-ray diffraction (XRD), and optical microscopy, this study investigates morphological and chemical changes in the material after 7 and 14 days of in-vivo oral exposure. Raman spectroscopy analysis revealed remarkable chemical stability, with no significant compositional changes observed after two weeks of exposure. Characteristic peaks of polyurethane-based materials were identified, confirming material homogeneity across measurement points. Furthermore, Principal Component Analysis (PCA) of the Raman spectroscopy data revealed no significant spectral variations over time. The stability of the material's crystalline structure, verified by XRD, further supports the resilience of 3D-printed aligners under intraoral conditions. However, optical microscopic analysis revealed localized surface wear, suggesting potential alterations in mechanical properties over time. Wear patterns correlated with masticatory forces, emphasizing patient-specific variations. This measurement campaign solidifies direct 3D printing as a reliable aligner production method, and provides valuable insights into the long-term behavior of this kind of aligners, paving the way for optimizing their design and manufacturing for enhanced clinical outcomes.**

***Index Terms*—Raman spectroscopy, 3D Printing, Orthodontic Aligners, Material Characterization.**

I. Introduction

In recent years, an increasing number of patients have preferred aesthetic and comfortable orthodontic treatments as an alternative to conventional fixed braces. Clear aligners have revolutionized orthodontic treatment by offering an aesthetically driven and patient-centered modality. Unlike traditional braces, clear aligners provide effective treatment for mild to moderate malocclusions with minimal impact on patients' quality of life. This increasing demand led to technological advancements in biomaterials, Computer-Aided Design (CAD), and Computer-Aided Manufacturing (CAM), fostering the spread of Clear Aligner Therapy (CAT) as a promising orthodontic solution. CAT typically involves the sequential use of transparent aligners that perfectly fit over the dentination, worn continuously except during meals and oral hygiene routines. Aligners are usually replaced every 1–2 weeks to achieve desired orthodontic movements [1]. The most common manufacturing process for clear aligners is vacuum thermoforming. Among them some of the most popular are the Invisalign® clear aligner system, which utilizes SmartTrack™ (LD30), a multilayer aromatic thermoplastic polyurethane/copolyester for its aligners; and Exceed30 a polymer made of polyurethane methylene diphenyl diisocyanate. The manufacturing process involves 3D scanning of a patient's teeth, digital treatment planning, 3D printing of models, and finally, vacuum thermoforming of the aligners over these models [2]. Recent advancements have introduced direct 3D printing techniques for clear aligner fabrication [3]. However, these innovations necessitate the development of novel materials with specific mechanical, optical, thermal, and chemical properties suitable for intraoral use. Tera Harz TC-85 (Graphy, Seoul, South Korea) is currently the only CE Class IIa-certified resin approved for commercial aligner production using direct 3D printing to overcome the limitations of existing thermoforming [4]–[6].

While this innovative material can simplify the manufacturing process, its long-term clinical behavior and the related degradation mechanisms are still underexplored.

Thus, this study aims to investigate the in-vivo degradation of 3D printed aligners produced with Tera Harz TC-85—a CE Class IIa-certified resin applying a multi-analytical measurement approach. In particular, the paper investigate the chemical composition, crystallinity, and surface morphology after intraoral exposure.

A. Background

The process of direct 3D printing eliminates the need for intermediary physical models, employed in thermoformed

aligners. It offers several advantages over conventional thermoforming, including reduced manufacturing time, improved patient fit, and a simpler workflow, reducing errors associated with analog impressions, leading to a more environmentally friendly production process with reduced waste and lower costs [7].

An ideal clear aligner material must exhibit excellent biocompatibility and possess optimal mechanical, optical, thermal, and chemical properties. While the clinical performance of thermoformed aligners is well-documented, data on the long-term clinical outcomes of 3D-printed aligners remains limited. Indeed, 3D printed aligners, while a revolutionary solution in orthodontics, can be susceptible to progressive degradation when exposed to the oral environment. Interactions with substances present in saliva, food, and beverages induce chemical and physical alterations in the polymeric material, compromising its mechanical properties and promoting deformation. These alterations can lead to reduced orthodontic treatment efficacy, increased risk of breakage, and the formation of bacterial biofilm, with potential implications for oral health.

