ACTA
STOMATOLOGICA
CROATICA
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Acta stomatol Croat. 2023;57(4):286-299.
DOI: 10.15644/asc57/4/1

ORIGINAL SCIENTIFIC PAPER
IZVORNI ZNANSTVENI RAD

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Differential Stability of One-layer and Three-layer Orthodontic Aligner Blends under Thermocycling: Implications for Clinical Durability

Diferencijalna stabilnost jednoslojnih i troslojnih ortodontskih alignera pod utjecajem termocikliranja: implikacije za kliničku trajnost

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Abstract
Objectives: To optimize the therapeutic usefulness of aligners, it is crucial to understand how their mechanical properties alter with time. **Materials and methods:** Specimens from four different brands, including Duran+, CA® Pro, Zendura A, and Zendura FLX, were produced for material testing of thermoplastic orthodontic aligners (TOA) using dimensions measuring 4mm x 10mm. Each brand's 24 samples were split into three groups as follows: G1 being thermoformed, G2 being thermoformed and underwent 500 thermocycles (simulating 7 days), and G3 being thermoformed and underwent 1000 thermocycles (simulating 14 days). Surface roughness, modulus of elasticity in bending, and spectrophotometry were used to assess the effect of aging on TOAs. **Results:** After 1000 thermocycles, Duran+ had the highest modulus of elasticity and differed statistically from all other groups. The intragroup comparison showed that only Duran+'s elastic modulus significantly changed after 1000 thermocycles in comparison with the control group. Surface roughness values (Ra), did not statistically differ among brands or thermocycling group measures. The change in chemical properties was not significant in any brand. **Conclusion:** One-layer PETG (Duran+) failed to demonstrate stability after *in vitro* aging, thus suggesting that clinicians should be aware of the change in mechanical properties when using one-layer PETG (Duran +) in a 2 weeks regime.

Received: October 25, 2023
Accepted: December 1, 2023

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MeSH Terms: Orthodontic Appliances; Materials Testing; Mechanical Tests
Author Keywords: Aligners; Orthodontic appliance; Mechanical properties; Chemistry

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Introduction

Clear aligners have gained immense popularity in orthodontic treatments, particularly among adult patients who appreciate their enhanced comfort and aesthetics (1). While aligners are effective in achieving proper leveling and alignment, they encounter challenges in certain tooth movements, such as extrusion, rotation, and torque control, which may not always be predictable (2-6). Additionally, aligners have shown limited effectiveness in correcting overbite and anteroposterior discrepancies, although they improve the alignment and interproximal contacts in certain malocclusions. However, compared to fixed appliances, clear aligners can yield comparable outcomes, especially for mild to moderate mal-

Uvod

Prozirni aligneri stekli su golemu popularnost u ortodontskim terapijama, posebice među odraslim pacijentima koji cijene njihovu veću udobnost i estetiku (1). Iako su učinkoviti u postizanju pravilnog niveliranja i poravnavanja, pojavljuju se izazovi pri određenim pomacima zuba poput ekstruzije, rotacije i kontrole priteznoga momenta, što se ne može uvijek predvidjeti (2 – 6). Uz to, aligneri su pokazali ograničenu učinkovitost u korekciji prijeklopa i anteroposteriornih diskrepancija, iako poboljšavaju poravnanje te interproksimalne kontakte kod određenih malokluzija. No u usporedbi s fiksnim napravama, prozirni aligneri mogu pružiti usporedive rezultate, posebno za blage do umjerene malokluocclusions. Studies show that aligners achieve about 50% accuracy in total types of tooth movements, with rotation being the least accurate (7). The effectiveness of clear aligners is influenced by various factors, including the used materials and the manufacturing process. Conventional, thermoformed orthodontic aligners (TOAs) are composed of thermoplastic resin polymers such as polyvinyl chloride (PVC), polyethylene terephthalate (PET), polyethylene terephthalate glycol (PETG), and polyurethane (PU) (8). Modifications in the physical characteristics of aligner materials, such as their hardness and elastic modulus, can affect the force delivery, and subsequently impact treatment effectiveness. Processes of thermoforming and aging have been shown to affect the properties of aligner materials, but there is a lack of consensus on their specific influence (9-13). To comprehensively understand the behavior of aligners, it is important to consider the mechanical and thermal stress they experience during daily wear. Short-term mechanical stress occurs during insertion and removal, while long-term stress results from the interaction between the aligners and misaligned teeth, as well as the pressure during chewing (14). Additionally, aligner materials may exhibit a force drop in the initial hours of use (15, 16). Previous studies have shown that thermal and mechanical loading significantly affect the mechanical properties of aligner materials, thus leading to changes in hardness, elasticity, and strength (13, 17-19). Also, studies have indicated that aligners may undergo changes in shape and composition in the oral environment due to factors such as temperature, humidity, and salivary enzymes (10, 20, 21). Understanding the mechanical behavior of aligners under various stresses is essential for optimizing their performance. While it has been demonstrated in earlier research that the chemical structures of EX30 aligners remain unchanged following intraoral aging (10), to our best knowledge, there have been no studies examining the alterations in the chemical structures of PETG, PU, and copolyester aligners. Due to the critical importance of the physical attributes of materials uti-lized in the manufacturing of TOAs, relying solely on technical data provided by suppliers may not be sufficient. Experimental assessment of these materials under various conditions is needed for precise evaluation of their efficacy. Following the thermoforming procedure, thermoplastic polymers may experience alterations in their mechanical properties, pointing to the need for testing post-thermoforming (9). Additionally, when used by patients, aligners are exposed to a harsh environment of the oral cavity that can potentially degrade their properties, thereby negatively affecting treatment effectiveness (10). This study aimed to determine changes in elastic modulus, surface roughness, and chemical composition of single and multi-layer TOAs after thermocycling.

Materials and methods

Sample preparation

The 4mm x 10mm dimensions for aligner material testing were used to create specimens of four brands: Duran+ (thickness 0.75mm), CA® Pro (thickness 0.75mm), Zendura A (thickness 0.76 mm), and Zendura FLX (thickness 0.76)

zije. U studijama se ističe da se alignerima postiže oko 50 % preciznosti u svim vrstama ortodontskih pomaka, pri čemu je rotacija najmanje precizna (7). Njihova učinkovitost ovisi o različitim čimbenicima, uključujući korištene materijale i proizvodni proces. Konvencionalni, termoformirani ortodontski aligneri (TOA) sastoje se od termoplastičnih smola poput polivinil klorida (PVC), polietilen tereftalata (PET), polietilen tereftalat glikola (PETG) i poliuretana (PU) (8). Modifikacije u fizikalnim karakteristikama materijala alignera, poput njihove tvrdoće i elastičnog modula, mogu utjecati na isporuku sile i posljedično na učinkovitost liječenja. Procesi termoformiranja i starenja pokazali su utjecaj na svojstva materijala za izradu alignera, ali nedostaje konsenzus o njihovu specifičnom utjecaju (9 – 13). Za sveobuhvatno razumijevanje ponašanja alignera važno je uzeti u obzir mehanički i toplinski stres kojemu su izloženi tijekom svakodnevnog nošenja. Kratkoročni mehanički stres nastaje tijekom umetanja i uklanjanja, a dugoročni zbog interakcije između alignera i nepravilno pozicioniranih zuba te pritiska tijekom žvakanja (14). Uz to, materijali alignera mogu pokazivati pad sile u početnim satima korištenja (15, 16). U dosadašnjim studijama autori su istaknuli da toplinsko i mehaničko opterećenje značajno utječe na mehanička svojstva materijala alignera te rezultira promjenama u tvrdoći, elastičnosti i čvrstoći (13, 17 – 19). Također upozoravaju da te naprave mogu doživjeti promjene u obliku i sastavu u oralnome okruženju zbog čimbenika kao što su temperatura, vlažnost i salivarni enzimi (10, 20, 21). Razumijevanje mehaničkog ponašanja alignera pod različitim stresom ključno je za optimizaciju njihovih performansi. Iako je u ranijim istraživanjima pokazano da se kemijske strukture alignera EX30 ne mijenjaju nakon intraoralnog starenja (10), koliko nam je poznato nije bilo studija u kojima su se ispitivale promjene u kemijskim strukturama alignera PETG, PU i kopoliestera. Zbog kritične važnosti fizikalnih svojstava materijala korištenih u proizvodnji TOA-e, oslanjanje isključivo na tehničke podatke proizvođača možda nije dovoljno. Eksperimentalna procjena tih materijala u različitim uvjetima nužna je za preciznu evaluaciju njihove učinkovitosti. Poslije termoformiranja, termoplastični polimeri mogu promijeniti mehanička svojstva, što upućuje na to da je potrebno testiranje nakon toga postupka (9). Osim toga, kada ih koriste pacijenti, aligneri su izloženi grubom okruženju usne šupljine koje može degradirati njihova svojstva i negativno utjecati na učinkovitost liječenja (10). Ovoj je studiji cilj utvrditi promjene u elastičnom modulu, u hrapavosti površine i kemijskom sastavu jednoslojnih i višeslojnih TOA poslije termocikliranja.

