Materialtechnische Untersuchungen von Alignermaterialien aus Formgedächtnispolymeren

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Abkürzungsverzeichnis

3PB	Drei-Punkt-Biegeversuch
3D-Aligner	3D-gedrucktem Harz
4D-Aligner	3D-gedrucktem Formgedächtnisharz
CP	CA Pro Aligner Folien
DMA	Dynamisch-mechanische Analyse
DSC	Dynamische Differenzkalorimetrie (Differential Scanning Calorimetry)
PETG	Polyethylenterephthalat Glykol
PP	Polypropylen
PS	Polystyrol
PU	Polyurethan
PV	Polyvinyl
PVC	Polyvinylchlorid
OMSS	Orthodontic Measurement and Simulation System
SMP	Shape Memory Polymers (Formgedächtnispolymere)
TC-85	Tera Harz TC-85 (Aligner Harz)
Tg	Glasübergangstemperatur
VHN	Vickers-Härtezahl
ZA	Zendura A Aligner Folien
ZF	Zendura FLX Aligner Folien

1. Deutsche Zusammenfassung

1.1 Einleitung

Unsichtbare Aligner sind beliebt, da sie ästhetisch ansprechend sind, Aligner-Therapien bieten im Vergleich zur konventionellen kieferorthopädischen Behandlung effektivere Möglichkeiten zur Förderung der Mundhygiene, da Patienten die Aligner tagsüber herausnehmen können.. (Ashari und Mohamed, 2016), weniger Zahnarztbesuche erfordern und technisch einfacher zu handhaben sind (Yassir et al., 2022). Die schrittweise Korrektor der Zahnfehlstellung erfolgt mithilfe von Alignern, die Translationen und Rotationen mit einer begrenzten Schrittgröße ermöglichen, über einen Zeitraum von 10-14 Tagen (Moutawakil et al., 2021; Tamer et al., 2019). Die begrenzte Zahnbewegung pro Aligner-Schiene erhöht die Anzahl der Schienen pro Behandlung, was die finanzielle Belastung, Kunststoffverbrauch und Umweltauswirkungen steigert (Elshazly et al. 2022). Die Integration intelligenter Materialien, wie Formgedächtnispolymeren, Shape Memory Polymers (SMPs), wurde vorgeschlagen (Elshazly et al., 2021; Elshazly et al., 2022; Lee et al., 2022). SMPs können temporäre Formen beibehalten und bei geeignetem Stimulus in ihre ursprüngliche Form zurückkehren (Lendlein und Kelch, 2002; Liu et al., 2007; Meng und Li, 2013).

Die klinische Wirksamkeit von durchsichtigen Alignern hängt von verschiedenen Faktoren ab (Upadhyay und Arqub, 2021; Yassir et al., 2022), wobei die Materialeigenschaften eine entscheidende Rolle spielen (Cremonini et al., 2022; Momtaz, 2016). Mehrschichtige Hybridmaterialien wurden entwickelt, um Einschränkungen einschichtiger Materialien zu überwinden, indem sie harte Außenschalen mit einer weicheren Innenschicht kombinieren, was zu verbesserten mechanischen Eigenschaften und höherem Patientenkomfort führt (Lombardo et al., 2016). Das herkömmliche Thermoformverfahren beeinträchtigt die mechanischen Eigenschaften von Aligner-Materialien (Dalaie et al., 2021; Golkhani et al., 2022). Als Alternative wurde der direkte 3D-Druck eingeführt, um kumulative Fehler zu eliminieren, mit dem Ziel höherer Präzision, besserer Designkontrolle, geringerer Komplexität der Lieferkette und niedrigeren Produktionskosten (Elshazly et al., 2022; Koenig et al., 2022; Lee et al., 2022; Peeters et al., 2019; Shivapuja et al., 2019; Tartaglia et al., 2021).

Bisher gibt es in der Literatur keinen umfassenden Überblick über die Materialeigenschaften von Alignern, die aus SMPs, 3D-gedrucktem Harz oder 3D-gedrucktem Formgedächtnisharz (4D-Aligner) hergestellt werden. Das Hauptziel dieser Studie besteht darin, physikochemische und mechanische Analyseergebnisse von 3D-gedruckten Formgedächtnis-Alignern (4D-Alignern) im Vergleich zu thermogeformten Alignern vorzustellen.

1.2 Materialien und Methoden

1.2.1 Materialien

Vier Materialien wurden in dieser Studie untersucht. Drei davon wurden durch Thermoverformung hergestellt, nämlich CA Pro (CP, Scheu-Dental, Iserlohn), Zendura A (ZA, Bay Materials, Fremont, USA) und Zendura FLX (ZF, Bay Materials, Fremont, USA). Das vierte Material wurde durch den 3D-Druckprozess hergestellt und trägt den Namen Tera Harz TC-85 (TC-85, Graphy, Seoul, Südkorea).

1.2.2 Vorbereitung der Proben

Die thermoplastischen Platten der drei Materialien (CP, ZA, ZF) wurden mit einem Biostar-Tiefziehgerät (Scheu-Dental GmbH, Iserlohn) gemäß aufgeführten Richtlinien des Herstellers tiefgezogen. Bei diesem Tiefziehverfahren wurden die Platten von 0,75 mm auf etwa 0,60 mm ausgedünnt (Elshazly et al., 2022). Die Proben wurden anschließend mittels einer Schere in rechteckige Streifen mit den Dimensionen 50 x 10 x 0,6 mm³ geschnitten. Im Gegensatz dazu erfolgte die Herstellung der TC-85-Proben direkt durch 3D-Druck in Form rechteckiger Streifen mit denselben Abmessungen von 50 x 10 x 0,6 mm³.

1.2.3 Prüfungen

1.2.3.1 Dynamische Differenzkalorimetrie (DSC)

Thermische Analysen wurden unter Stickstoffatmosphäre mit einem Differential-Scanning-Kalorimeter (STARe SW Mettler Toledo V16.10; Greifensee, Schweiz) durchgeführt (n=2). Die Glasübergangstemperatur (Tg) für jedes Material wurde durch Identifizierung des Mittelpunkts im zweiten Heizzyklus bestimmt.

