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Physiochemical and mechanical characterisation of orthodontic 3D printed aligner material made of shape memory polymers (4D aligner material)

Islam Atta [a], Christoph Bourauel [a], Yasmine Alkabani [b], Nesreen Mohamed [c], Hoon Kim [d], Abdulaziz Alhotan [e], Ahmed Ghoneima [f], Tarek Elshazly [a,f,*]

[a] Oral Technology, Dental School, University Hospital Bonn, Bonn, Germany
[b] Restorative and Dental Materials Department, National Research Centre, Giza, Egypt
[c] Faculty of Dentistry, Charite University, Berlin, Germany
[d] Research Institute of Agriculture and Life Sciences, College of Agriculture and Life Sciences, Seoul National University, Seoul, Republic of Korea
[e] Department of Dental Health, College of Applied Medical Sciences, King Saud University, Riyadh, Saudi Arabia
[f] Department of Orthodontics and Pediatric Dentistry, Hamdan Bin Mohammed College of Dental Medicine (HBMCDM), Mohammed Bin Rashid University of Medicine and Health Sciences (MBRU), Dubai, United Arab Emirates

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ABSTRACT

Objectives: To conduct a physiochemical and mechanical material analysis on 3D printed shape-memory aligners in comparison to thermoformed aligners.
Materials and methods: Four materials were examined, including three thermoformed materials: CA Pro (CP), Zendura A (ZA), Zendura FLX (ZF), and one 3D printed material: Tera Harz (TC-85). Rectangular strips measuring 50 × 10 × 0.5 mm were produced from each material. Five tests were conducted, including differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), shape recovery tests, three-points bending (3 PB), and Vickers surface microhardness (VH).
Results: DSC recorded glass transition temperatures (Tg) at 79.9 °C for CP, 92.2 °C for ZA, 107.1 °C for ZF, and 42.3 °C for TC-85. In DMA analysis at 20–45 °C, a prominent decrease in storage modulus was observed, exclusively for TC-85, as the temperature increased. Notably, within the temperature range of 30–45 °C, TC-85 exhibited substantial shape recovery after 10 min, reaching up to 86.1 %, while thermoformed materials showed minimal recovery (1.5–2.9 %). In 3 PB test (at 30, 37, 45 °C), ZA demonstrated the highest force at 2 mm bending, while TC-85 exhibited the lowest. Regarding VH at room temperature, there was a significant decrease for both ZA and ZF after thermoforming. ZA had the highest hardness, followed by ZF and TC-85, with CP showing the lowest values.
Conclusions: TC-85 demonstrates exceptional shape memory at oral temperature, improving adaptation, reducing force decay, and enabling, together with its higher flexibility, extensive tooth movement per step. Additionally, it maintains microhardness similar to thermoformed sheets, ensuring the durability and effectiveness of dental aligners.
Clinical relevance: The 3D printed aligner material with shape memory characteristics (4D aligner) has revolutionized the orthodontic aligner field. It showed mechanical properties more suitable for orthodontic treatment than thermoforming materials. Additionally, it offers enhanced control over aligner design and thickness, while optimizing the overall workflow. It also minimizes material wastage, and reduces production expenses.

1. Introduction

Invisible aligners have become increasingly a popular alternative to fixed orthodontic devices. Patients find them more appealing due to their aesthetically clear appearance. Moreover, their removability contributes to maintaining improved oral hygiene standards (Ashari and Mohamed, 2016). Furthermore, they require fewer dental appointments, saving both time and money for clinicians and patients. Technically, they are also easier to manage in everyday practice compared to fixed appliances (Yassir et al., 2022). Clear aligner treatment is defined

* Corresponding author. Oral Technology, Dental School, University Hospital Bonn, Welschnonnenstr. 17, 53111, Bonn, Germany.
E-mail address: elshazly@uni-bonn.de (T. Elshazly).

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by a gradual incremental correction of tooth malalignment. Typically, each aligner has a limited step size and can achieve tooth movements of only 0.2–0.3 mm for translations and 1°–3° for rotations per tooth. Patients are instructed to wear each aligner in the series for at least 20 h daily within a specified intervals of 10–14 days, before switching to a new aligner (Moutawakil et al., 2021; Tamer et al., 2019).

The clinical efficacy of clear aligners can be affected by a multitude of factors (Yassir et al., 2022; Upadhyay and Arqub, 2022). The properties of aligner materials remain one of the most essential aspects in determining their mechanical and clinical features (Cremonini et al., 2022; Momtaz, 2016). Conventional thermoformed aligners are made of a single layer of plastic sheets made of either polyvinyl (PV), polyvinyl chloride (PVC), polyethylene terephthalate glycol (PETG), polypropylene (PP), polystyrene (PS), or polyurethane (PU) (Cremonini et al., 2022; Thukral and Gupta, 2015; Martorelli et al., 2013; Elshazly et al., 2021). More recently, multi-layer hybrid materials have been developed to address the limitations of single-layer materials. These hybrid materials consist of a combination of tough outer shells and a softer inner layer, resulting in enhanced mechanical properties as well as more patient comfort (Lombardo et al., 2016).

The conventional manufacturing process through thermoforming was observed to have an adverse impact on the mechanical properties of aligner materials (Golkhani et al., 2022; Dalaie et al., 2021). Hence, as an alternative approach, direct 3D printing of aligners has been introduced recently (Koenig et al., 2022; Shivapuja et al.; Lee et al., 2022; Jindal et al., 2019). The 3D printing process eliminates the cumulative errors caused by the conventional thermoforming workflow (Tartaglia et al., 2021). Additionally, 3D printing offers enhanced precision, increased control over aligner design and thickness (Elshazly et al., 2022a; Jindal et al., 2020), reduced supply chain complexity, diminished material wastage, as well as lower production costs (Elshazly et al., 2021, 2022b; Jindal et al., 2020; Peeters et al., 2019).