Materijali i metode

Priprema uzoraka

Dimenzije 4 mm x 10 mm korištene su za izradu uzoraka četiriju vrsta alignera: Duran+ (debljina 0,75 mm), CA® Pro (debljina 0,75 mm), Zendura A (debljina 0,76 mm) i Zendura FLX (debljina 0,76 mm) (tablica 1.) (22). Duran+, poznat

Table 1 Manufacturers' information on the tested materials
Tablica 1. Podatci proizvođača o ispitanim materijalima

TOA brand	Product data sheet material • Materijal po proizvođaču	Manufacturer • Proizvođač
Duran +	Polyethylenterephthalat-Glycol Copolyester (PET-G) • Kopoliester polietilentereftalat-glikol (PET-G)	Scheu Dental GmbH, Iserlohn, Germany • Njemačka
CA Pro	ABA three-layer material consisting of Copolyester (A) and thermoplastic elastomer (B) • ABA troslojni materijal koji se sastoji od kopoliestera (A) i termoplastičnog elastomera (B)	Scheu Dental GmbH, Iserlohn, Germany • Njemačka
Zendura A	Thermoplastic polyurethane • Termoplastični poliuretan	Bay Materials, Fremont, CA , USA • SAD
Zendura FLX	Thermoplastic polyurethane and polyester (3-layer) • Termoplastični poliuretan i poliester (3 sloja)	Bay Materials, Fremont, CA , USA • SAD

(Table 1.) (22) Duran+ is known as PETG, a clear copolymer with strong mechanical properties, formability, and resistance to fatigue and deformation. Unlike many thermoplastics, it does not require pre-drying for thermoforming due to its low hygroscopy. Zendura®, categorized as thermoplastic polyurethane (TPU), stands out for its versatility, abrasion resistance, elasticity, and clarity. TPU's unique two-phase microstructure enhances its durability under stress. While, CA Pro and Zendura FLX are considered copolyester blends (20, 23-25). A total of 24 samples from each brand were prepared for the study, with 8 samples allocated to each in vitro aging group.

Thermoforming process

To shape the TOA materials, they were initially heated and exposed to a vacuum process, following the guidelines provided by the manufacturer. This process was carried out on a circular SS (stainless-steel) plate with a diameter of 110 mm and a thickness of 10 mm. The thermoforming procedure was conducted using a BioStar VI vacuum forming machine (Scheu-Dental GmbH, Iserlohn, Germany).

In vitro aging

To assess the durability of the four TOA materials, they were subjected to thermocycling after the thermoforming process. In this study, the samples underwent 500 and 1000 thermocycles using the thermocycler 1100 (SD-Mechatronik, Westerham, Germany) to simulate 7 and 14 days of intraoral use. Gale and Darvell's proposal posits that 10,000 cycles could reasonably replicate around one year of *in vivo* functionality, with a range of 20 to 50 cycles being analogous to the wear endured within a single day (26). Since orthodontic aligners are worn for 7 days, this translates to an equivalence of 350 thermal cycles. Furthermore, following the ISO 11405 guidelines, the application of 500 thermal cycles spanning temperatures from 5°C to 55°C is recognized as suitable for mimicking the short-term aging of dental materials. Taking this into consideration, our study adopted 500 and 1000 thermal cycles to simulate the intraoral usage of orthodontic aligners over periods of 7 and 14 days respectively, ensuring both high reproducibility and methodical consistency (27). Before thermocycling, the samples were submerged in distilled water at a temperature of 37 °C for 24 hours. During the thermocycling process, the samples were exposed to temperatures of 5 °C and 55 °C for a dwelling time of 15 seconds, followed by a dripping time of 10 seconds. Each brand's 24 samples were split into three groups as follows: Group 1 being thermoformed, Group 2 being thermoformed

kao PETG, prozirni je kopolimer s jakim mehaničkim svojstvima, oblikovnošću i otpornošću na zamor i deformaciju. Za razliku od mnogih termoplastika, ne zahtijeva prethodno sušenje za termoformiranje zbog svoje niske higroskopnosti. Zendura®, kategorizirana kao termoplastični poliuretan (TPU), ističe se otpornošću na trošenje te elastičnošću i prozirnošću. Dvofazna mikrostruktura TPU-a povećava njezinu izdržljivost pod stresom. CA Pro i Zendura FLX smatrani su mješavinama kopoliestera (20, 23 – 25). Ukupno 24 uzorka svakog proizvoda pripremljena su za studiju, s 8 uzoraka dodijeljenih svakoj skupini za starenje *in vitro*.

Proces termoformiranja

Za oblikovanje materijala TOA-e inicijalno su zagrijavani i izloženi vakuumskom procesu, slijedeći upute proizvođača. Taj proces proveden je na kružnoj ploči od nehrđajućeg čelika (SS) promjera 110 mm i debljine 10 mm. Postupak termoformiranja obavljen je s pomoću BioStar VI vakuumformirajućeg stroja (Scheu-Dental GmbH, Iserlohn, Njemačka).

Starenje *in vitro*

Da bi se procijenila izdržljivost četiriju materijala TOA-e, poslije termoformiranja bili su podvrgnuti i termocikliranju. U ovoj studiji uzorci su bili 500 i 1000 puta podvrgnuti termociklusima koristeći se termociklerom 1100 (SD-Mechatronik, Westerham, Njemačka) kako bi se simuliralo 7 i 14 dana intraoralne upotrebe. Gale i Darvell ističu da 10 000 ciklusa može simulirati otprilike jednu godinu funkcionalnosti *in vivo*, s rasponom od 20 do 50 ciklusa koji su analogni trošenju tijekom jednog dana (26). Budući da se ortodontski aligneri nose 7 dana, to se prevodi na ekvivalent od 350 termalnih ciklusa. Nadalje, slijedeći smjernice ISO 11405, primjena 500 termalnih ciklusa u rasponu temperatura od 5 °C do 55 °C prepoznata je kao prikladna za simuliranje kratkoročnog starenja dentalnih materijala. Uzimajući to u obzir, naša studija usvojila je 500 i 1000 termalnih ciklusa kako bi simulirala intraoralnu upotrebu ortodontskih alignera tijekom 7, odnosno 14 dana, osiguravajući visoku reproducibilnost i metodološku dosljednost (27). Prije termocikliranja uzorci su bili 24 sata uronjeni u destiliranu vodu na temperaturi od 37 °C. Tijekom procesa termocikliranja uzorci su bili izloženi temperaturama od 5 °C i 55 °C s vremenom zadržavanja od 15 sekunda, poslije čega je slijedilo vrijeme kapanja od 10 sekunda. 24 uzorka svakog proizvođača podijeljena su u tri grupe kako slijedi: grupa 1 – termoformirani, grupa 2 – termoformi i provedeni kroz 500 termociklusa (simulirajuand underwent 500 thermocycles (simulating 7 days), and Group 3 being thermoformed and underwent 1000 thermocycles (simulating 14 days).

Modulus of elasticity in bending (Flexural modulus)

The elastic modulus is a measure of a material's ability to resist temporary deformation, also known as elastic deformation. When subjected to stress, materials initially demonstrate elastic behavior, wherein they deform in response to the stress but return to their original shape once the stress is removed (28). The elastic modulus of the materials was determined through a three-point bending test, conducted on a Mark-10 testing machine with IntelliMESUR® software (Mark-10 Corporation, Copiague, NY, USA), with a span length of 8 mm (22). The specimens were loaded at a speed of 1 mm/min, reaching a maximum deflection of 5 mm (29). Utilizing a mathematical framework grounded in the Euler–Bernoulli beam theory, we conducted calculations for various parameters within the scope of linear elasticity. These calculated values were then contrasted with the measurements taken, enabling a comprehensive comparison between theoretical predictions and actual observed data (30). The elastic modulus, expressed in gigapascals (GPa), was calculated using the equation:

$$E = F_1 * L^3 / (4 * b * h^3)$$

F_1 represents the highest load observed in the linear portion of the load-deflection curve, d corresponds to the deflection magnitude at F_1, l indicates the span length between the supports, b denotes the width of the test sample, and h represents its height measured right before testing.

Surface roughness

Surface roughness measurements were made using a high-precision profilometer, the Mitutoyo SJ-210 surface roughness tester (Mitutoyo, Japan), following the ISO 4287:1997 standard (31). The top sides of the specimen were assessed to determine the roughness parameter Ra. The vertical roughness parameter Ra, considered in this study, represents the average arithmetic deviation of the profile, calculated by dividing the total roughness amplitude by the unit length of the surface. Three replicates per specimen were performed at different locations within a diameter of 5 mm from the center, from which the mean value was calculated and used as the statistical unit.