1.2.3.2 Dynamisch-mechanische Analyse (DMA)

Für die DMA wurden jeweils drei Proben pro Material vorbereitet (n=3). Die Untersuchung wurde mithilfe eines dynamisch-mechanischen Analysators (DMA Q800; TA-Instruments, New Castle, USA) im Modus der Spannungsrelaxation durchgeführt. Die Tests wurden bei Temperaturen von 20, 25, 30, 35, 40 und 45 °C durchgeführt, mit einer Frequenz von 0 bis 100 Hz und einer Dehnungsrate von 0,1 %.

1.2.3.3 Prüfung der Formerholung

Die Beurteilung der Formerholung wurde bei drei verschiedenen Temperaturen (30 °C, 37 °C und 45 °C) mit insgesamt 18 Proben für jedes Material durchgeführt. Die Proben wurden einem speziellen Verfahren unterzogen, bei dem sie erhitzt, gebogen, gekühlt und anschließend in Wasserbädern getestet wurden. Dabei wurden der ursprüngliche Biegewinkel (θ initial) und der nachfolgende Erholungswinkel (θ final) gemessen. Der prozentuale Anteil der Formerholung wurde mithilfe der folgenden Gleichung 1 berechnet:

$$Formerholung \ \% = \frac{(\theta \ final)}{(\theta \ intial)} \times 100 \qquad (1)$$

1.2.3.4 Drei-Punkt-Biegeversuch (3PB)

Für die Messung der maximalen Kraft wurde ein spezieller biomechanischer Messaufbau verwendet (Orthodontic Measurement and Simulation System, OMSS; Oralmedizinischse Technologie, Universitätsklinikum Bonn, Bourauel et al. 1992).Dabei wurden die Proben in einer Drei-Punkt-Konfiguration mit einer Spannweite von 24 mm um 2 mm ausgelenkt. Dieser Aufbau ermöglichte Experimente bei verschiedenen Temperaturen (30 °C, 37 °C und 45 °C) und umfasste insgesamt 18 Proben für jedes Material, wobei jeweils 6 Proben pro Erholungstemperatur vorgesehen waren (n=6).

1.2.3.5 Mikrohärte der Oberfläche

Die Oberflächenmikrohärte wurde bei Raumtemperatur mit einem Vickers-Mikrohärteprüfgerät (Qness 60 M Evo; QATM, Mammelzen) gemessen, wobei eine Kraft

von 9,8 N für 10 Sekunden angewendet wurde. In jeder Probe wurden fünf Eindrücke mit einem Mindestabstand von 50 μm erzeugt, und die durchschnittliche Vickers-Härtezahl (VHN) wurde berechnet. Bei den thermoformbaren Platten (CP, ZA, ZF) wurden Härteprüfungen sowohl am Ausgangsmaterial als auch nach dem Thermoformen durchgeführt, mit insgesamt 12 Proben für jedes Material (6 Proben für jede Phase). Für TC-85 wurde die Härteprüfung nur nach dem Nachhärtungsprozess durchgeführt (n=6).

1.3 Statistische Analyse

Numerische Daten wurden durch Mittelwert und Standardabweichung dargestellt und auf Normalverteilung mittels Shapiro-Wilk-Test geprüft. Oberflächenhärte-Daten wurden normalverteilt analysiert durch einfaktorielle ANOVA mit Tukey's post-hoc Test. Andere Daten wurden nicht-parametrisch mittels Kruskal-Wallis-Test und Dunn's post-hoc Test mit Bonferroni-Korrektur untersucht. Das Signifikanzniveau wurde auf $p < 0,05$ festgelegt, und die Analyse erfolgte mit R-Softwareversion 4.1.3 für Windows, bereitgestellt von der R Foundation for Statistical Computing in Wien, Österreich.

1.4 Ergebnisse

1.4.1 Ergebnisse der DSC-Analyse

Durch DSC-Analysen wurden folgende Tg-Werte ermittelt: 79,9 °C für CP, 92,2 °C für ZA, 107,1 °C für ZF und 42,3 °C für TC-85. TC-85 zeigte eine bemerkenswerte strukturelle Stabilität, wohingegen DMA-Tests im Temperaturbereich von 20 °C bis 45 °C bei diesem Material deutliche Schwankungen aufzeigten.

Die Darstellungen in **Abb. 1 bis 3** bieten die Ergebnisse der DSC-Analyse für ZF (vor und nach Thermoformen) sowie TC-85. Anhand dieser Graphen lassen sich die verschiedenen Glasübergangstemperaturen (Tg) für die Materialien ZF und TC-85 ableiten.