The limited tooth movement per each single aligner splint results in an increase of the number of splints per treatment. This escalation not only amplifies the financial burden per treatment, but also significantly increases plastic consumption, which is a matter of environmental concern (Elshazly et al., 2022b). Additionally, a greater quantity of aligner splints per treatment introduces an elevated risk of divergence between the intended treatment plan and the actual clinical results (Upadhyay and Arqub, 2022). In order to address these challenges and enhance the adaptability of aligners in oral conditions, the integration of smart materials, such as shape memory polymers (SMPs), was proposed (Elshazly et al., 2021, 2022b; Lee et al., 2022).

SMPs are dynamic polymers which can undergo a change in their macroscopic configuration when subjected to specific stimuli. These materials effectively can maintain a temporary shape until they are exposed to a proper stimulus, at which they promptly return to their original form (Meng and Li, 2013; Lendlein and Kelch, 2002). The shape memory mechanism of SMPs has two key associations, first is the presence of a stable polymer network that determines the initial shape of the material, and second is a reversible polymer network that allows the material to transform into a temporary shape (Elshazly et al., 2022b; Meng and Li, 2013). SMPs possess the ability to attain higher strain levels and can adopt multiple temporary shapes. This distinctive feature is attributed to the presence of multiple phases within the material, each phase is characterized by a different shape recovery temperature (Liu et al., 2007).

To the best of our knowledge, a comprehensive overview of the material properties of aligners made from either shape memory polymers, 3D printed resin or the 3D printed shape memory resin (referred to as 4D aligners) is still lacking in the literature. In this context, the primary objective of this study is to present data derived from the physiochemical and mechanical analysis of 3D printed shape-memory aligners (4D aligners) in comparison to thermoformed aligners.

2. Materials and Methods

2.1. Materials

Four materials were investigated in the current study, three of them are thermoformed materials; namely CA Pro (CP), Zendura A (ZA), Zendura FLX (ZF), and one is a 3D printed material; namely Graphy Tera Harz TC-85 (TC-85) (Table 1).

2.2. Specimens preparation

Thermoplastic sheets of the three materials (CP, ZA, ZF) underwent a thermoforming process using a Biostar thermoforming device (Scheu-Dental GmbH, Iserlohn, Germany), following the manufacturer's guidelines outlined in Table 1. This thermoforming process resulted in the sheets thinning from 0.75 mm to approximately 0.6 mm (Golkhani et al., 2022), reassured with a digital caliper (Fisher Scientific International Inc., Hampton, NH, USA) and the resulting specimens were then cut into rectangular strips measuring 50 × 10 × 0.6 mm using scissors. The edges of these specimens were refined using a polishing machine (Fig. 1). On the other hand, TC-85 specimens were directly 3D printed in strip rectangular form with dimensions of 50 × 10 × 0.6 mm, as showed in the 3D model in Fig. 1.

2.3. Testing

2.3.1. Differential scanning calorimetry (DSC)

Thermal analyses were executed utilizing a differential scanning calorimeter (STARe SW Mettler Toledo V16.10; Greifensee, Switzerland). Each specimen was exposed to two heating cycles to 240 °C and one cooling cycle to −40 °C, with a cooling/heating rate 10 °C/min. The analyses were performed under nitrogen atmosphere. The glass transition temperature (Tg) was ascertained by identifying the midpoint in the second heating cycle (Fig. 2, and Supplements 1–3). Two specimens (n = 2) were tested for each material, and the average Tg value was subsequently calculated.

2.3.2. Dynamic mechanical analysis (DMA)

Three specimens per material (n = 3) were prepared for DMA. The test was done using a dynamic mechanical analyzer (DMA Q800; TA Instruments, New Castle, USA) with frequency 0–100 Hz and strain rate 0.1 % in stress relaxation mode, at temperatures 20, 25, 30, 35, 40, and 45 °C.

2.3.3. Shape recovery test

Shape recovery assessment was conducted at three distinct temperatures: 30 °C, 37 °C, and 45 °C. For each material, a total of 18 specimens were prepared, with 6 specimens designated for each recovery temperature (n = 6). The specimens underwent a specific process, in which they were initially softened by heating in boiling water at 100 °C, then bent to 180°. Subsequently, the specimens were rapidly cooled in cold water for 1 min to gain hardness while maintaining the deformed bent shape. These specimens were then refrigerated at 4 °C for 1 h to preserve their temporary shape until testing. To assess the extent of shape recovery within an oral environment, each specimen was immersed in a water bath for 10 min at 30 °C, 37 °C, and 45 °C. The ImageJ software (National Institutes of Health, Maryland, USA) was employed to measure both the initial bending angle (θ initial) and the subsequent recovery angle (θ final) (Fig. 3). Subsequently, the shape recovery percentage was computed using the following equation:

$$\text{Shape Recovery } \% = \frac{\theta \text{ final}}{\theta \text{ initial}} \times 100$$

2.3.4. Three-point bending test (3 PB)

A custom-made mechanical setup (Orthodontic measurement and

Table 1
Data on the investigated aligner materials, specifying the manufacturer, thickness of the sheets, thermoforming or 3D printing conditions, and the material composition (Manufacturers' data).