ATR-FTIR analysis

Infrared spectra were obtained using an Alpha ATR-FT-IR spectrometer (Bruker Optics, Germany) coupled with attenuated total reflectance technique (ATR) with diamond crystal as a single-reflection element. The spectra were acquired over the 4000-400 cm^{-1} range using a resolution of 4 cm^{-1}, and the final spectra were obtained by averaging 10 scans. For the instrument control, baseline correction (concave rubber band correction), spectra normalization, and automatic determination of band wavenumbers (peak picking) OPUS 7.0 software were used. The spectrum of each sample was recorded at least two times to check measurement reproducibility. We employed a precise and meticulous meth-

ći 7 dana) i grupa 3 – termoformirani i provedeni kroz 1000 termociklusa (simulirajući 14 dana).

Modul elastičnosti pri savijanju

Modul savijanja mjera je sposobnosti materijala da se odupre privremenoj deformaciji, također poznatoj kao elastična deformacija. Kada su izloženi naprezanju, materijali inicijalno demonstriraju elastično ponašanje, pri čemu se deformiraju kao odgovor na naprezanje, ali se vraćaju u izvorni oblik kada naprezanje prestane (28). Modul savijanja materijala određen je trotočkastim testom savijanja na testnom uređaju Mark-10 sa softverom IntelliMESUR® (Mark-10 Corporation, Copiague, NY, SAD), s rasponom duljine od 8 mm (22). Uzorci su opterećeni brzinom od 1 mm/min., dosežući maksimalnu defleksiju od 5 mm (29). Koristeći se matematičkim okvirom utemeljenim na teoriji greda Euler-Bernoullija, dobili smo izračune za različite parametre unutar okvira linearne elastičnosti. Te izračunate vrijednosti zatim su uspoređene s izmjerenim vrijednostima, omogućujući sveobuhvatnu usporedbu između teorijskih predviđanja i stvarno promatranih podataka (30). Elastični modul, izražen u gigapaskalima (GPa), izračunat je s pomoću jednadžbe:

$$E = F_1 * L^3 / (4 * b * h^3)$$

F_1 je najveće opterećenje zabilježeno u linearnom dijelu krivulje opterećenja-defleksije, d odgovara veličini defleksije na F_1, l označava raspon duljine između potpora, b označava širinu uzorka ispitivanja, a h njegovu visinu izmjerenu neposredno prije testiranja.

Hrapavost površine

Mjerenja hrapavosti površine provedena su korištenjem visokopreciznog profilometra Mitutoyo SJ-210 testera hrapavosti površine (Mitutoyo, Japan), slijedeći ISO 4287:1997 standard (31). Gornje strane uzorka ocjenjivane su da bi se odredio parametar hrapavosti Ra. Vertikalni parametar hrapavosti Ra, razmatran u ovoj studiji, prosječno je aritmetičko odstupanje profila izračunato dijeljenjem ukupne amplitude hrapavosti s jediničnom duljinom površine. Tri ponavljanja po uzorku obavljena su na različitim mjestima unutar promjera od 5 mm od centra, iz čega je izračunata prosječna vrijednost koja se koristila kao statistička jedinica.

ATR-FTIR analiza

Infracrveni spektri dobiveni su korištenjem spektrometra Alpha ATR-FTIR (Bruker Optics, Njemačka) uparenog s tehnikom atenuirane totalne refleksije (ATR) s dijamantom kao elementom za jednostruku refleksiju. Spektri su snimljeni u rasponu od 4000 do 400 cm^{-1} s rezolucijom od 4 cm^{-1}, a konačni spektri dobiveni su prosječenjem 10 skeniranja. Za kontrolu instrumenta, korekciju osnovne linije (konkavna korekcija gumene trake), normalizaciju spektara i automatsko određivanje valnih brojeva bendova (odabir vrhova) korišten je softver OPUS 7.0. Spektar svakog uzorka sniman je najmanje dva puta da bi se provjerila reproducibilnost mjerenja. Koristili smo se preciznom i temeljitom

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od to isolate the central and outer layers of the material for Fourier Transform Infrared Spectroscopy (FTIR) analysis. To achieve this, we utilized a high-quality precision scalpel manufactured by Fisherbrand (Fisher Scientific Company L.L.C., Pennsylvania, USA). Prior to dissection, the sample was demarcated using a fine-tipped marker to establish a clear guide for the incision. Utilizing a high-precision scalpel, an incision was initiated through the middle at a predetermined point on the sample. During this process, care was taken to exert steady pressure to circumvent tearing or misalignment, thus ensuring the integrity of the sample. After separation, a marker was used to mark outer and inner layer.

Statistical analysis

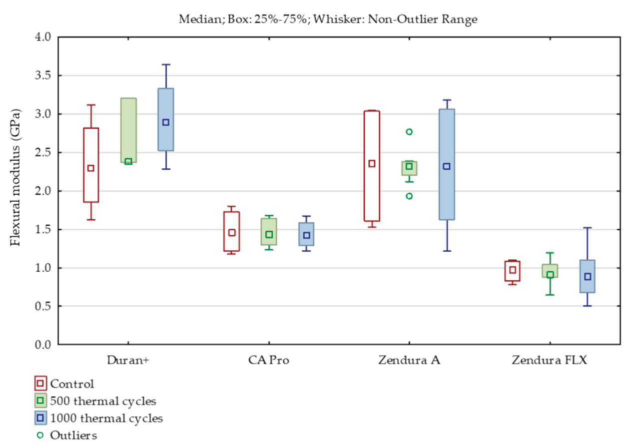
A priori statistical analysis was performed to ensure adequate statistical power in the study. Considering the study design, the comparison of flexural modulus and surface roughness of 4 brands of TOAs after thermoforming, ther-

metodom za izolaciju središnjih i vanjskih slojeva materijala za Fourierovu transformacijsku infracrvenu spektroskopsku (FTIR) analizu. Za to smo upotrijebili visokokvalitetni precizni skalpel proizveden u Fisherbrandu (Fisher Scientific Company L.L.C., Pennsylvania, SAD). Prije disekcije uzorak je obilježen preciznim markerom kako bi se uspostavio jasan vodič za rez. Koristeći se visokopreciznim skalpelom, incizija je počela na unaprijed određenoj točki na uzorku. Tijekom toga procesa pazilo se da se čini stalni pritisak kako bi se izbjeglo kidanje ili nesklad i osiguravalo očuvanje integriteta uzorka. Poslije razdvajanja, markerom su označeni vanjski i unutarnji sloj.

Statistička analiza

A priori statistička analiza provedena je da bi se osigurala adekvatna statistička snaga u studiji. Uzimajući u obzir dizajn studije, usporedba modula savijanja i hrapavosti površine četiriju marki TOA-e poslije termoformiranja, termo-

1



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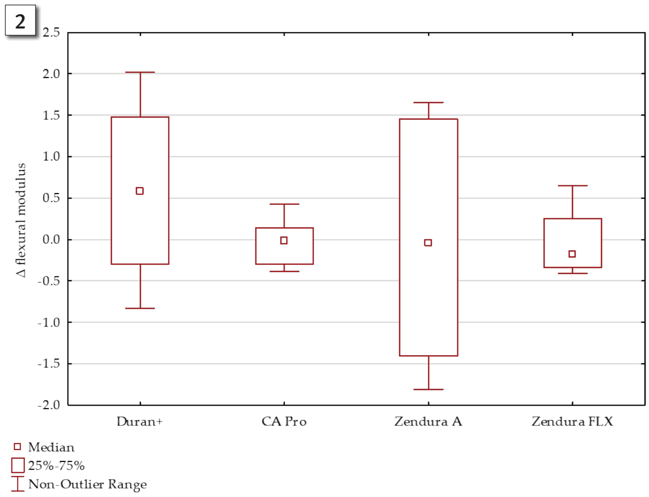

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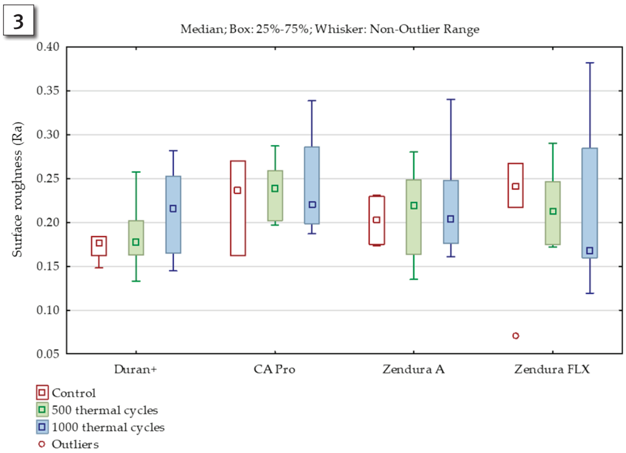