In **Tab. 1** sind die ermittelten Glasübergangstemperaturen (Tg) mittels differentieller Scanning-Kalorimetrie (DSC) für die verschiedenen Aligner-Materialien aufgeführt.
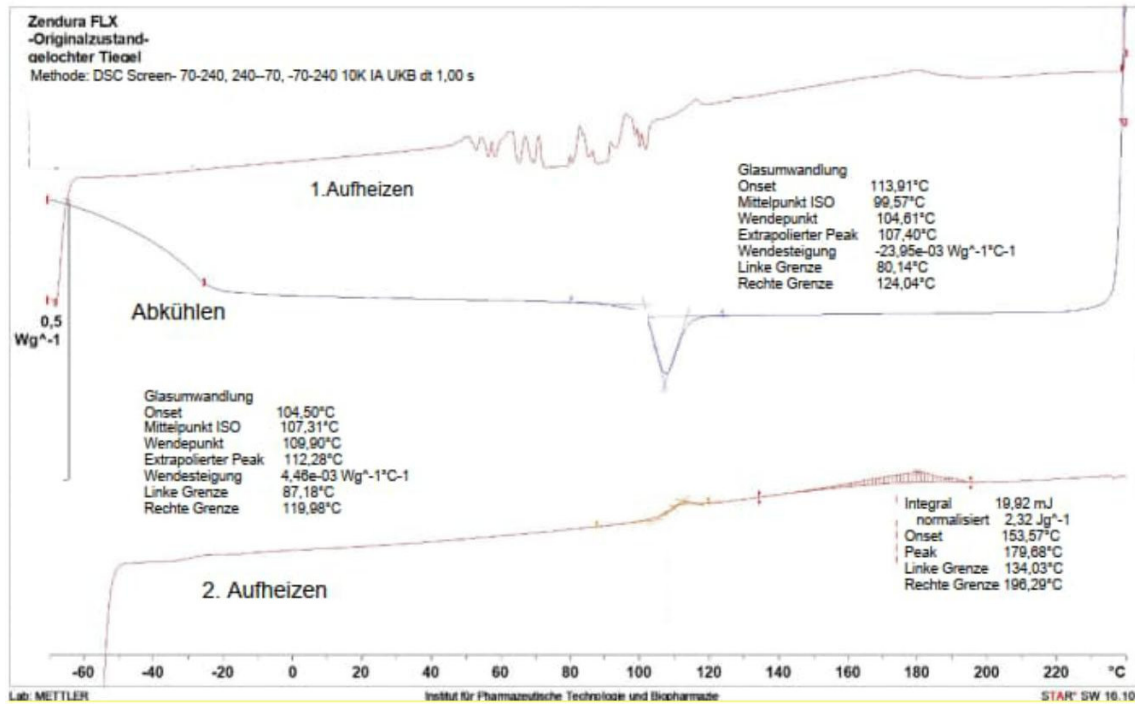
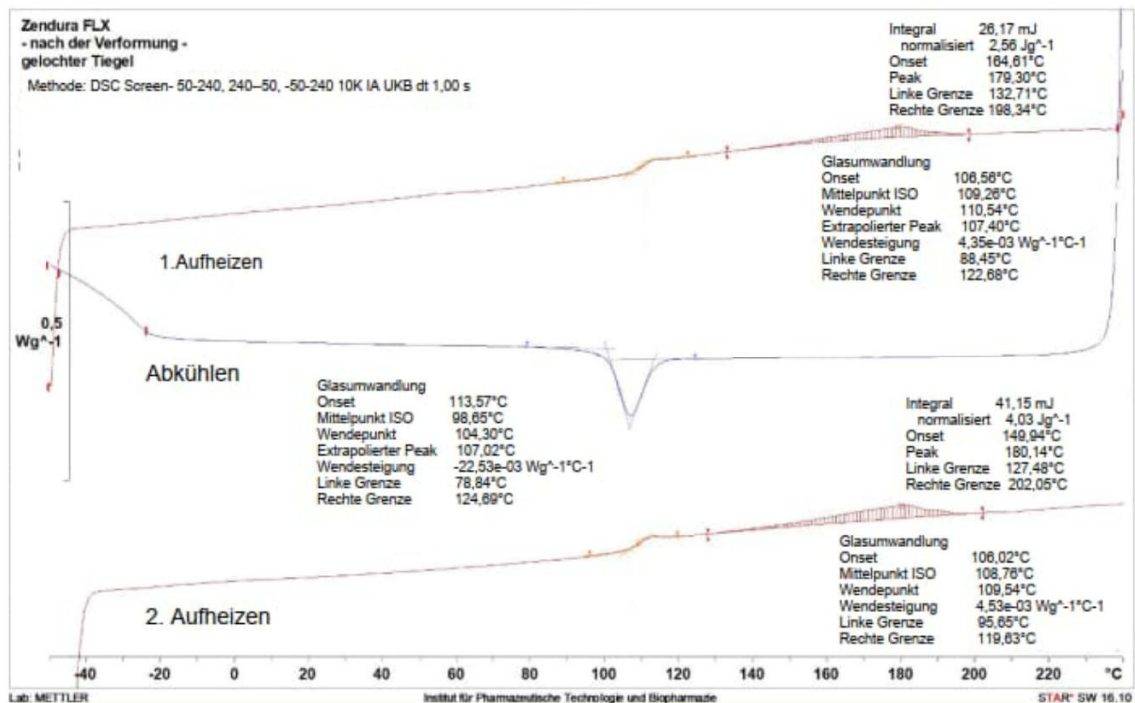**Abb.1:** DSC-Messung für das Zendura FLX im Originalzustand

Abb. 2: DSC-Messung für das Zendura FLX nach der thermischen Verformung
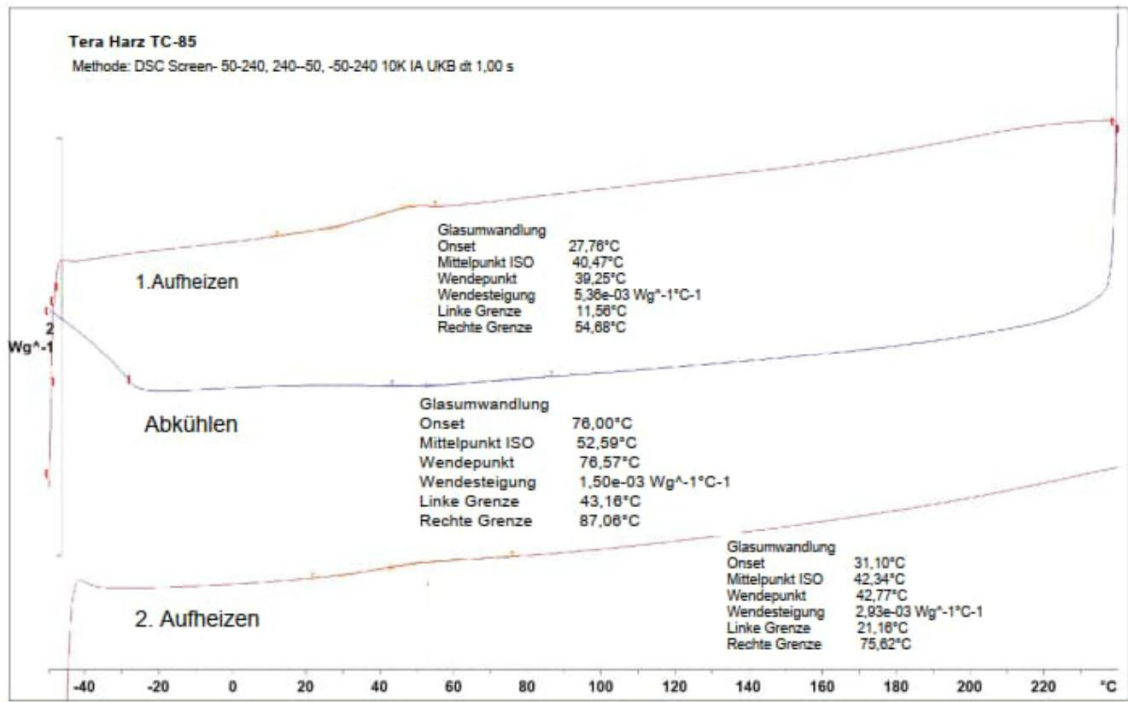
Abb. 3: DSC-Messung für Tera Harz (TC-85)