Name	Manufacturer	Thermoforming Code/Thickness	Thermoforming/3D Printing Conditions	Material Composition
CA® Pro (CP)	Scheu-Dental (Iserlohn, Germany)	Code (112)/0.75 mm	Thermoforming: Heating for 25 s at 220 °C, and pressure-forming at 4.8 bar, then cooling for 60 s	Three-layer sheet of a soft thermoplastic elastomeric layer between two hard layers of co-polyester
Zendura A™ (ZA)	Bay Materials (Fremont, USA)	Code (162)/0.75 mm	Thermoforming: Heating for 50 s at 220 °C, and pressure-forming at 4.8 bar, then cooling for 60 s	Single-layer sheet of thermoplastic polyurethane (TPU)
Zendura FLX™ (ZF)	Bay Materials (Fremont, USA)	Code (162)/0.75 mm	Thermoforming: Heating for 50 s at 220 °C, and pressure-forming at 4.8 bar, then cooling for 60 s	Three-layer sheet of a middle thermoplastic soft elastomeric TPU layer and two hard layers of co-polyester
Tera Harz TC-85[1] **(TC-85)**	Graphy (Seoul, South Korea)	N/A /0.6 mm	3D printing was done using a DLP-type 3D printer (Uniz NBEE; Uniz, CA, USA) (layer thickness of 100 μ), followed by UV light photo-curing (wavelength: 405 nm) under N_2 conditions for 25 min using a special post-curing device (Tera Harz Cure; Graphy, South Korea)	Urethane acrylate oligomer with acrylic monomers

[1] TC-85 is a CE, FDA, and KFDA Certified material.

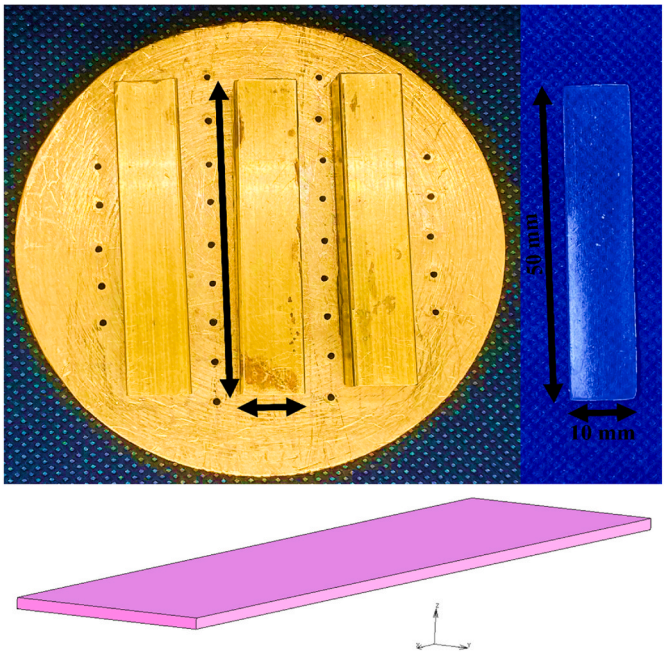

Fig. 1. A custom–made metal mold used for thermoforming of aligners sheets to produce test specimens in specific dimensions (Upper left), a test specimen in the form of rectangular strip (50 × 10 × 0.6 mm) (Upper right), a 3D model used for the 3D printing of strips made from TC-85 aligner material with the following dimensions: X = 50 mm, Y = 10 mm, Z = 0.6 mm (Lower).

simulation system, OMSS; Oral Technology, University Hospital Bonn, Bonn, Germany) (Bourauel et al., 1992) was employed to measure the maximum force when each specimen was deflected by 2 mm at a three point configuration with a span length of 24 mm. This mechanical setup was equipped with a temperature-controlled cabin, enabling the tests to be conducted at various temperatures, specifically 30 °C, 37 °C, and 45 °C. For each material, a total of 18 specimens were prepared, with 6 specimens designated for each recovery temperature (n = 6).

2.3.5. Surface microhardness

Surface microhardness was measured using a Vickers microhardness tester (Qness 60 M Evo; QATM, Mammelzen, Germany) at room temperature. To create indentations, a load of 1.96 N (200 g force) was applied for a duration of 10 s (HV 0.2). In each sample, five indentations were generated with a minimum separation of 50 μ between them. The mean Vickers hardness number (VHN) was then calculated for each sample. For the thermoformable sheets (CP, ZA, ZF), hardness tests were conducted on both the as-received material and after thermoforming, with a total of 12 samples for each material (6 specimens for each stage). In the case of TC-85, hardness testing was performed only after the post-curing process (n = 6).

2.4. Statistical analysis

Numerical data were represented as mean and standard deviation (SD) values. Shapiro-Wilk's test was used to test for normality. Surface hardness data were normally distributed and were analyzed using one-way ANOVA followed by Tukey's post hoc test. Other data were non-parametric and were analyzed using Kruskal-Wallis test followed by Dunn's post hoc test with Bonferroni correction. The significance level was set at $p < 0.05$ within all tests. Statistical analysis was performed with R statistical analysis software version 4.1.3 for Windows (R Foundation for Statistical Computing, Vienna, Austria).

3. Results

DSC analysis in the range from −40 °C to 240 °C showed Tg at 79.9 °C for CP, 92.2 °C for ZA, and 107.1 °C for ZF, while TC-85 showed a much lower Tg of 42.3 °C (Table 2). Furthermore, structural stability in TC-85 material was observed, which differs from the behavior in other thermoformable materials (Fig. 2, Supplements 1–3).

DMA was conducted within the temperature range of 20 °C–45 °C. The thermoformable materials (CP, ZA, ZF) showed minimal variations in storage modulus with increasing temperature or frequency. In contrast, TC-85 displayed a prominent decrease in the storage modulus as the temperature increased, together with an elevation of the storage modulus on increasing frequency. Additionally, the storage modulus was around 1000 MPa for CP, approximately 1500 MPa for ZA, and roughly 800 MPa for ZF. While, the storage modulus of TC-85 displayed considerable fluctuations in response to variations in both temperature and frequency, ranging from 100 MPa to as high as 3000 MPa (Fig. 4).

The shape recovery evaluation (at 30 °C, 37 °C, and 45 °C) pointed to negligible shape recovery characteristics (1.5 %–2.9 %) among the three thermoformed materials, namely CP, ZA, and ZF. On the opposite, the TC-85 material displayed 8.4 % recovery at 30 °C, which increased dramatically with higher temperatures reaching 54.9 % at 37 °C and 86.1 % at 45 °C (Table 3).