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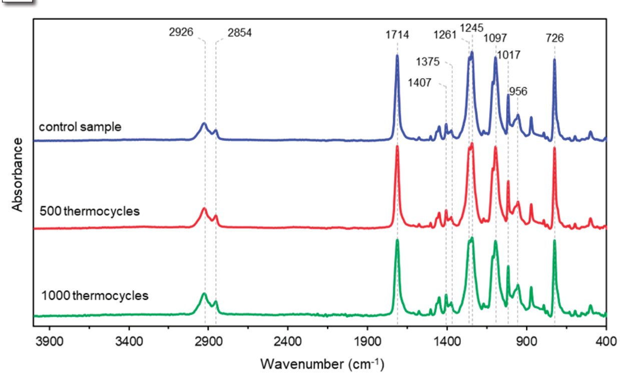
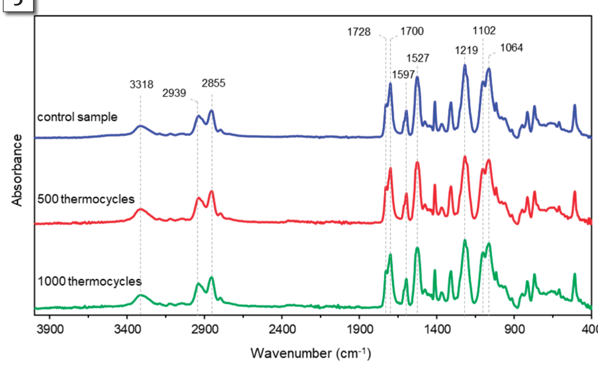


Figure 1 Flexural modulus (GPa) after 500 and 1000 thermocycles.
Slika 1. Modul savijanja (GPa) poslije 500 i 1000 termociklusa
Figure 2 Change in flexural modulus (GPa) after 1000 thermocycles. (Median and interquartile range)
Slika 2. Promjena modula savijanja (GPa) poslije 1000 termociklusa (medijan i interkvartilni raspon)
Figure 3 Surface roughness values (Ra) after 500 and 1000 thermocycles.
Slika 3. Vrijednosti hrapavosti površine (Ra) poslije 500 i 1000 termociklusa
Figure 4 FTIR spectra of the outer layer of Zendura FLX.
Slika 4. FTIR spektri vanjskog sloja Zendure FLX

moforming and 500 thermal cycles, and thermoforming and 1000 thermal cycles indicated F test groups for sample size analysis: ANOVA: Fixed effects, special, main effects, and interactions, effect size f (0.4), α err prob. (0.05), and power (0.8) = 93. Every TOA brand should have 24 samples, 8 in each *in vitro* aging group to achieve the appropriate power. An analysis of data normality using the Shapiro–Wilk test and asymmetry tests revealed a non-normal distribution of flexural modulus and surface roughness values. Change in flexural modulus after 1000 thermal cycles revealed non-normally distributed data, while the change in surface roughness was normally distributed. A comparison between brands was made using the Kruskal-Wallis test and one-way ANOVA test with post-hoc Dunn's and Tukey HSD test, respectively. This analysis was conducted using the program Statistica (TIBCO® Statistica™ Version 14.0.0.15, Palo Alto, CA, USA).

formiranja i 500 termalnih ciklusa te termoformiranja i 1000 termalnih ciklusa, upozorila je na F testne skupine za analizu veličine uzorka: ANOVA: fiksni efekti, posebni, glavni efekti i interakcije, veličina efekta f (0,4), α err prob. (0,05) i snaga (0,8) = 93. Svaka marka TOA-e trebala bi imati 24 uzorka, 8 u svakoj skupini za starenje *in vitro* kako bi se postigla odgovarajuća snaga. Analiza normalnosti distribucije podataka s pomoću Shapiro-Wilkova testa i testova asimetrije otkrila je nenormalnu distribuciju vrijednosti modula savijanja i hrapavosti površine. Promjena u modulu elastičnosti poslije 1000 termalnih ciklusa otkrila je nenormalno raspoređene podatke, a promjena u hrapavosti površine bila je normalno raspoređena. Usporedba između proizvoda obavljena je korištenjem Kruskal-Wallisova testa i jednosmjerne ANOVA-e, s post-hoc Dunnovim i Tukeyevim HSD testom. Ta analiza provedena je u programu Statistica (TIBCO® Statistica™ Verzija 14.0.0.15, Palo Alto, CA, SAD).

5



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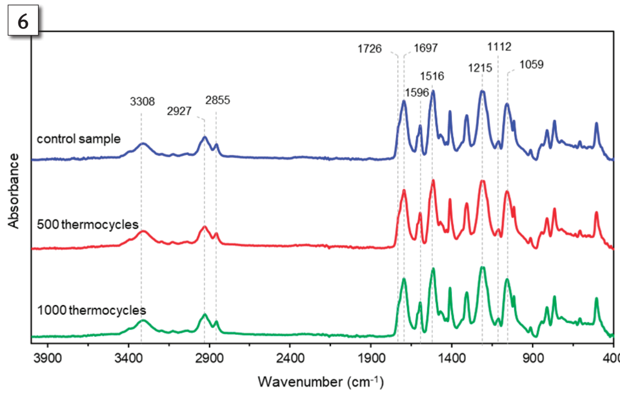

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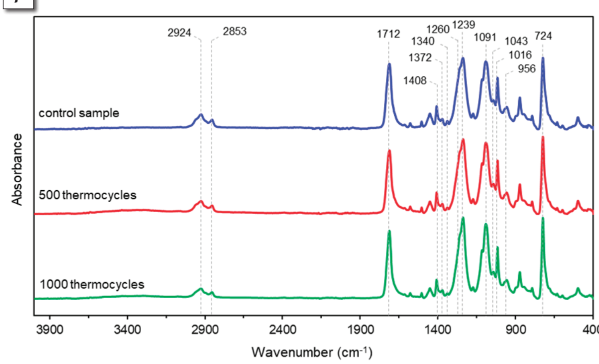

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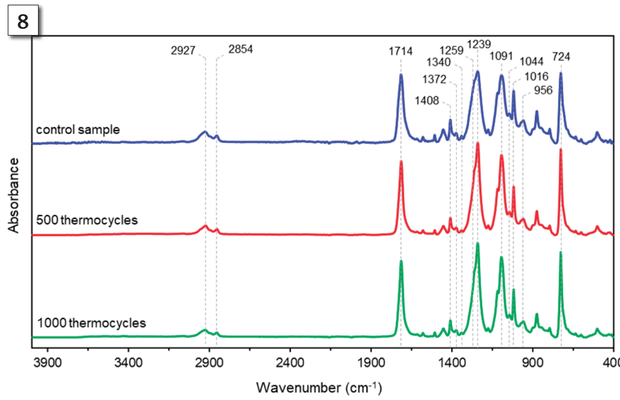

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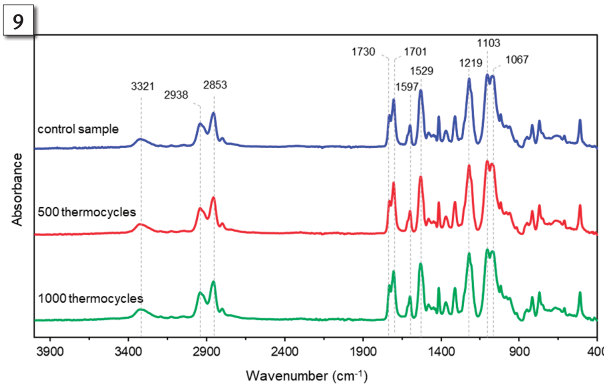

Figure 5 FTIR spectra of the central layer of Zendura FLX.
Slika 5. FTIR spektri središnjeg sloja Zendure FLX
Figure 6 FTIR spectra of Zendura A.
Slika 6. FTIR spektri Zendure A
Figure 7 FTIR spectra of Duran +.
Slika 7. FTIR spektri Durana+
Figure 8 FTIR spectra of the outer layer of CA Pro.
Slika 8. FTIR spektri vanjskoga sloja materijala CA Pro
Figure 9 FTIR spectra of the central layer of CA Pro.
Slika 9. FTIR spektri središnjeg sloja materijala CA Pro

Results

Modulus of elasticity in bending (Flexural modulus)

The *in vitro* aging effect on flexural modulus after 500 and 1000 thermocycles of thermoformed orthodontic aligner (TOA) materials is presented in Figure 1. In the initial values, Duran + had significantly higher modulus values than Zendura FLX (p<.001) and CA Pro (p=.005). After 500 thermocycles, neither brand showed a significant change in modulus (p=.394). Still, significant differences were observed between Duran + and all other brands, Zendura A (p=.048), Zendura FLX, and CA Pro (p<.001). After 1000 thermocycles, as well, no change in modulus was observed in either brand, but Duran + modulus values were significantly higher when compared to the control (initial values) (p<.001). When comparing change from initial values and values after 1000 thermocycles, the highest change in modulus had Duran + (0.78 GPa, IQR 0.41 - 0.95), and significantly differed from all others: Zendura A (p=.026), Zendura FLX (p=.023) and CA Pro (p=.016) (Figure 2). As presented in the figure, Duran + increased, Zendura A slightly decreased and Zendura FLX and CA Pro showed stability.