Understanding the mechanisms of aligner degradation is crucial for the development of new materials and clinical protocols that can mitigate these effects and ensure the maximum efficacy of orthodontic treatments. Rigorous in-vitro and in-vivo evaluations are crucial to assess the safety and long-term performance of these materials.

The existing scientific evidence on Tera Harz TC-85 3D printed aligners is focused on the study of several properties, such as their dimensional accuracy and thickness [4], [8], [9], the mechanical properties [8], [10], [11] and the cytotoxicity [8], [12]. In addition, some studies have been performed to evaluate the degree of conversion on the Tera Harz TC-85 polymer [8], [13] and the impact of UV light during printing [8], [14]. Notwithstanding, the majority of these studies are focused on in-vitro testing, and the effect of intraoral exposure on the properties of 3D-printed materials is still largely unexplored. Some in-vivo studies have been performed to investigate the thickness of the 3D printed materials [15], the effect of intraoral aging on the mechanical properties [16], or the surface properties of the aligners, such as roughness and porosity [17], but the long-term clinical behavior of 3D-printed aligners remains largely unexplored.

B. The proposed measurement approach

There is a need for a methodological approach that can systematically characterize 3D printed material and their stability after clinical application. Non-destructive spectroscopic techniques offer a powerful tool for analyzing the chemical and structural properties of materials across various fields, including industry, food, medicine, cultural heritage, and dentistry [18]–[26].

Among these, Raman spectroscopy proved its capability of tracking molecular changes [22], while, X-ray diffraction (XRD) can be used to assess the crystalline structure of polymers [26], and optical microscopy can help assess the morphological properties of the surface.

Therefore, this in-vivo study proposes a multi-analytical measurement approach that combines Raman Spectroscopy, X-ray diffraction, and Optical Microscopy) to provide a comprehensive characterization of the material properties of Tera Harz TC-85 3D printed aligners. This includes the study of elemental composition, chemical and molecular stability, and crystallinity, providing valuable insights into their degradation mechanisms related to the exposure to oral environments. In particular, the study has been performed on a set of Tera Harz TC-85 3D-printed aligners. The aligners are characterized before and after exposure to the oral environment for 7 and 14 days (with an average daily exposure of 20-22 h, and removed only due to food ingestion), to simulate typical clinical conditions.

II. Materials and Methods

Ten patients undergoing orthodontic treatment with clear aligners fabricated via direct 3D printing using Tera Harz TC-85 resin (Graphy, Seoul, South Korea) were enrolled in this study conducted at the Orthodontics Department of the Dental School, University of Turin. Inclusion criteria were: age ≥ 18 years, periodontal pocket depth ≤ 4 mm, plaque index $< 15\%$, absent or reduced tooth mobility, stable and persistent occlusal trauma, absence of caries, and patient motivation. Each patient wore an aligner for 7 days (t_1) and then 14 days (t_2), for a total of 20 aligners. Raman spectroscopy analyses were initially conducted on a sample of unworn aligners (t_0, n=3 Tera Harz TC-85) to verify homogeneity in the composition of the aligners. Subsequently, Raman and XRD analyses were conducted on aligners worn for 7 (t_1) and 14 (t_2) days. XRD was performed on the aligners at t_0, t_1, and t_2 to assess their crystalline structure. Optical microscopy was employed to evaluate any morphological changes at t_0, t_1, and t_2.

A. Raman spectroscopy (RS)

Raman spectroscopy was employed to identify the material's chemical composition and detect any alterations induced by oral exposure, such as the presence of foreign substances or polymer degradation. Raman analysis was performed using a portable BWTeK Raman spectrometer equipped with a 785 nm laser and a BAC151 Raman microscope. Measurements were acquired on the aligner's surface with a $\sim$50 μm spot size. The emitted signal was collected by a BTC675N® spectrometer, in the range between 65 cm^{-1} and 3350 cm^{-1} , with a resolution of 6 cm^{-1} . Measurements were performed directly on the sample surface. The measurements were carried out using the following parameters: laser power of 20 mW, integration time of 10 s, and 16 repetitions for each area. The Raman analysis involved the outermost layer of the material, on three positions of each aligner: the working cusp of the first right molar (p1), working cusp of the first left molar (p2), and incisal edge of the central incisor (p3). The analysis of three different surfaces allowed for evaluation in areas subjected to different levels of mechanical stress. Raman spectra were collected before (t_0)