Tab. 1: Glasübergangstemperatur (Tg) mittels differentieller Scanning-Kalorimetrie (DSC) für verschiedene Alignermaterialien

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

1.4.2 Ergebnisse des Formerholungstests

Bezüglich der Formerholung wurde festgestellt, dass CP, ZA und ZF bei Temperaturen von 30 °C, 37 °C und 45 °C vernachlässigbare Rückverformungsraten aufwiesen (1,5 % - 2,9%), während TC-85 bei höheren Temperaturen eine deutliche Rückverformung aufwies. Die Ergebnisse des Rückformungstest für den CP, ZA; ZF und TC-85 werden in **Tab. 2** zusammengefasst.

Tab. 2: Rückformungsgrade und -rate bei verschiedenen Temperaturen für ZA

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

1.4.3   Ergebnisse des Vickers-Mikrohärtetests

Vor dem Thermoformen wies ZA die höchste Vickers-Mikrohärte auf, während sich nach dem Thermoformen ZA und ZF signifikant verringerten und CP unverändert blieb. TC-85 zeigte vergleichbare Härtegrade wie thermogeformtes ZF bei Raumtemperatur. **Tab. 3** zeige die Vickers-Mikrohärte für den CP, ZA, ZF und TC-85 vor – und nach Thermoformung bei Raumtemperatur.

Tab. 3: Vickers-Mikrohärte für den CP, ZA, ZF und TC-85 bei Raumtemperatur

	Oberflächenhärte (Mittelwert ± SA)				p-value
	CA Pro	**Zendura A**	**Zendura FLX**	**TC-85**	
Originalzustand	2.7 ± 0.1^{Ca}	13.4 ± 0.3^{Aa}	10.3 ± 0.2^{Ba}	NA	<0.001*
Thermoformen/ 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	

1.4.4 Ergebnisse des Drei-Punkt-Biegeversuchs

Im 3PB-Test erzielte ZA die höchsten Kraftwerte bei 30 °C und 37 °C, während TC-85 durchweg die niedrigsten Werte aufwies. **Abb. 4** zeige die Maximal erforderliche Biegekraft für eine 2-mm-Durchbiegung durch Alignermaterialien bei den untersuchenden Temperaturen.
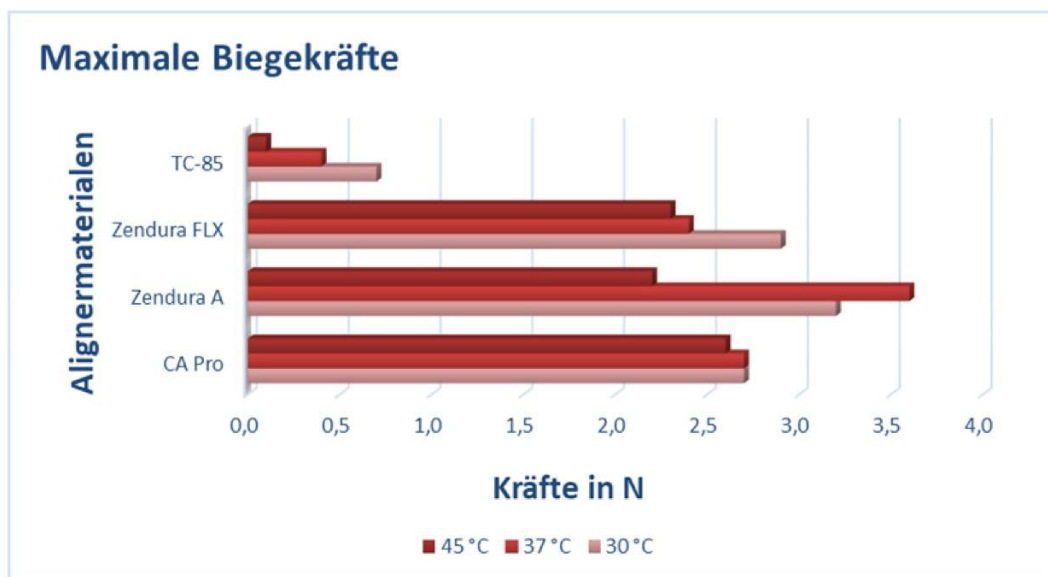

Abb. 4: Maximal erforderliche Biegekraft für eine 2-mm-Durchbiegung durch Alignermaterialien bei den untersuchenden Temperaturen

1.5 Diskussion

Die traditionelle Methode zur Herstellung von thermoformbaren Alignern durch Tiefziehen anhand von Zahnmodellen kann zu Ungenauigkeiten und ungleichmäßiger Dicke der Aligner führen.(Elshazly et al., 2022), was Unsicherheiten in der Leistung und den Behandlungsergebnissen verursacht (Min et al., 2010; Park et al., 2023). Ein vorgeschlagenes 3D-Druckverfahren (Tartaglia et al., 2021) und die Verwendung von Formgedächtnispolymeren sollen diese Probleme angehen und die Effektivität der Aligner verbessern (Chen et al., 2023; Elshazly et al., 2023; Lombardo et al., 2016; Vardimon et al., 2010). Die spezielle langfristige Formgedächtnisfähigkeit trägt zur verbesserten Anpassung des Aligners bei, erleichtert dessen Platzierung und sorgt für eine gleichbleibende Kraftausübung auf den Zähnen. (Elshazly et al., 2021; Elshazly et al.,s 2022).

Das Ziel dieser Studie bestand darin, die physikochemischen und mechanischen Eigenschaften von 3D-gedruckten Formgedächtnis-Alignern im Vergleich zu thermoformbaren Alignern zu untersuchen.