Surface roughness

The *in vitro* aging effect on surface roughness after 500 and 1000 thermocycles of TOA materials is presented in Figure 3. Initial values (control group) of surface roughness were highest in Zendura A (0.24, IQR 0.2 - 0.27), followed by CA Pro (0.24, IQR 0.22 - 0.25), Zendura FLX (0.2, IQR 0.18 - 0.23), and Duran + (0.18, IQR 0.16 - 0.18). Surface roughness values (Ra), did not statistically differ among brands or thermocycling group measures. The highest change in surface roughness was presented in Duran + after 1000 cycles (0.04 Ra, SD 0.058), while the lowest one was in CA Pro (0.003 Ra, SD 0.11).

Spectrophotometry

FTIR spectra of control aligner samples and the samples subjected to the aging process are shown in Figures 4-9. Zendura FLX is a three-layer aligner material for which the FTIR technique confirmed that the outer layers are made of the same copolymer material based on polyethylene terephthalate glycol (PETG). The FTIR spectrum (Figure 4) is dominated by strong absorption bands attributed to stretching of carbonyl group at 1714 cm^{-1}, vibrational modes of C (=O)-O esters groups visible as weakly separated maxima at 1261 and 1245 cm^{-1}, symmetrical stretching vibrations of C-O glycol bonds at 1097 cm^{-1} as well as out of plane bending vibration of C−H bonds in aromatic ring at 726 cm^{-1}. The in-plane C–H stretching band of the aromatic ring is also present in the spectra and is located at 1017 cm-1. Weak but informative peaks at 1407 cm^{-1} and 1375 cm^{-1} are associated with the in-plane deformation of the aromatic ring and wagging of glycol CH2 groups in gauche conformation, respectively. Medium absorption at 956 cm^{-1} is characteristic for C–H stretching of cyclohexylene ring and represents an important difference between FTIR spectra of PETG and PET that does not contain this band. Other important features of PETG spectra are stretching vibrations of the C–H bonds in methy-

Rezultati

Modul elastičnosti pri savijanju

Učinak starenja *in vitro* na modul elastičnosti pri savijanju poslije 500 i 1000 termociklusa termoformiranih ortodontskih alignera (TOA) prikazan je na slici 1. U početnim vrijednostima Duran+ imao je značajno veće vrijednosti modula od Zendure FLX (p <.001) i CA Proa (p = .005). Poslije 500 termociklusa, ni jedan proizvod nije pokazao značajnu promjenu u modulu (p=.394). Ipak, značajne razlike uočene su između Durana+ i svih ostalih marki – Zendure A (p=.048), Zendure FLX i CA Pro (p < .001). Poslije 1000 termociklusa također nije zapažena promjena u modulu ni u jednom proizvodu, ali su vrijednosti modula Duran+ bile značajno veće u usporedbi s kontrolom (početne vrijednosti) (p < .001). Uspoređujući promjene od početnih vrijednosti i vrijednosti poslije 1000 termociklusa, najveću promjenu u modulu imao je Duran+ (0,78 GPa, IQR 0,41 – 0.95) i značajno se razlikovao od svih ostalih: Zendure A (p =.026), Zendure FLX (p = .023) i CA Pro (p = .016) (slika 2.). Kao što se vidi na slici, Duran+ je porastao, Zendura A je neznatno smanjena, a Zendura FLX i CA Pro pokazali su stabilnost.

Hrapavost površine

Učinak starenja *in vitro* na hrapavost površine poslije 500 i 1000 termociklusa materijala TOA-e prikazan je na slici 3. Početne vrijednosti (kontrolna grupa) hrapavosti površine bile su najveće kod Zendure A (0,24, IQR 0,2 – 0,27), slijedi CA Pro (0,24, IQR 0,22 – 0,25), Zendura FLX (0,2, IQR 0,18 – 0,23) i Duran+ (0,18, IQR 0,16 – 0,18). Vrijednosti hrapavosti površine (Ra) nisu se statistički razlikovale između proizvoda ili režima termocikliranja. Najveća promjena u hrapavosti površine zabilježena je za Duran+ poslije 1000 ciklusa (0,04 Ra, SD 0,058), a najmanja za CA Pro (0,003 Ra, SD 0,11).

Spektrofotometrija

FTIR spektri kontrolnih uzoraka alignera te uzoraka podvrgnutih procesu starenja prikazani su na slikama od 4. do 9. Zendura FLX troslojni je materijal za koji je FTIR analiza potvrdila da su vanjski slojevi napravljeni od istoga kopolimernog materijala na bazi polietilen tereftalat glikola (PETG). FTIR spektar (slika 4.) dominiran je jakim apsorpcijskim trakama pripisanima istezanju karbonilne skupine na 1714 cm^{-1}, vibracijskim modovima C(=O)-O esterskih skupina vidljivima kao slabo odvojeni maksimumi na 1261 i 1245 cm^{-1}, simetričnim istezanjem vibracija C−O glikolnih veza na 1097 cm^{-1} te vanjskom savijanjem vibracija C−H veza u aromatskom prstenu na 726 cm^{-1}. Traka istezanja C–H veza aromatskog prstena također je prisutna u spektru i nalazi se na 1017 cm^{-1}. Slabi, ali informativni vrhovi na 1407 cm^{-1} i 1375 cm^{-1} povezani su s deformacijom u ravnini aromatskoga prstena i mahanjem glikolnih CH_2 grupa u *gauche* konformaciji. Srednja apsorpcija na 956 cm^{-1} karakteristična je za C–H istezanje cikloheksilenog prstena i važna je razlika između FTIR spektara PETG-a i PET-a koji ne sadrži tu traku. Ostale važne značajke spektara PETG-a su istezanja vibracija C–H veza u metilenskim grupama vidljivim na 2926 i 2854 cm^{-1} (32,33).

lene groups visible at 2926 and 2854 cm^{-1} (32, 33).

FTIR spectrum of the central layer in Zendura FLX (Figure 5) shows a profile of polyurethane-based (PU) materials, where the most prominent peaks are connected with characteristic urethane –NH–CO–O– group. The spectrum contains a broad absorption in the range 3420–3210 cm^{-1} with the maximum at 3318 cm^{-1} which originates from stretching vibrations of the N–H bonds, while the non-hydrogen bonded and hydrogen bonded carbonyl groups are represented by weakly separated bands at 1728 cm^{-1} and 1700 cm^{-1}, respectively. Polyurethane systems are also characterized by the bending of the N–H group, which, coupled with the stretching of –C–C and –C–N bonds, contributes to the band at 1527 cm^{-1}. The medium band at 1597 cm^{-1} arises from C=C stretching vibrations in the aromatic ring. Intense vibrational mode at 1219 cm^{-1} is assigned as stretching vibrations of the C–O bond, followed by a region characteristic for C−O−C stretching vibrations (1102 and 1064 cm^{-1}). The C-H stretching region between 3000 and 2800 cm^{-1} exhibits absorptions of antisymmetric and symmetric vibrations of methylene groups (2939 and 2855 cm^{-1}) (32,34).

FTIR analysis of other aligners revealed that Zendura A consists of a single-layer material based on polyurethane (Figure 6), Duran + is PETG (Figure 7), while three-layer CA Pro aligner, as well as Zendura FLX, consists of outer PETG layers (Figure 8) and the central polyurethane-based material (Figure 9). The FTIR spectra of all polyurethane and PETG materials coincide to a large extent.

The FTIR spectra of all PU-based and PETG materials coincide to a significant extent but still with certain differences that could affect their properties. One of them is observed in the spectra of the Duran + aligner and outer layers of the CA Pro aligner. Namely, in comparison with the outer layer of the Zendura FLX aligner, new bands at 1340 and 1044 cm-1 are observed. According to the literature, the band at 1340 cm-1 originates from the wagging of glycol CH2 groups in trans conformation, while the small peak at 1044 cm-1 is assigned as gauche C–O asymmetric stretching (35).

FTIR spectroscopy was also used to monitor possible chemical changes in materials during the aging cycles. Comparing the spectra of control aligner samples with the spectra of samples that have aged in 500 and 1000 thermocycles it was found that none of the analyzed material underwent changes in chemical composition that could be measured by the applied FTIR spectroscopy technique.

Discussion

The importance of having reliable and affordable aligners cannot be overstated. Due to the critical importance of the mechanical properties of materials used in the production of clear aligners, relying solely on technical data provided by suppliers may not be sufficient. Experimental assessment of these materials under various conditions is needed to accurately evaluate their efficacy. The thermoforming process can induce alterations in the mechanical properties of thermoplastic polymers, underscoring the necessity for con-

FTIR spektar središnjega sloja u Zenduri FLX (slika 5.) prikazuje profil materijala na bazi poliuretana (PU) gdje su najistaknutiji vrhovi povezani s karakterističnom uretanskom –NH–CO–O– grupom. Spektar sadržava široku apsorpciju u rasponu od 3420 do 3210 cm^{-1} s maksimumom na 3318 cm^{-1} koji potječe od istezanja vibracija N–H veza, a nevezane i vezane vodikove karbonilne skupine predstavljene su slabo odvojenim trakama na 1728 cm^{-1} i 1700 cm^{-1}. Poliuretanske sustave također karakterizira savijanje N–H skupine koje, u kombinaciji s istezanjem –C–C i –C–N veza, pridonosi traki na 1527 cm^{-1}. Srednja traka na 1597 cm^{-1} nastaje od istezanja C = C vibracija u aromatskom prstenu. Intenzivan vibracijski mod na 1219 cm^{-1} dodijeljen je kao istezanje vibracija C–O veze, te regije karakteristične za C−O−C istezanja vibracija (1102 i 1064 cm^{-1}). Regija istezanja C−H između 3000 i 2800 cm^{-1} pokazuje apsorpcije antisimetričnih i simetričnih vibracija metilenskih grupa (2939 i 2855 cm^{-1}) (32, 34).