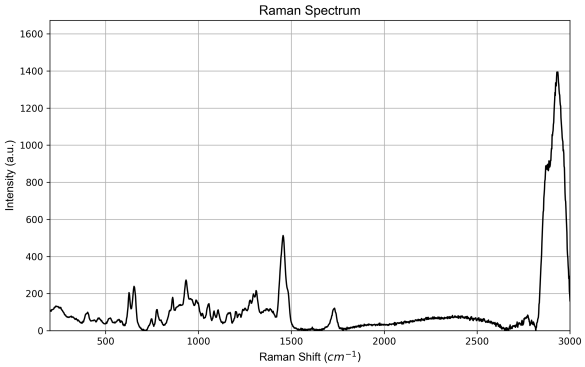

Fig. 1: Representation Raman spectrum at t_0 of Tera Harz TC-85 aligner.

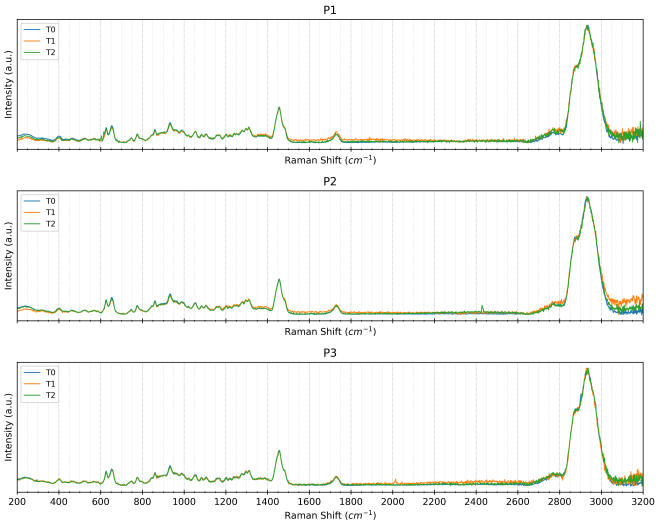

Fig. 2: Representative Raman spectra at p1, p2 and p3 of Tera Harz TC-85 aligners at t_0 in blu, t_1 in orange and, t_2 in green.

and after the oral exposure or 7 (t_1) and 14 (t_2) days, for all the samples.

The spectra were analyzed after baseline correction to remove background signals. Subsequently, the most prominent peaks (Fig. 1) were examined, and their association with various functional groups was determined through a literature review [24], [27].

The acquired Raman spectra were processed using Principal Component Analysis (PCA) by means of a Python script. The pre-processing involved the following steps: the region between 500 cm^{-1} and 2000 cm^{-1} was selected; the baseline was removed by asymmetric least square smoothing; the Savitzky-Golay filter was applied using a window length of 15 cm^{-1} and first-derivative spectra were obtained; Standard Normal Variate Transformation was performed; and the Principal Components were computed.

B. X-ray diffraction (XRD)

XRD was employed to collect information about the crystalline structure and phase composition of the investigated materials. The analysis were performed at t_0, t_1, and t_2 using the PANalytical X'Pert PRO diffractometer. The generator settings were configured at 40 mA and 40 kV, with a scanning range of 10° to 70°. Phase identification and changing in the crystalline structures was carried out using HighScore Plus software.

C. Optical Microscopy (OM)

The Zeiss Stereo Discovery V12 microscope was used to examine the aligners' surface and images were obtained using the Axiocam 208 color (Carl Zeiss Microscopy GmbH, Jena, Germany) with magnification: 20X, 40X, 60X. Microscopic images of the aligners were collected at t_0, t_1, and t_2. The surfaces of the aligners at positions p1, p2, and p3 were evaluated under varying magnifications, enabling a detailed visual analysis of the aligner surfaces before and after oral exposure. This approach facilitated the assessment of potential damage caused by use.