In the 3 PB test (at 30 °C, 37 °C, and 45 °C), the highest force measurements were observed for ZA at both 30 °C and 37 °C, while TC-85 consistently exhibited the lowest values across all temperatures. At 30 °C, there was no significant statistical difference between the ZF and CP groups, but at oral temperature (37 °C), the CP group displayed higher force values. At 45 °C, there was no significant statistical difference

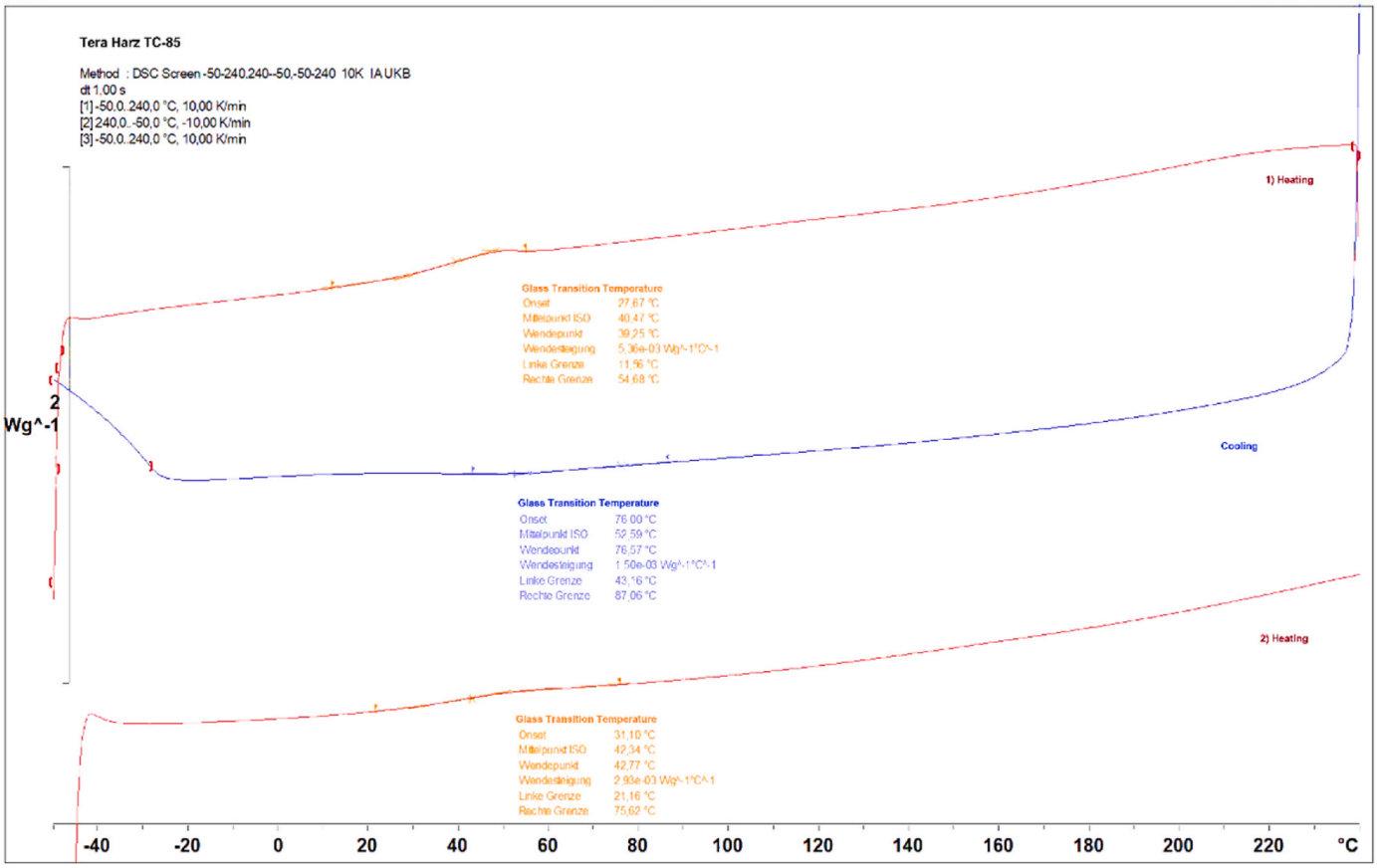

Fig. 2. Differential scanning calorimetry (DSC) graph for a 3D printed aligner material (Tera Harz TC-85).

among the three thermoformed materials (CP, ZA, ZF). As the temperature rises, CP maintains consistent force levels, in contrast to other materials that exhibit a decrease in force over time (Fig. 5).

Among the as-received thermoformable sheets, the highest Vickers microhardness values were recorded for ZA, followed by ZF, and then CP. A significant reduction in microhardness was observed after thermoforming in both ZA and ZF, whereas CP exhibited no change. TC-85 displayed hardness values that were comparable to the thermoformed ZF at room temperature (Table 4).

4. Discussion

Conventional manufacturing process of thermoformed aligners involves printing of dental models followed by thermoforming of plastic sheets. This process is accompanied with many geometric inaccuracies and irregularity of the thickness of the aligner (Elshazly et al., 2022a), leading to uncertainties in aligner performance and treatment outcomes (Park et al.; Min et al., 2010a). To address this drawback, a 3D printing procedure has been proposed (Tartaglia et al., 2021). Furthermore, an important concern associated with conventional aligners is their susceptibility to stress relaxation while being worn, which leads to a reduction in the applied force. This phenomenon typically occurs within a few hours of the aligner being inserted into the patient's mouth (Lombardo et al., 2016; Elshazly et al., 2023a; Chen et al., 2023; Vardimon et al., 2010). For such reasons, continuous advancements are undertaken to enhance orthodontic aligner effectiveness and patient experience, such as the utilization of shape memory polymers (SMPs) (Elshazly et al., 2021, 2022b; Lee et al., 2022). The unique long-term shape memory property enhances aligner's adaptation, facilitates its placement, and maintains consistent pressure by aligner on the teeth (Elshazly et al., 2021, 2022b). With that in mind, the aim of this research was to shed light on the physiochemical and mechanical properties of 3D printed shape-memory aligners as compared to thermoformed ones.