FTIR analiza ostalih alignera otkrila je da se Zendura A sastoji od jednoslojnog materijala na bazi poliuretana (slika 6.), Duran+ je PETG (slika 7.), a troslojni CA Pro aligner, kao i Zendura FLX, sastoji se od vanjskih slojeva PETG-a (slika 8.) i središnjeg materijala na bazi poliuretana (slika 9.). FTIR spektri svih poliuretanskih i PETG materijala u velikoj se mjeri podudaraju.

FTIR spektri svih materijala na bazi PU-a i PETG-a u značajnoj se mjeri podudaraju, ali i dalje s određenim razlikama koje bi mogle utjecati na njihova svojstva. Jedna od razlika primijećena je u spektrima alignera Duran+ i vanjskih slojeva CA Pro alignera. Naime, u usporedbi s vanjskim slojem Zendura FLX alignera, uočene su nove trake na 1340 i 1044 cm^{-1}. Prema literaturi, traka na 1340 cm^{-1} potječe od *wagging* glikolnih CH_2 grupa u transkonformaciji, a mali vrh na 1044 cm^{-1} dodjeljuje se kao *gauche* C–O asimetrično istezanje (35).

Spektroskopija FTIR također je korištena za praćenje mogućih kemijskih promjena u materijalima tijekom ciklusa starenja. Usporedbom spektara kontrolnih uzoraka alignera sa spektrima uzoraka koji su podvrgnuti 500 i 1000 puta termociklusima, utvrđeno je da se ni u jednom od analiziranih materijala nisu dogodile promjene u kemijskom sastavu koje bi mogle biti mjerene primijenjenom tehnikom spektroskopije FTIR.

Rasprava

Od iznimne je važnosti da su aligneri pouzdani i pristupačni. Zbog kritične važnosti mehaničkih svojstava materijala korištenih u proizvodnji prozirnih alignera, oslanjanje isključivo na tehničke podatke koje daju proizvođači možda nije dovoljno. Eksperimentalna procjena tih materijala u različitim uvjetima nužna je za točnu evaluaciju njihove učinkovitosti. Proces termoformiranja može inducirati promjene u mehaničkim svojstvima termoplastičnih polimera, što ističe potrebu za provođenjem testova poslije faze termoformiraducting tests after the thermoforming stage (9). Additionally, when used in the oral cavity, aligners are exposed to a harsh environment that can potentially degrade their properties, thereby negatively affecting treatment effectiveness (10). The aim of this study was to investigate the effects of thermocycling on four commonly used TOA materials: Duran+®, Zendura A®, Zendura FLX, and CA Pro® through various tests such as three-point bending, spectrophotometry, and surface roughness measurements. The materials were subjected to thermoforming followed by thermocycling to simulate real-world conditions. By conducting thermocycling, the goal was to identify the materials that maintained optimal mechanical properties even after undergoing in vitro aging, to minimize costs and ensure the effectiveness of orthodontic treatment. Previous research has offered valuable insights into the mechanical characteristics of various thermoplastic materials used in aligners and retainers. However, comparing these studies is challenging due to the diverse array of experimental designs and methodologies employed (22,26,36-41). Furthermore, there is a lack of ISO specifications or national standards particularly addressing the assessment of mechanical properties of TOA materials. While some test standards, such as ISO 20795-2 for orthodontic base polymers (42), have been published and utilized in the literature, they mainly focus on stiffer orthodontic materials that experience more uniform material stress and possess greater thicknesses. An example is the use of polymethyl methacrylate (PMMA) in the fabrication of Hawley retainers (22).

In a previous investigation by Iijima et al. (19), the impact of thermocycling on the mechanical characteristics of TOA materials (PETG, PP, and PU) was examined. The aforementioned TOA materials underwent thermocycling for 500 and 2500 cycles, with temperature variations between 5 and 55 °C. The results showed that after 500 cycles, the hardness values of the materials remained relatively unchanged, while there was a significant decrease in their elastic modulus values. Nevertheless, in contrast to the present study, where most materials exhibited an increase in flexural modulus values after thermocycling, the previous research observed a significant decline in elasticity after 2500 thermal cycles for the majority of thermoplastics. A recent study by Albilali et al. (43) who studied the effects of thermocycling on the mechanical properties of PETG and PU materials, revealed results in agreement with ours, namely that thermocycling leads to an increase in the elastic modulus of the material. Furthermore, the investigation conducted by Dalaie et al. (29) examined the impact of thermocycling on the flexural modulus and hardness of PETG aligner materials, specifically Duran and Erkodur. Their findings revealed a slight increase in the flexural modulus after thermocycling, although this increase did not reach statistical significance. It is worth noting that the limited number of cycles (200) employed in their study might have contributed to that outcome.

Our study indicates that only the PETG material (Duran+) showed a dramatic change in the modulus of elasticity, compared to single-layer and multi-layer PU as well as copolyester, which showed stability, regardless of the number of cycles. Duran + is an amorphous transparent copo-

nja (9). Osim toga, kada se koriste u usnoj šupljini, aligneri su izloženi grubom okruženju koje može degradirati njihova svojstva i negativno utjecati na učinkovitost liječenja (10). Cilj ove studije jest istražiti učinke termocikliranja na četirima često korištenim TOA materijalima: Duran+®, Zendura A®, Zendura FLX i CA Pro® i to različitim testovima kao što su trotočkasto savijanje, spektrofotometrija i mjerenje hrapavosti površine. Materijali su bili podvrgnuti termoformiranju, a zatim termocikliranju da bi se simulirali stvarni uvjeti. Provođenjem termocikliranja cilj je bio identificirati materijale koji su zadržali optimalna mehanička svojstva čak i poslije starenja *in vitro*, kako bi se minimizirali troškovi i osigurala učinkovitost ortodontskog liječenja. Dosadašnja istraživanja omogućila su vrijedan uvid u mehaničke karakteristike različitih termoplastičnih materijala korištenih u alignerima i retainerima. No usporedba tih studija izazovna je zbog raznolikosti eksperimentalnih dizajna i korištenih metodologija (22, 26, 36 – 41). Osim toga, nedostaje ISO specifikacija ili nacionalni standardi posebno usmjereni na procjenu mehaničkih svojstava materijala TOA-e. Iako su neki testni standardi, poput ISO 20795-2 za ortodontske bazične polimere (42), objavljeni i korišteni u literaturi, oni se uglavnom fokusiraju na kruće ortodontske materijale koji doživljavaju uniformnije naprezanje i imaju veću debljinu. Primjer je korištenje polimetilmetakrilata (PMMA) u izradi retainera Hawley (22).

U istraživanju Iijime i suradnika (19) istražen je utjecaj termocikliranja na mehaničke karakteristike materijala TOA-e (PETG, PP i PU). Spomenuti materijali bili su termociklirani u 500 i 2500 ciklusa, s temperaturnim varijacijama između 5 i 55 °C. Rezultati su pokazali da poslije 500 ciklusa vrijednosti tvrdoće materijala ostaju razmjerno nepromijenjene, ali se značajno smanjuju vrijednosti elastičnih modula. No za razliku od ove studije u kojoj je većina materijala pokazala povećanje vrijednosti modula savijanja poslije termocikliranja, u dosadašnjim istraživanjima uočen je značajan pad elastičnosti poslije 2500 termalnih ciklusa za većinu termoplastika. Nedavna studija Albilalija i suradnika (43), koja je istraživala učinke termocikliranja na mehanička svojstva materijala PETG i PU, predstavila je rezultate u skladu s našima, naime, da termocikliranje povećava elastični modul materijala. Također u istraživanju koje je proveo Dalaie sa suradnicima, (29) ispitivao se utjecaj termocikliranja na modul elastičnosti pri savijanju i na tvrdoću materijala alignera PETG, posebno Durana i Erkodura. Njihovi rezultati otkrili su blagi porast modula elastičnosti pri savijanju poslije termocikliranja, iako to povećanje nije dostignulo statističku značajnost. Potrebno je napomenuti da je ograničen broj ciklusa (200) korištenih u njihovoj studiji mogao pridonijeti tom rezultatu.