III. Results

Fig. 1 shows a representative indexed Raman spectrum acquired at t_0 on the aligners. The identified peaks correspond to those typically associated with polyurethane-based materials, as reported in several studies [6], [28]. The following key Raman bands were identified: the aromatic ring Ph-C-H in-plane H bend at 626 cm^{-1}; the C=C bonds at 655 cm^{-1} and 746 cm^{-1}; the C-C stretching (ring breathing) and C-O stretching at 861 cm^{-1}; the ether group C-O-C at 1106 cm^{-1} band; the 1279 cm^{-1} band corresponds to C-N stretching and N-H bending in amide III; the methylene groups CH_2 bands at 1455 cm^{-1}; the urethane group δ(CH), urethane amide III, with bands at 1310 cm^{-1}, and the ester ν(C=O), urethane amide I ν(C=O) at 1730 cm^{-1}; and the CH_2 stretching, at 2929 cm^{-1} [29], [30]. To evaluate the uniformity of the material across different regions, the Raman spectra at points p1, p2, and p3 acquired at t_0 (before the exposure to the intraoral environment) were compared (Fig. 2). No significant differences were observed, i.e., no peak shifting or shifts, broadening, or intensity changes in peaks, suggesting that the material exhibits chemical uniformity across all points of interest and throughout the examined sample.

Analogous results are obtained in the spectra acquired after exposure to the oral environment for each sample at t_1 and at t_2 (Fig. 2) in all the investigated areas (p1, p2, and p3). PCA was performed on the data obtained from the Raman spectroscopy study to highlight any differences due to oral exposure. The scores are presented in Fig. 3. Specifically, where different colors were assigned to the datasets corresponding to t_0, t_1, and t_2.

From the PC1-PC2, PC1-PC3, and PC2-PC3 plots, it is evident that the measurements do not form distinct clusters. This indicates that no significant changes in the spectra were observed, even after exposure to the oral cavity. Indeed, the

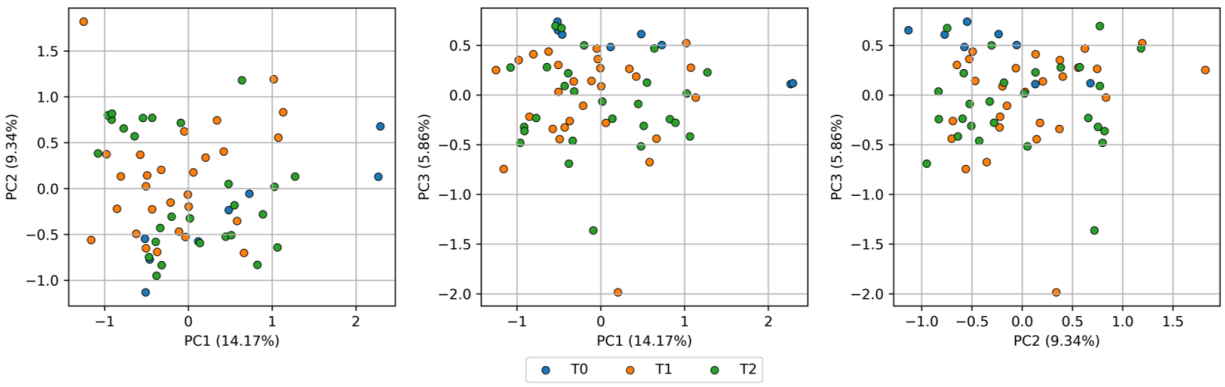

Fig. 3: Score plots of the first three components (PC1-PC2, PC1-PC3 and PC2-PC3) calculated from Raman spectra. Statistical model on all patients. The percent variance acquired by each PC is shown in the parentheses along each axis.

spectra exhibit no noticeable differences in terms of peak position, width, shape, or intensity.

The result of the XRD analysis of the aligners performed at t_0, t_1, and t_2 is shown in Fig. 4. The diffractograms show a broad peak at 2θ angles around 16° and 40°, which indicate an amorphous structure of the material. The results revealed similar diffraction patterns before and after intraoral use (t_0 , t_1 , and t_2). This suggests that the crystalline structure of the aligner materials remained consistent throughout the exposure period as shown in Fig. 4. The diffractograms acquired at t_1, and t_2 show sharp peaks at about 29°, 35°, 39°, 43°, 47°, 48°, 57°, 64°, and 65°, which can be assigned at calcium carbonate (ICDD database, reference 00-005-0586). Deposits of calcium carbonate on the surface of the aligners can be due to the exposure to the oral environment, and in particular to localised calcification processes of the biofilm, as reported in [24], [31], [32] and which may be due to the exposure to the oral environment, in particular the saliva. Regarding