The DSC test is a thermo-analytical technique used to examine material structural behavior and phase changes at varying temperatures. It plays a crucial role in understanding the properties of polymers and is used to measure the glass transition temperature (Tg) (Schick, 2009). The Tg represents the temperature range at which a thermosetting polymer undergoes a transition from a glassy rigid state to a rubbery more flexible state. At temperatures higher than Tg, Van der Waals interactions are weakened, allowing movement of polymer chains (Zin et al., 2019).

Current DSC results revealed major differences between the investigated materials, where TC-85 exhibited a remarkably lower Tg of 42.3 °C, compared to CP, ZA, and ZF, whose Tg were 79.9 °C, 92.2 °C, and 107.1 °C respectively. This variation in Tg can be attributed to the composition of each material outlined in Table 1. The investigated thermoformed aligner materials (CP, ZA, ZF) are made up of PETG, TPU, or a hybrid multi-layer mixture of TPU and PETG, with different degrees of crystallinity which affect the properties of each aligner (Daniele et al., 2021). Multi-layered CP exhibits Tg within the typical range of PETG-based polymers (79.9 °C) and some TPU-based polymers (Iijima et al., 2015). Conversely, the heightened Tg observed in multi-layered ZF (107.1 °C) can be attributed to its increased crystallinity (Daniele et al., 2021), a characteristic that is also reflected in its higher hardness value recorded in the current study.

Moreover, PETG and TPU are high molecular weight copolymers that possess aromatic rings which lead to a strong pi-pi stacking interaction, and hence a high Tg (Hunter and Sanders, 1990). However, TC-85 is composed of an aliphatic vinyl ester–urethane polymer, with methacrylate functionalization, as revealed by a recent ATR-FTIR study (Can et al., 2022). The interactions between the aliphatic polymer chains, as

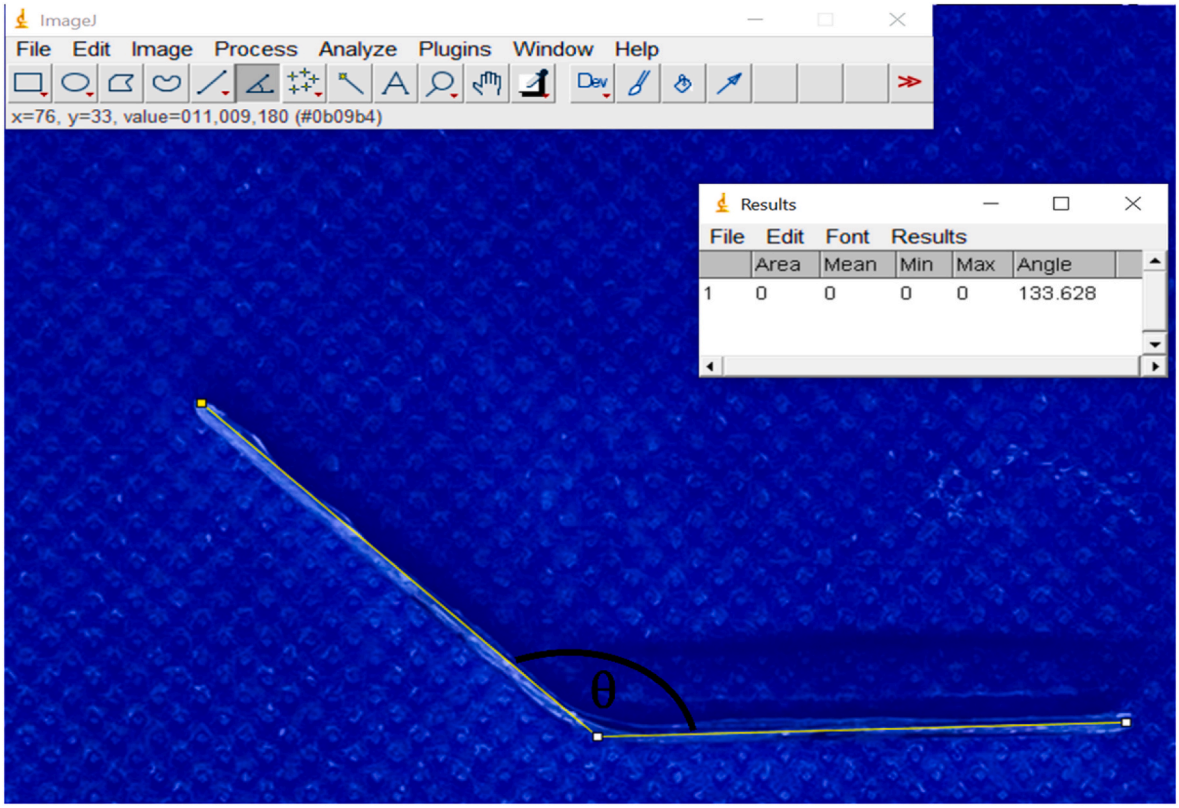

Fig. 3. Measurement of the initial angle (θ initial) and the recovery angle (θ final) of aligner material strips using ImageJ software in order to calculate the shape recovery percentage.

Table 2
Glass Transition Temperature (Tg) measured by differential scanning calorimetry (DSC) for different orthodontic aligner materials.