Naša studija pokazuje da je samo materijal PETG (Duran+) pokazao drastičnu promjenu u modulu elastičnosti u usporedbi s jednoslojnim i višeslojnim PU-om te kopoliesterom koji su pokazali stabilnost, bez obzira na broj ciklusa. Duran+ amorfni je prozirni kopolimer polietilen tereftalata (PET). Ima izvrsna mehanička svojstva, dimenzijsku stabilnost, otpornost na zamor, optičke kvalitete i oblikovljivost (23). Niska mu je higroskopnost i lako se proizvodi zato što prethodno sušenje obično nije potrebno prije termoformiranja. S druge strane, Zendura je klasificirana kao termoplastičlymer of polyethylene terephthalate (PET). It possesses excellent mechanical properties, dimensional stability, fatigue resistance, optical qualities, and formability (23). It has low hygroscopicity and is easily manufacturable, as pre-drying is typically not necessary before thermoforming. On the other hand, Zendura is classified as thermoplastic polyurethane (TPU). It is recognized as one of the most versatile engineering thermoplastics, offering high abrasion resistance, elasticity, good transparency, and excellent shear strength (20,24). TPU possesses a two-phase microstructure composed of soft and hard segments. Under stress, the soft segments tend to orient perpendicularly and subsequently break into smaller pieces, enabling further deformation (25). Elevated temperatures and moist conditions can result in polymer oxidation, which some researchers suggest is the cause behind the observed increase in elastic modulus or stiffness (44). However, copolyesters exhibit low resistance to hydrolysis (45). PET polymers are susceptible to elevated temperatures ranging from 100 to 130 °C, which can result in warping, bending, and deformation (45). Aforementioned, could be a possible explanation for the change in elastic modulus presented in PETG only. Numerous studies have examined the impact of thermal cycling on various mechanical properties of PETG TOA materials (13, 29). However, there is a scarcity of research focusing specifically on the impact of thermal cycling on surface roughness (13, 29). Measurements of surface roughness were conducted after undergoing thermoforming alone and thermoforming followed by thermocycling. In the control group, which involved only thermoforming, no statistically significant differences in surface roughness were observed among the materials, with Zendura A having the highest values and Duran + the lowest. After thermocycling with both regimes, Duran + (PETG) exhibited the highest change in surface roughness compared to single or multilayer PU or copolyester. Moreover, the surface roughness of all materials did not increase significantly after thermocycling. A recent study found that the PETG material demonstrated susceptibility to external factors that can cause instability such as thermocycling and brushing. Thermocycling increased both roughness and mass while brushing predominantly led to an increase in roughness and a decrease in mass (40). A possible explanation for significant results could be a greater number of cycles used (1500) compared to this study. Thermocycling is a method employed to replicate challenging conditions similar to those experienced in the oral environment, involving frequent temperature fluctuations and increased moisture levels over a specified duration (46). When materials are subjected to thermocycling, their mechanical properties change due to both extreme temperature variations and water absorption (13, 46). Thermoplastic materials, including PETG, have been reported to exhibit higher water absorption rates, in comparison to copolyesters, which further contribute to alterations in their mechanical properties (11,13,23,46). When the water absorption of a material increases, it becomes more susceptible to degradation, exhibiting more noticeable signs of deterioration (48). Additionally, research has demonstrated that higher temperatures facilitate greater permeation of water molecules into the material. Consequent-

ni poliuretan (TPU). Prepoznata je kao jedan od najsvestranijih inženjerskih termoplastika jer nudi visoku otpornost na habanje, elastičnost, dobru prozirnost i izvrsnu čvrstoću na smicanje (20, 24). TPU posjeduje dvofaznu mikrostrukturu sastavljenu od mekih i tvrdih segmenata. Pod stresom se meki segmenti teže orijentiraju okomito i poslije se razbijaju u manje komade omogućujući daljnju deformaciju (25). Povišene temperature i vlažni uvjeti mogu rezultirati oksidacijom polimera, što neki istraživači sugeriraju kao uzrok za povećanu elastičnost ili krutost (44). Međutim, kopoliesteri pokazuju nisku otpornost na hidrolizu (45). Polimeri PET-a osjetljivi su na povišene temperature u rasponu od 100 do 130 °C, što može rezultirati savijanjem, uvijanjem i deformacijom (45). Gore spomenuto moglo bi biti objašnjenje za promjenu u elastičnom modulu prikazanom samo u PETG-u. Više studija istraživalo je utjecaj termocikliranja na različita mehanička svojstva materijala TOA-e PETG-a (13, 29). No malo je istraživanja usmjerenih posebno na utjecaj termocikliranja na hrapavost površine (13, 29). Mjerenja hrapavosti površine obavljena su samo poslije termoformiranja i termoformiranja praćenog termocikliranjem. U kontrolnoj skupini, koja je uključivala samo termoformiranje, nije bilo statistički značajnih razlika u hrapavosti površine među materijalima, pri čemu je Zendura A imala najviše vrijednosti, a Duran+ najmanje. Poslije termocikliranja s oba režima, Duran+ (PETG) pokazao je najveću promjenu u hrapavosti površine u usporedbi s jednoslojnim ili višeslojnim PU-om ili kopoliesterom. Nadalje, hrapavost površine svih materijala nije se značajno povećala poslije termocikliranja. Nedavna studija otkrila je da materijal PETG pokazuje osjetljivost na vanjske čimbenike koji mogu prouzročiti nestabilnost, kao što su termocikliranje i četkanje. Termocikliranje je povećalo i hrapavost i masu, a četkanje je uglavnom rezultiralo povećanjem hrapavosti i smanjenjem mase (40). Moguće objašnjenje za značajne rezultate mogao bi biti veći broj ciklusa korištenih (1500) u usporedbi s ovom studijom. Termocikliranje je metoda koja se koristi za repliciranje uvjeta sličnih onima u oralnome okruženju, uključujući česte fluktuacije temperature i povećanu razinu vlage tijekom određenog razdoblja (46). Kada su materijali podvrgnuti termocikliranju, njihova se mehanička svojstva mijenjaju zbog ekstremnih varijacija temperature i apsorpcije vode (13, 46). Termoplastični materijali, uključujući PETG, pokazali su veće stope apsorpcije vode u usporedbi s kopoliesterima, što dodatno pridonosi promjenama njihovih mehaničkih svojstava (11, 13, 23, 46). Kada se poveća apsorpcija vode, materijal postaje osjetljiviji na degradaciju, pri čemu se pojavljuju vidljiviji znakovi propadanja (48). Uz to, istraživanja su pokazala da više temperature olakšavaju veću permeaciju molekula vode u materijal. Stoga, kako se intraoralna temperatura povećava, tako se povećava i količina apsorbirane vode (48). Osim što se suočavaju s izazovima koje postavljaju salivarni enzimi, visoka vlažnost i povremene i kontinuirane sile, retineri su izloženi fluktuacijama temperature (49). Poslije konzumacije toplih napitaka ili jela, temperatura unutar usne šupljine može dosegnuti do 57 °C i može biti potrebno nekoliko minuta da se vrati na svoju početnu vrijednost (49). Mehanička svojstva materijala TOA-e mogu biti negativno pogođena tim fluktuacijama temperature (11, ly, as the intraoral temperature rises, the extent of water absorption also increases (48). In addition to facing challenges posed by salivary enzymes, high humidity, and intermittent and continuous forces, retainers are exposed to fluctuations in temperature (49). Following the consumption of hot beverages or foods, the temperature within the oral cavity can reach up to 57 °C, and it may require several minutes for it to revert to its initial values (49). The mechanical properties of the TOA material can be negatively affected by these temperature fluctuations (11, 19, 29, 49, 50). When a material is exposed to a moist environment, it undergoes a chemical reaction known as hydrolysis, where water reacts with the polymer matrix. This process results in the deterioration of the material through hydrolytic reactions and causes swelling (48, 51). Additionally, water permeates the polymer's structure, acting as a spacer between polymer chains and resulting in hygroscopic expansion (48, 52). In consequence, the weight and volume of TOA specimens increase (53). Previous studies have shown that water primarily penetrates the amorphous regions of polymers, while the crystalline regions remain relatively unaffected (51). PETG is considered to exhibit more stability than other materials in humid environments due to its high degree of crystallinity (53). Furthermore, Zhang et al. (54) suggest that a modified blend of PC, PETG, and TPU material exhibits a lower water absorption rate compared to PETG alone, which is an explanation for greater change in Duran + than in Zendura A, Zendura FLX, and CA Pro in our study. In this study, the impact of aging on clear aligners was examined. However, it is important to consider that factors such as wear (55), brushing (40), and other cleaning protocols (41) have the potential to modify the surface properties of TOA materials. In a recent study (41), the surface roughness of PETG material was investigated after exposure to chemical and mechanical cleaning procedures, namely alkaline peroxide tablets (Corega+), a toothbrush, and a combination of the two. The findings indicate that these cleaning procedures have the potential to alter the mechanical properties of TOA materials. Furthermore, almost all of the tested cleaning methods resulted in a significant increase in the surface roughness of the PETG material. While most of the tested materials, excluding Duran +, demonstrated stability in the modulus of elasticity during *in vitro* aging, it has been confirmed that the outer layers of the three-layer blends consist of PETG, while the inner layers consist of PU. However, it is important to consider the potential factors contributing to the varying modulus of elasticity between Zendura FLX and CA Pro materials. Specifically, Duran + and the outer layers of the CA Pro aligner exhibited a new band at 1340 cm^{-1}, originating from the wagging motion of glycol CH2 groups in the trans conformation. This band is commonly used to assess sample crystallinity, assuming that only trans chains can form crystals and that amorphous regions primarily consist of gauche conformations. However, a detailed analysis of the 1340 cm^{-1} band revealed that using the equations of Belali and Vigourex (56) to extract crystallinity values from oriented PET films is erroneous (57). These equations assume that the crystalline regions are unoriented and the amorphous regions mainly consist of 19, 29, 49, 50). Kada je materijal izložen vlažnom okruženju, nastaje kemijska reakcija poznata kao hidroliza, u kojoj voda reagira s polimernom matricom. Taj proces rezultira propadanjem materijala zbog hidrolitičke reakcije i uzrokuje ekspanziju (48, 51). Nadalje, voda prodire u strukturu polimera te djeluje kao razmak između polimernih lanaca rezultirajući hidroskopskim širenjem (48, 52). Kao rezultat toga povećavaju se težina i volumen uzoraka TOA-e (53). Dosadašnje studije pokazale su da voda primarno prodire u amorfne dijelove polimera, a kristalni dijelovi ostaju relativno netaknuti (51). PETG se smatra stabilnijim od drugih materijala u vlažnim okruženjima zbog visokoga stupnja kristalnosti (53). Nadalje, Zhang i suradnici (54) sugeriraju da modificirana mješavina PC, PETG i TPU materijala pokazuje nižu stopu apsorpcije vode u usporedbi samo s PETG-om, što je objašnjenje za veću promjenu u Duranu+ u usporedbi sa Zendurom A, Zendurom FLX i CA Proom u našoj studiji. U ovoj studiji istražen je utjecaj starenja na prozirne alignere. No važno je uzeti u obzir da čimbenici kao što su trošenje (55), četkanje (40) i drugi protokoli čišćenja (41), imaju potencijal za mijenjanje površinskih svojstava materijala TOA-e. U nedavnoj studiji (41) istraživana je hrapavost površine materijala PETG poslije izlaganja kemijskim i mehaničkim postupcima čišćenja, naime alkalnim peroksidnim tabletama (Corega+), četkicom za zube i njihovom kombinacijom. Rezultati upozoravaju na to da ti postupci čišćenja imaju potencijal za promjenu mehaničkih svojstava materijala TOA-e. Nadalje, gotovo sve testirane metode čišćenja rezultirale su značajnim povećanjem hrapavosti površine materijala PETG. Iako je većina testiranih materijala, osim Durana+, pokazala stabilnost u modulu elastičnosti tijekom starenja *in vitro*, potvrđeno je da se vanjski slojevi troslojnih mješavina sastoje od PETG-a, a unutarnji od PU-a. No važno je uzeti u obzir potencijalne čimbenike koji pridonose različitom modulu elastičnosti između materijala Zendura FLX i CA Pro. Konkretno, Duran+ i vanjski slojevi alignera CA Pro pokazali su novu traku na 1340 cm^{-1} koja potječe od kretanja *wagging* glikolnih CH_2 grupa u transkonformaciji. Ta se traka često koristi za procjenu kristalnosti uzoraka, pretpostavljajući da samo translanci mogu formirati kristale i da se amorfna područja uglavnom sastoje od *gauche* konformacija. No detaljna analiza trake na 1340 cm^{-1} otkrila je da je korištenje jednadžbi Belalija i Vigourexa (56) za izvlačenje vrijednosti kristalnosti iz orijentiranih PET filmova pogrešno (57). Te jednadžbe pretpostavljaju da su kristalne regije neorijentirane i da se amorfne regije uglavnom sastoje od *gauche* konformera. U slučaju orijentiranih uzoraka, broj transkonformera u amorfim regijama značajno se povećava, što dovodi do umjetno visokog očitanja kristalnosti za traku na 1340 cm^{-1} (57). Budući da se zna da povećana kristalnost poboljšava modul savijanja i čvrstoću u polimerima, ta razlika objašnjava razliku u modulu elastičnosti pri savijanju između proizvoda CA Pro i Zendura FLX, oba od kojih su PETG/PU mješavine.