In den DSC- und DMA-Tests wurden aufgrund von Literaturstudien, Testcharakteristiken und Empfehlungen lediglich zwei Proben als ausreichend betrachtet. Bei den Versuchen zur Formerholung, zur Oberflächenmikrohärte sowie zum Drei-Punkt-Biegetest waren jedoch mehrere Durchläufe erforderlich, um eine statistisch aussagekräftigere Analyse zu gewährleisten. Nach der Berechnung der Stichprobengröße es wurde festgestellt, dass sechs Proben pro Gruppe notwendig sind, um die Standardabweichung zu minimieren.

Die durch den DSC-Test gemessene Tg steht für den Temperaturbereich, in dem das Polymer von einem glasartig starren zu einem gummiartig flexiblen Zustand übergeht (Schick, 2009; Zin et al., 2019). Die aktuellen DSC-Ergebnisse zeigen signifikante Tg-Unterschiede zwischen den Materialien, wobei TC-85 mit 42,3 °C deutlich niedriger liegt als CP, ZA und ZF mit 79,9 °C, 92,2 °C bzw. 107,1 °C. Diese Variation lässt sich auf die unterschiedlichen Zusammensetzungen der Materialien zurückführen, wobei thermoformbare Alignermaterialien (CP, ZA, ZF) aus PETG, TPU oder einer hybriden mehrschichtigen Mischung, mit unterschiedlichem Kristallinitätsgrad, bestehen (Daniele et al., 2021; Iijima et al., 2015). PETG und TPU sind hochmolekulare Copolymere mit aromatischen Ringen, was zu einer starken pi-pi-Wechselwirkung und einer hohen Tg führt (Hunter und Sanders, 1990). Im Gegensatz dazu besteht TC-85 aus einem aliphatischen Vinyl ester–Urethan-Polymer (Can et al., 2022), zeigt schwächere Wechselwirkungen und somit eine niedrigere Tg (Olabis et al., 2012). Die DSC-Kurve für TC-85 beginnt bei 30,4 °C, was auf klare Formgedächtniseigenschaften im Mund hinweist. Die DSC-Diagramme zeigen, dass TC-85 bei höheren die Temperaturen strukturelle Stabilität behält, was klinische Vorteile bei der Sterilisation des Aligners bieten könnte. Dies erfordert jedoch weitere Forschung.

Außerdem hat DMA sich als wichtiges Instrument zur Untersuchung des Verhaltens von Polymerstrukturen erwiesen, um Polymerrelaxationen zu erforschen und zu verstehen, wie Polymere auf verschiedene Spannungs- und Temperaturbedingungen reagieren

(Zin et al., 2019). Die Ergebnisse der laufenden DMA-Analyse, insbesondere die signifikanten Abweichungen des Speichermoduls im Temperaturbereich von 20 °C bis 45 °C für das TC-85-Material, weisen auf potenzielle klinische Vorteile hin, indem sie helfen könnten, den Kraftabfall zu minimieren und die kieferorthopädische Kraft der Aligner aufrechtzuerhalten (Lee et al., 2022).

Der Mechanismus des Formgedächtnisses in thermoreaktiven SMPs beruht auf mindestens zwei strukturellen Phasen: einer stabilen Netzwerkphase, die die ursprüngliche Form bestimmt, und einer reversiblen Schaltphase, die die vorübergehende Form herstellt (Elshazly et al., 2021; Elshazly et al., 2022). Die Temperatur der Formerholung hängt mit der Tg der reversiblen Umschaltphase zusammen (Elshazly et al., 2021; Lee et al., 2022), was mit den aktuellen Ergebnissen von DSC, DMA und Formerholung übereinstimmt. Das TC-85-Material zeigt eine geringe Formwiederherstellung bei 30 °C und nimmt mit steigender Temperatur zu, während thermogeformte Aligner nur geringe Formwiederherstellung zeigen, da der Testtemperaturbereich (30, 37, 40 °C) weit unter ihrem Tg liegt.

Die Biegefestigkeit während der Durchbiegung, gemessen mit dem 3PB-Test, ist eine wichtige mechanische Eigenschaft bei der Analyse von kieferorthopädischen Aligner-Materialien (Elshazly et al., 2022; Ryu et al., 2018). Die Ergebnisse des Tests bestätigen, dass einlagige Aligner-Bögen wie ZA im Vergleich zu mehrlagigen Bögen höhere Steifigkeit und Anfangskräfte aufweisen (Lombardo et al., 2016), was mit den Speichermodulwerten aus der DMA-Analyse übereinstimmt. Thermogeformte Aligner zeigen eine höhere Festigkeit als TC-85 Aligner, was auch mit früheren Studien übereinstimmt (Lee et al., 2022).

TC-85 zeigt im Vergleich zu herkömmlichen thermogeformten Materialien eine geringere Biegekraft, was besser mit empfohlenen kieferorthopädischen Kräften von 0,1 bis 1,2 N (Proffit et al., 2000) für verschiedene Zahnbewegungen vereinbar ist. Die Formgedächtniseigenschaft ermöglicht konstante Kräfte auf den Zähnen bei normaler Körpertemperatur, was potenziell eine größere Zahnbewegung pro Schritt erlaubt und die Anzahl benötigter Aligner reduzieren könnte. Studien zu 4D-Materialien (Elshazly et al., 2022) und

kieferorthopädischen Drähten aus SMP (Nakasima et al., 1991) unterstützen diese Annahme.

Ein enger Zusammenhang besteht zwischen der Härte des Aligners und dem Ausmaß der von ihm ausgeübten Kraft (Kohda et al., 2013). Signifikante Unterschiede in den Härtemessungen der getesteten Materialien zeigen einen direkten Zusammenhang mit der Materialzusammensetzung (Pratto et al., 2022). Die Mikrohärte von CP bleibt nach der Thermoformung konstant, während sie bei ZA und ZF abnimmt, was auf eine verringerte Kristallinität zurückzuführen ist (Daniele et al., 2021). TC-85 zeigt ähnliche Härte wie ZF (Can et al., 2022) und einen hohen Speichermodul bei Raumtemperatur, der jedoch bei höheren Temperaturen abnimmt, was möglicherweise die mechanischen Eigenschaften beeinflusst.