Material	CA Pro	Zendura A	Zendura FLX	TC-85
Tg (°C)	79.9	92.2	107.1	42.3

in TC-85, are comparatively weaker than those observed aromatic chains, as in PETG and TPU (Olabis, 2012). Consequently, TC-85 exhibits a lower Tg. It's also important to highlight that in the present study, the Tg is represented as the midpoint of the DSC curve, yet the actual shape memory behavior is observed from the initiation of the DSC curve. The DSC curve for TC-85 begins at 30.4 °C, which is below the typical oral temperature, providing clear evidence that TC-85 exhibits shape memory properties within the oral cavity.

Lee et al. (2022) reported Tg of TC-85 at 69.85 °C using DMA. This discrepancy arises because the two different applied techniques, DSC and DMA, assess various manifestations of the glass transition, whereas Tg recorded by DMA has higher values (Dalaie et al., 2021). DSC is primarily responsive to alterations in heat capacity, whereas DMA is attuned to a mechanical relaxation phenomenon and depends on the mechanical frequency executed by the test (Gracia-Fernández et al., 2010). Using DSC, Daniele et al. (2021) reported the Tg of 96.9 °C for ZF, which differs from our findings (107.1 °C). This disparity could be attributed to variations in the methodology employed to determine Tg from their DSC results. Also, in our study, Tg was determined by identifying the midpoint during the second heating cycle, whereas the midpoint during the cooling cycle was found to be 97.5 °C.

Furthermore, current DSC graphs revealed that TC-85 material maintains its structural stability at elevated temperatures, a characteristic may be attributed to its cross-linked structure. This behavior contrasts with that observed in other thermoformed materials, which undergo phase changes at higher temperatures. This can offer clinical advantages by enabling the disinfection or, more precisely, sterilization of the aligner both before and during its use. However, additional research is required to ensure that sterilization at elevated temperatures will not have an adverse impact on the aligner's performance.

DMA has proven to be an important tool for examining the behavior of polymer structures, exploring polymer relaxations, and understanding how polymers respond to various stress and temperature conditions. Below Tg, where the polymer is in a glassy state, the storage modulus, which is the ratio of viscous stress to strain, is usually high. At Tg, storage modulus decreases rapidly, where the polymer starts to shift to the rubbery state (Zin et al., 2019). In this context, the results of the ongoing DMA analysis may become clearer, particularly with regard to the significant discrepancies in storage modulus observed between 20 °C and 45 °C for the TC-85 material, whose Tg is 42.3 °C. For the thermoformed materials, storage modulus showed almost no changes since the temperature range lies way below their Tg as recorded by the DSC. Also, the increase in storage modulus with increasing frequency in TC-85 material indicates a gradual increase in static force during cyclic loads, this might offer clinical advantages since it can help minimize force decay and preserve the orthodontic force exerted by the aligners (Lee et al., 2022).

The shape memory mechanism in thermo-responsive SMPs relies on the presence of at least two structural phases: a stable network phase that defines the original shape and a reversible switching phase that establishes the temporary shape. Each of these phases possesses distinct chemical characteristics and exhibits different Tg. The shape recovery temperature is related to Tg of the reversible switching phase (Elshazly et al., 2021, 2022b). This aligns with the interpretation of the current DSC, DMA, and shape recovery outcomes. Shape recovery test is used to determine how much the material will retain its original form after exposure to a suitable thermal stimulus (Elshazly et al., 2021; Lee et al., 2022). The TC-85 material showed low recovery of 8.4 % at 30 °C, which