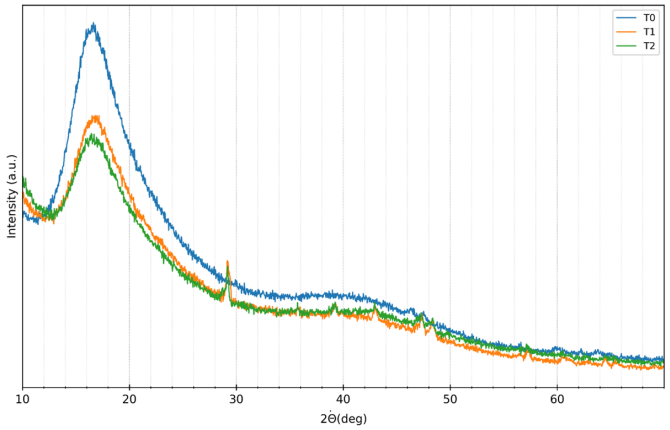

Fig. 4: Representative XRD diffractogram of a Tera Harz TC-85 aligner (at t_0 in blu, t_1 in orange and, t_2 in green).

optical microscopy, different positions on the aligner exhibited varying degrees of wear. This was attributed to the intensity and distribution of masticatory forces, which vary depending on the position analyzed and individual patient variability. An example of the images captured at positions p1, p2, and p3 during the different periods (t_0, t_1, and t_2), is presented in Fig. 5. This analysis underscores the importance of correlating wear patterns with masticatory dynamics to improve aligner durability and patient-specific treatment outcomes.

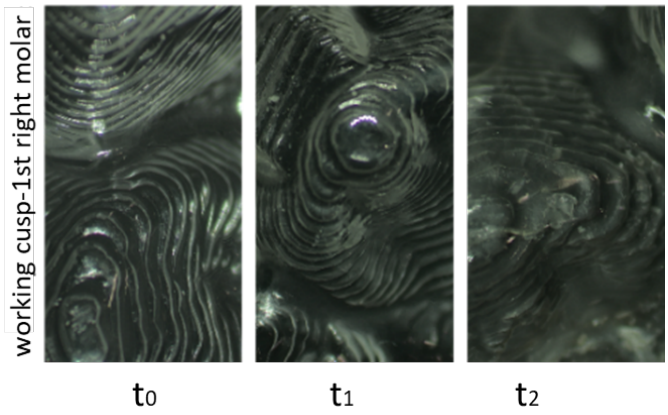

Fig. 5: Representative optical microscope images (Magnification: 20X) representing the surface of a Tera Harz TC-85 aligner at t_0, t_1, and t_2 at point p1.

IV. Discussion

The results obtained demonstrate a good homogeneity of the material constituting the aligners, as confirmed by Raman spectroscopy analyses. The absence of significant variations in chemical composition in different regions of the aligners, both before and after oral exposure, suggests a remarkable stability of the material. The absence of significant variations in the XRD diffraction pattern further confirms the stability of the material's crystalline structure at different time points. However, optical microscopy analysis revealed different surface wear in the three examined positions, suggesting potential alterations in mechanical properties following clinical use.

These results indicate that while maintaining a uniform chemical composition, the aligners may undergo long-term surface deterioration, with potential implications for the duration of orthodontic treatment. Further studies are needed to correlate the observed surface modifications with the mechanical properties and to assess their clinical impact.

V. Conclusions

This integrated measurement approach effectively evaluated the chemical stability of directly Tera Harz TC-85 3D-printed orthodontic aligners subjected to exposure to the oral environment. Raman spectroscopy results demonstrated excellent chemical stability of the material, with no significant compositional changes observed after two weeks of use. However, it is important to note that chemical stability does not preclude the possibility of alterations at the surface level or in mechanical properties, which could affect the long-term clinical performance of the aligners. Further studies, focused on the mechanical properties and durability of the aligners, are therefore necessary to provide a comprehensive understanding of their clinical performance. The preliminary results obtained in this study contribute to solidifying the position of direct 3D printing as a reliable production method for orthodontic aligners, opening up new perspectives for the development of increasingly personalized and effective materials and treatment protocols. Future research will focus on evaluating mechanical property changes during oral exposure and assessing the potential release of microplastics, ensuring both durability and patient safety.

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