Die vorliegende Studie weist Einschränkungen auf, da der Einfluss der Mundalterung auf die Materialien nicht berücksichtigt wurde, und die rechteckige Form der Prüfkörper von der klinischen Aligner-Form abweicht (Elshazly et al., 2023; Kwon et al., 2008). Weiterführende Studien mit vollanatomischen Alignern und verschiedenen Testbedingungen sind notwendig, ebenso wie experimentelle und klinische Untersuchungen für eine umfassende Bewertung von Alignern aus Formgedächtnispolymeren und 3D-Druckkunststoff.

1.6   Schlussfolgerungen

Die Untersuchung von thermogeformten und 3D-gedruckten Aligner-Materialien hebt die beeindruckenden Formgedächtniseigenschaften von Tera Harz TC-85 hervor, bedingt durch seine niedrige Glasübergangstemperatur von 42,3 °C. Im Gegensatz zu herkömmlichen thermogeformten Materialien weist das 3D-gedruckte TC-85 eine geringere Biegekraft auf, behält jedoch die Fähigkeit zur konstanten Kraftausübung auf den Zähnen bei normaler Körpertemperatur bei. Interessanterweise zeigt TC-85 auch eine vergleichbare Härte im Vergleich zu herkömmlichen thermogeformten Platten.

1.7 Zusammenfassung

Zielsetzung: Physikochemische und mechanische Analyse von 3D-gedruckten Alignern mit Formgedächtniseigenschaften im Vergleich zu thermoformten Alignern. **Materialien und Methoden**: Vier Materialien, darunter die thermoformbaren Varianten CA Pro (CP), Zendura A (ZA), Zendura FLX (ZF) sowie das 3D-Druckmaterial Tera Harz (TC-85), wurden in rechteckigen Streifen (50x10x0,5 mm^3) getestet. Fünf Tests wurde durchgeführt, darunter Dynamische Differenzkalorimetrie (DSC), dynamische mechanische Analyse (DMA), Tests zur Formerholung, Drei-Punkt-Biegung (3PB) und Vickers-Oberflächenmikrohärte (VH). **Ergebnisse**: In der DSC zeigten sich Glasübergangstemperaturen (Tg) von 79,9 °C für CP, 92,2 °C für ZA, 107,1 °C für ZF und 42,3 °C für TC-85. Die DMA offenbarte einen signifikanten Abfall des Speichermoduls im Temperaturbereich von 20-45 °C, insbesondere bei TC-85. Bei Temperaturen von 30-45 °C erreichte TC-85 nach 10 Minuten eine erhebliche Formerholung von bis zu 86,1 %, während thermogeformte Materialien lediglich eine geringe Erholung von 1,5-2,9 % aufwiesen. Im 3PB (bei 30, 37, 45 °C) erzielte ZA die höchste Kraft bei 2 mm Biegung, während TC-85 die geringste aufwies. Die VH nahm nach der Thermoformung sowohl bei ZA als auch bei ZF deutlich ab, wobei ZA die höchste Härte aufwies, gefolgt von ZF und TC-85, während CP die niedrigsten Werte aufwies. **Schlussfolgerung**: Die Formgedächtniseigenschaften von Tera Harz TC-85 werden durch seine niedrige Glasübergangstemperatur von 42,3 °C betont. Im Vergleich zu herkömmlichen thermogeformten Materialien hat das 3D-gedruckte TC-85 eine geringere Biegekraft, behält jedoch die Fähigkeit zur konstanten Kraftausübung auf den Zähnen bei normaler Körpertemperatur bei und zeigt eine vergleichbare Härte.

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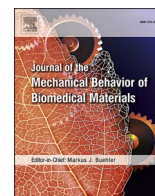
Veröffentlichung

Physiochemical and Mechanical Characterisation of Orthodontic 3D Printed Aligner Material made of Shape Memory Polymers (4D Aligner Material)

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

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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 $50 \times 10 \times 0.5$ 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

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

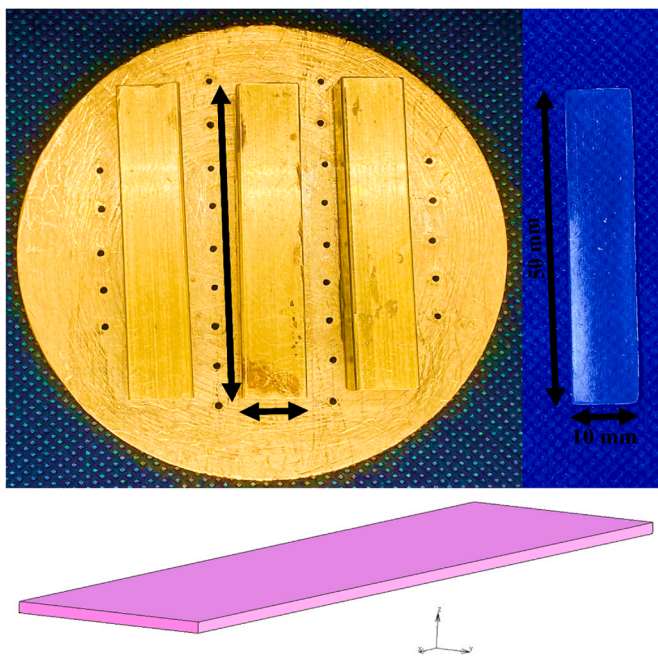[1] TC-85 is a CE, FDA, and KFDA Certified material.