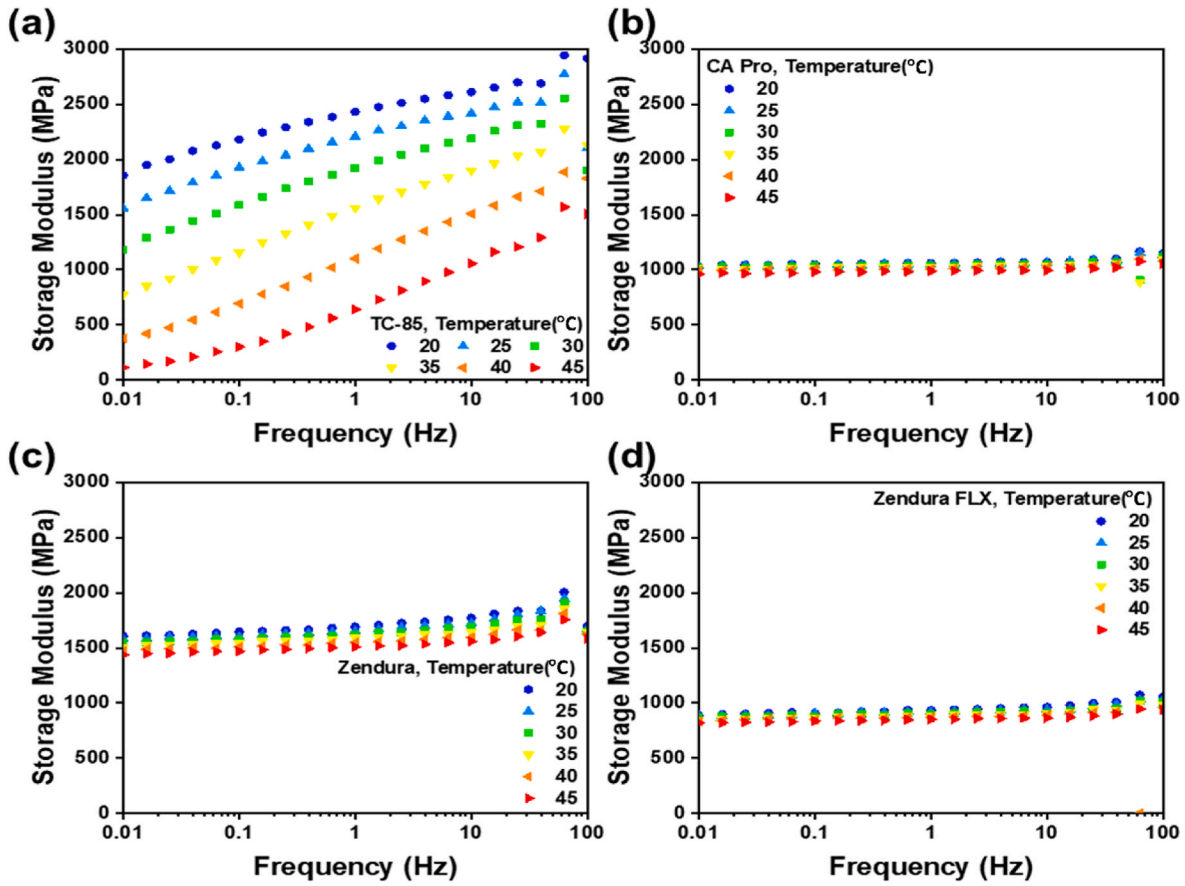

Fig. 4. Dynamic mechanical analysis (DMA) at different temperatures for different aligner materials; a) Tera Harz TC-85, b) CA Pro, c) Zendura A, d) Zendura FLX.

Table 3
Intergroup comparison of shape recovery angle and recovery percentage at different temperatures for different aligner materials.

Temperature		CA Pro	Zendura A	Zendura FLX	TC-85	p-value
30 °C	**Recovery Angle (Degree)**	3.2 ± 1.0^{B}	3.0 ± 0.9^{B}	2.7 ± 1.2^{B}	15.2 ± 4.5^{B}	<0.001*
	Recovery%	1.8 %	1.7 %	1.5 %	8.4 %	
37 °C	**Recovery Angle (Degree)**	4.0 ± 0.9^{B}	3.5 ± 0.8^{B}	3.3 ± 1.0^{B}	98.8 ± 6.2^{A}	<0.001*
	Recovery%	2.2 %	1.9 %	1.9 %	54.9 %	
45 °C	**Recovery Angle (Degree)**	5.2 ± 1.9^{B}	4.0 ± 1.4^{B}	3.7 ± 1.6^{B}	155.0 ± 5.7^{A}	<0.001*
	Recovery%	2.9 %	2.2 %	2.0 %	86.1 %	

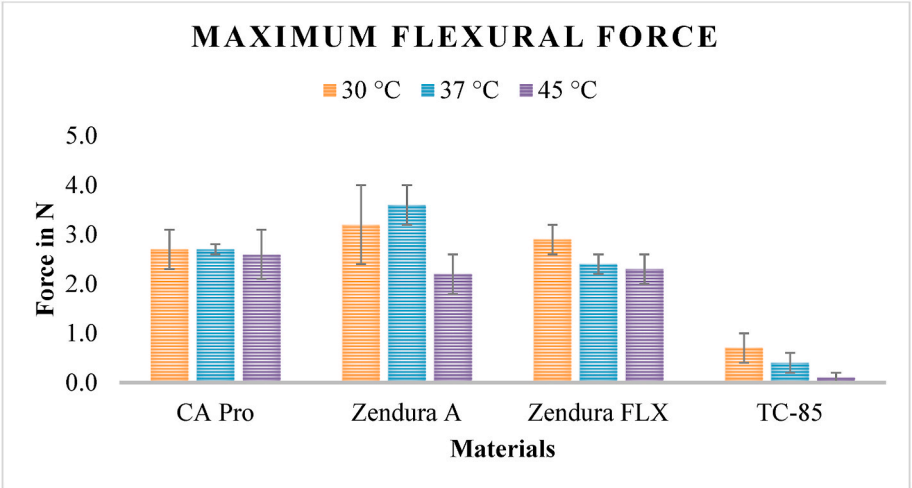

Fig. 5. Maximum flexural force on a 2 mm deflection for different aligner materials at different temperatures.

Table 4
Vickers microhardness values for different orthodontic aligner materials at room temperature.

Stage	Surface hardness (Mean ± SD)				p-value
	CA Pro	Zendura A	Zendura FLX	TC-85	
As-received	2.7 ± 0.1^{Ca}	13.4 ± 0.3^{Aa}	10.3 ± 0.2^{Ba}	NA	<0.001*
Thermoformed/3D Printed	2.7 ± 0.1^{Ca}	12.0 ± 0.2^{Ab}	7.9 ± 0.3^{Bb}	8.1 ± 0.9^{B}	<0.001*
p-value	0.899	<0.001*	<0.001*	NA	

Different upper and lowercase superscript letters indicate a statistically significant difference within the same horizontal row and vertical column respectively; *significant ($p < 0.05$).

is rational since it is 12 °C below the Tg (42.3 °C). This shape recovery increased dramatically with temperature to reach 54.9 % at 37 °C, and up to 86.1% at 45 °C, in agreement with the findings of Lee et al. (2022). However, Lee et al. documented that the complete shape recovery process takes longer than 1 h to reach 100%. On the other hand, thermoformed aligners exhibited very minimal recovery (1.5 %–2.9 %), since the test temperature range (30, 37, 40 °C) is far below their Tg (Table 2). This small recovery percentage with thermoformed sheets may be attributed to their stress relaxation property (Wang et al., 2017). Furthermore, TPU-based materials comprise alternating sequences of rigid and flexible segments, which facilitate the manifestation of a shape memory effect but become more pronounced at elevated temperatures (Elshazly et al., 2021; Iijima et al., 2015).