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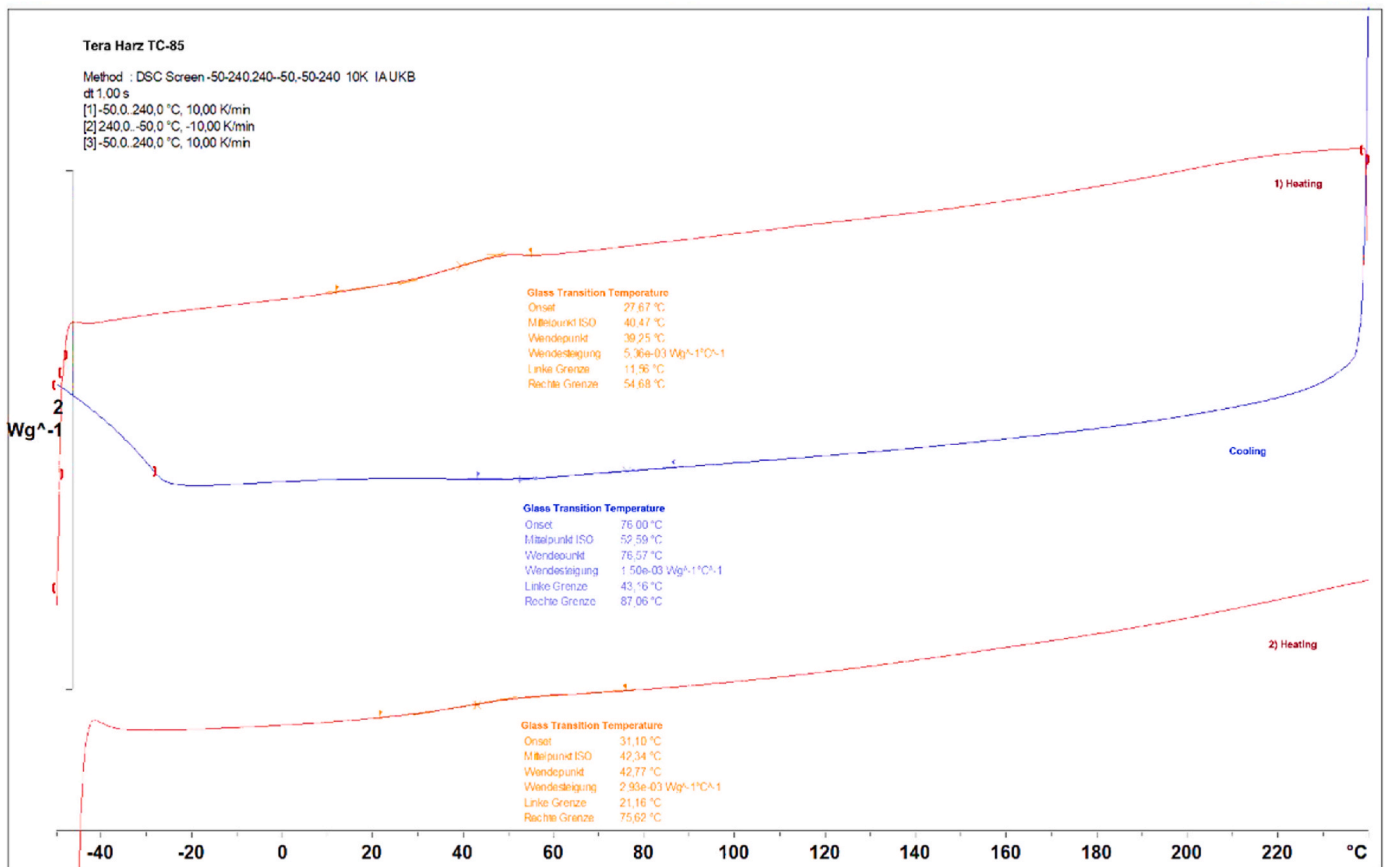
Fig. 2. Differential scanning calorimetry (DSC) graph for a 3D printed aligner material (Tera Harz TC-85).

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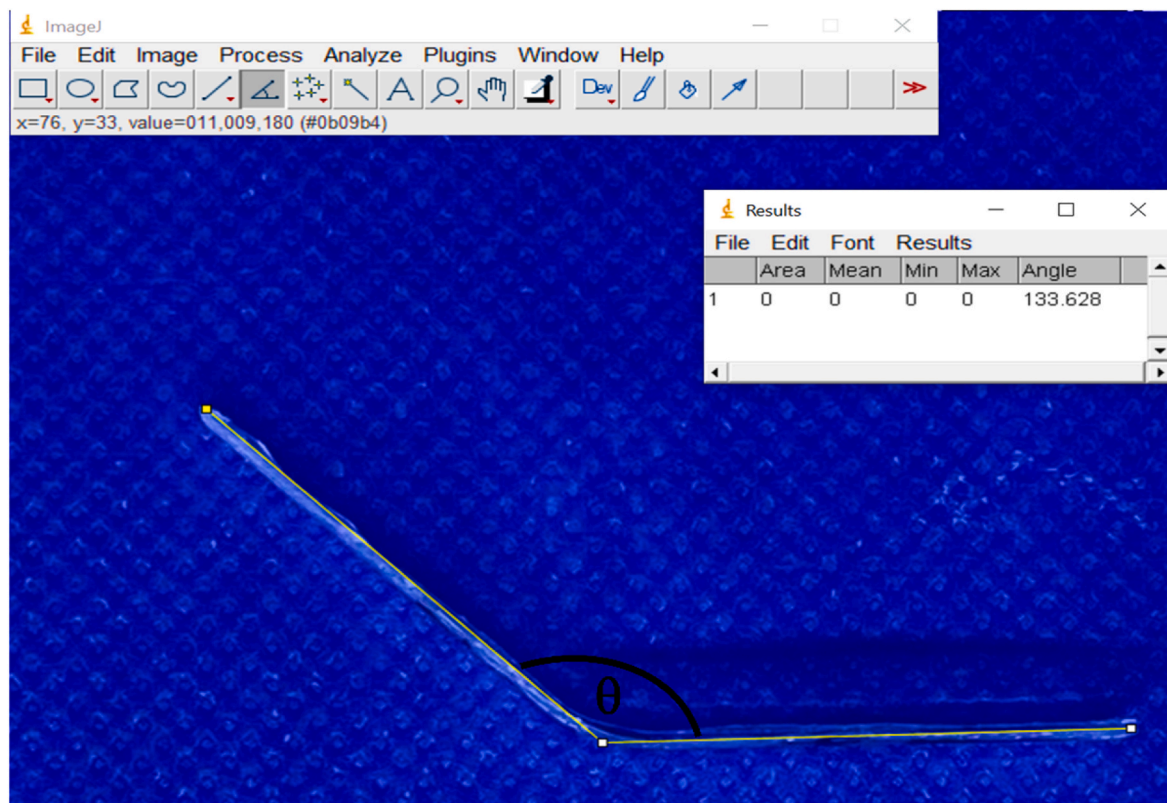
Fig. 3. Measurement of the initial angle (θ initial) and the recovery angle (θ final) of aligner material strips using ImageJ software in order to calculate the shape recovery percentage.

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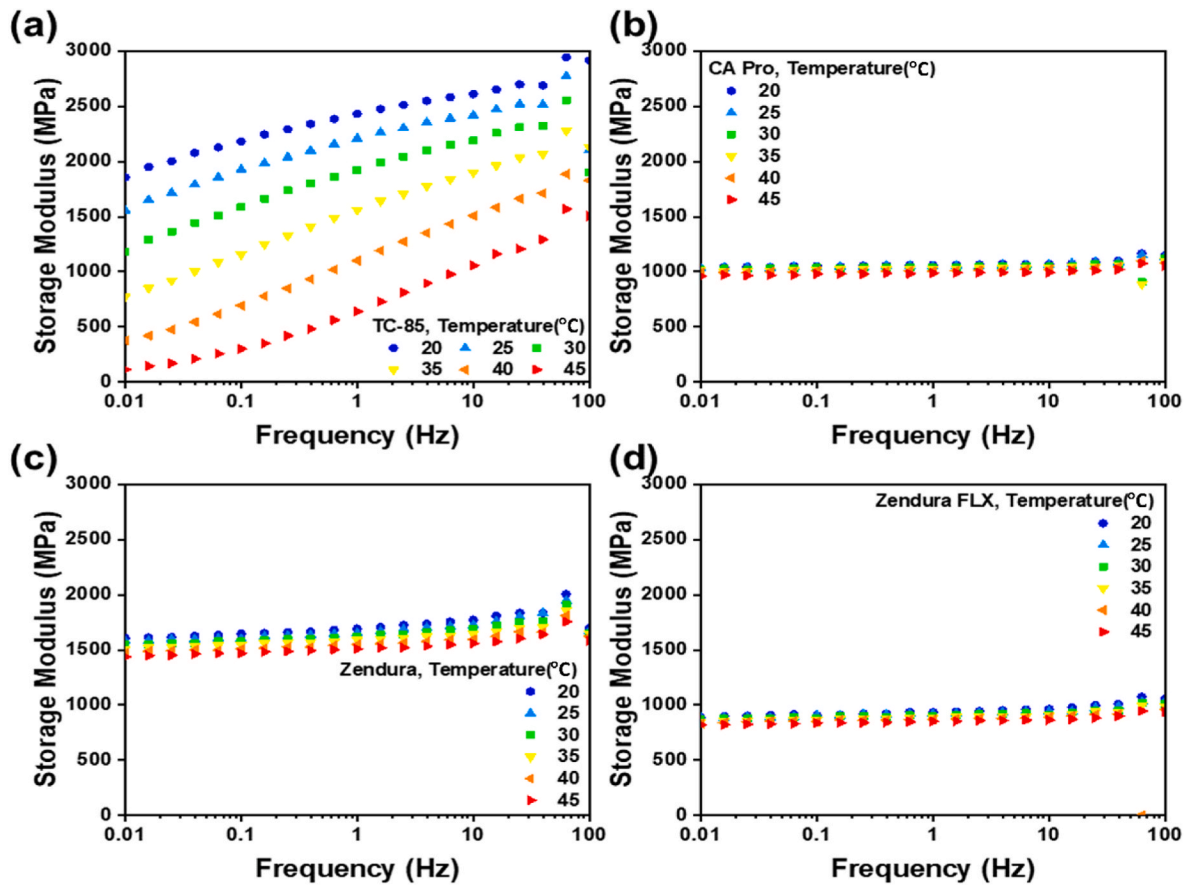
Fig. 4. Dynamic mechanical analysis (DMA) at different temperatures for different aligner materials; a) Tera Harz TC-85, b) CA Pro, c) Zendura A, d) Zendura FLX.

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

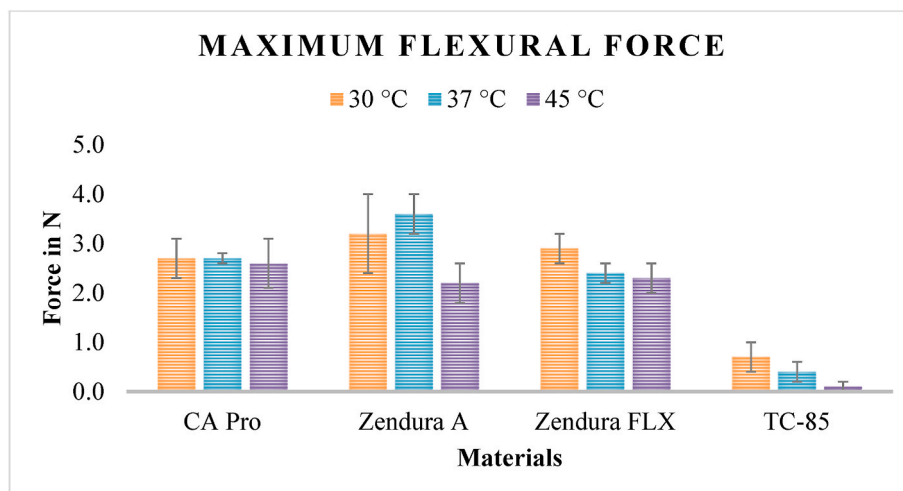| Temperature		CA Pro	Zendura A	Zendura FLX	TC-85	p-value
30 °C	**Recovery Angle (Degree)**	3.2 ± 1.0^B	3.0 ± 0.9^B	2.7 ± 1.2^B	15.2 ± 4.5^B	<0.001*
	Recovery%	1.8 %	1.7 %	1.5 %	8.4 %	
37 °C	**Recovery Angle (Degree)**	4.0 ± 0.9^B	3.5 ± 0.8^B	3.3 ± 1.0^B	98.8 ± 6.2^A	<0.001*
	Recovery%	2.2 %	1.9 %	1.9 %	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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During the preparation of this work the authors used ChatGPT AI tool in order to improve the readability of the English language. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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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