One important mechanical property to be considered during mechanical analysis of orthodontic aligner materials is the flexure strength during deflection, measured by 3 PB test. It assess the effectiveness of aligners in facilitating tooth movement, with the concept that the malaligned tooth applies deflection to the aligner while the adjacent teeth serve as anchorage points, similar to the behavior of a bow (Elshazly et al., 2022b; Ryu et al., 2018). The flexural force is directly proportional to the flexure modulus and the third power of the thickness in the bending direction (Elshazly et al., 2022b). The study design was implemented to replicate the aligner deflection caused by a 2 mm malalignment of upper central incisor. Hence, the span length in the 3 PB test, representing the distance between the two supports, was established at 24 mm, equal to the combined average widths of the two maxillary central incisors and one lateral incisor. The specimen was vertically deflected at its center, reaching a maximum of 2 mm (Kwon et al., 2008; Elshazly et al., 2023b).

Many studies (Elshazly et al., 2022b; Ryu et al., 2018; Kwon et al., 2008; Min et al., 2010b) used this test to determine the maximum flexural strength of the aligner materials. The outcomes of the current 3 PB test come in agreement with Lombardo et al. (2016) that the single-layer aligner sheets, like ZA, exhibit significantly greater stiffness compared to multi-layer aligner sheets, such as CP and ZF, leading to a higher generation initial forces. It can also be argued that ZA is exclusively composed of TPU, which inherently possesses higher rigidity compared to PETG (Olabis, 2012). This observation aligns with the storage modulus values recorded for each material through DMA. Also, consistent with Lee et al. (2022), conventional thermoformed aligners exhibited significantly higher strength compared to TC-85 aligners.

In clinical practice, orthodontic forces ranging from 0.1 to 1.2 N are recommended, with the specific force level depending on the type of tooth movement required (Proffit et al., 2000). The study outcomes showed that the low flexural force of TC-85, in contrast to conventional thermoformed materials, is more compatible to orthodontic tooth movement. Moreover, due to the shape memory characteristic of TC-85, the aligners can consistently exert orthodontic forces on the teeth at standard body temperature, with no discernible force decay. This combination can also allow an extended elastic range and thus a more substantial degree of tooth movement per step without inducing permanent deformation for the aligner or any violation to the biological structures. This capability may serve as a potential approach to reduce the number of aligners required for a treatment regimen. In the same context, Elshazly et al. (2022b) measured forces generated by 4D materials in the range of 0.3 N–0.7 N. Additionally, Nakasima et al. (1991) reported the capability of orthodontic wires made of SMPs to generate gentle but persistent forces suitable for orthodontic tooth movements.

Surface hardness is an important parameter in evaluation of orthodontic appliances. It is an indication of appliance surface roughness, color stability, ability to retain plaque, and crack initiation with subsequent fracture (Maleki et al., 2023). Moreover, there is a strong relation between the hardness of aligner and the amount of applied force by it (Kohda et al., 2013). Several previous studies (Dalaie et al., 2021; Albilali et al., 2023; Alhendi et al., 2022) on aligner materials have reported hardness measurements using the Vickers method. The deliberate and well-founded selection of a Vickers hardness tester to evaluate the hardness of the polymer sheet is based on its versatility and suitability for a broad spectrum of materials, encompassing polymers (Low, 1998). In the present study, there were significant variations in hardness measurements among the four tested materials. A direct correlation can be established between hardness on one side and the material composition on the other side (Pratto et al., 2022). The microhardness value remained consistent for CP after undergoing thermoforming, while it exhibited a significant decrease for both the ZA and ZF groups. That can be attributed to a decrease in the crystallinity fraction, resulting from the relaxation occurring between polymer chains (Pratto et al., 2022), especially that ZF showed high crystallinity (Daniele et al., 2021).

The hardness values of the TC-85 material remained similar to those of the ZF material, in agreement with a recent study (Can et al., 2022). According to the current DMA results, at room temperature (25 °C), TC-85 exhibits a high storage modulus compared to other thermoformed materials. However, this modulus significantly decreases at elevated temperatures, potentially affecting its mechanical properties, including hardness. It's important to note that one limitation of the present study is that the hardness tests were conducted at room temperature. Therefore, to obtain hardness values more relevant to clinical conditions, a specialized setup should be employed to measure hardness at various temperatures.

Indeed, there are other limitations of the present study. Firstly, it did not account for the potential influence of oral aging conditions on the physiochemical and mechanical characteristics of the examined materials. Secondly, the geometric configuration of the test specimens, being rectangular, is different from the actual shape of clinical aligners, potentially introducing variances in their mechanical properties (Elshazly et al., 2023a; Kwon et al., 2008). Also in reference to the 2D shape recovery test, previous studies on shape memory polymers have documented it as a proof of concept and preliminary assessment (Lendlein and Kelch, 2002). Nonetheless, it is crucial to recognize that the 3D behavior of the aligner splint may differ. Hence, further studies are necessary to explore additional characteristics using full anatomical aligners and across diverse testing conditions. Furthermore, additional experimental studies and clinical trials are essential for a comprehensive assessment of the performance and long-term implications associated with clear aligners fabricated using shape memory polymers and 3D printing resin.

5. Conclusion

The material assessment of thermoformed and 3D printed aligner materials revealed the subsequent observations:

a) The glass transition temperature of thermoformed aligner materials exceeds the range of oral temperatures, but for Tera Harz TC-85 3D printed aligner material, its Tg is 42.3 °C, and DSC heat absorption curve starts at 30.4 °C, enabling the aligners to adapt and activate their shape memory properties under oral conditions.

b) Tera Harz TC-85 3D printed materials showed excellent shape memory in the oral temperature range (4D property). This allows for better adaptation and less force loss.
c) Thermoformed single-layer sheets (such as Zendura A) exhibit greater stiffness compared to thermoformed multi-layer sheets (such as Zendura FLX and CA Pro). In turn, thermoformed sheets demonstrate higher stiffness levels than 3D printed Tera Harz TC-85 at oral temperature.
d) The hardness of the 3D printed Tera Harz TC-85 material is comparable to that of thermoformed conventional sheets.

Compliance with ethics requirements

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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