U ovoj studiji je trošenje materijala TOA-e simulirano termocikliranjem tijekom 7 i 14 dana. No važno je priznati da bi to moglo biti ograničenje studije jer broj termalnih ciklusa možda ne odgovara točnom broju dana starenja TOA materijala. Ograničenje ove studije potencijalna je prisutnost

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gauche conformers. In the case of oriented specimens, the number of trans conformers in the amorphous regions significantly increases, leading to an artificially high crystallinity reading for the 1340 cm^{-1} band (57). Since increased crystallinity is known to enhance Young's modulus and strength in polymers, this discrepancy explains the difference in modulus of elasticity between CA Pro and Zendura FLX, both of which are PETG/PU blends.

In this study, the wear of the TOA material was simulated through thermocycling for 7 and 14 days. However, it is crucial to acknowledge that this may be a limitation of the study as the number of thermal cycles may not precisely correspond to the exact number of days of aging of the TOA material. A limitation of this study is the potential presence of changes in the materials that, while detectable at a microscopic or molecular level, may not have a discernible clinical impact or affect patient outcomes. The use of standardized rectangular samples in this study is a limitation, since in clinical practice, TOAs are individually formed based on a plaster or 3D-printed model that replicates the patient's teeth. The absence of evaluating TOAs shaped to match the patient's dentition may have overlooked potential differences resulting from sample shape variations. Despite incorporating the respective thicknesses of 0.75 mm and 0.76 mm into our calculations for the modulus, a limitation of our study remains the assumption that this minor variation in thickness between materials does not substantially affect the overall mechanical property results. Moreover, thermocycling was carried out without any external force or loading. In reality, however, the aging process of the orthodontic aligner will occur under stress. Thermocycling treatments might not offer sufficient data to simulate real-world problems. Further research is required to provide more comprehensive findings. Additionally, it is important to assess the materials' tear strength, tensile strength, and creep. Furthermore, clinical studies should be conducted to investigate the effects of intraoral aging on the properties of diverse materials employed in the fabrication of TOAs.

Conclusion

One-layer PETG (Duran+) failed to demonstrate stability after *in vitro* aging, suggesting that clinicians should be aware of the change in mechanical properties when using it in a 2-week regime. Although both three-layer blends consist of PETG, while the inner layers consist of PU, the wagging of glycol CH2 groups in trans conformation are contributing factors to the varying modulus of elasticity between Zendura FLX and CA Pro materials.

Conflict of interest

The authors report no conflict of interest.

Author's contribution: **S. M.** – Supervision Project; **L.Š., K.S.** and **S.M** – Conceptualization and Methodology; **A. J., S. M.** – Validation, **L. Š., I. B.** – Investigation; **L. Š., I. B.** – Formal analysis; **L. Š.** – Data curation; **L. Š., S. M.** – Writing - Original draft; **A. J., K. S., I. B.**– Writing - Reviewing and Editing. All authors approved the final version.

promjena u materijalima koje, iako detektibilne na mikroskopskoj ili molekularnoj razini, možda nemaju jasno kliničko značenje ili utjecaj na ishode pacijenata. Ograničenje je i korištenje standardiziranih pravokutnih uzoraka u ovoj studiji, zato što se u kliničkoj praksi TOA individualno oblikuje na temelju sadrenoga ili 3D-ispisanoga modela koji replicira zube pacijenta. Izostanak evaluacije TOA oblikovanih prema zubima pacijenta mogao je zanemariti potencijalne razlike koje proizlaze iz varijacija oblika uzoraka. Unatoč uključivanju debljina od 0,75 mm i 0,76 mm u naše izračune za modul, ograničenje za ovu studiju ostaje pretpostavka da ta manja varijacija u debljini između materijala ne utječe značajno na ukupne rezultate mehaničkih svojstava. Nadalje, termocikliranje je provedeno bez vanjskog opterećenja. No u stvarnosti proces starenja ortodontskog alignera bit će pod naprezanjem. Samo termocikliranje možda neće pružiti dovoljno podataka za simulaciju stvarnih problema. Potrebna su daljnja istraživanja da bi se dobili sveobuhvatniji rezultati. Uz to, važno je procijeniti čvrstoću na kidanje te čvrstoću na zatezanje i puzanje materijala. Trebale bi se također provesti kliničke studije da bi se istražili učinci intraoralnog starenja na svojstva različitih materijala korištenih u izradi TOA-e.

Zaključak

Jednoslojni PETG (Duran+) nije pokazao stabilnost poslije starenja *in vitro*, što sugerira da bi kliničari trebali biti svjesni promjene u mehaničkim svojstvima pri korištenju u režimu od 2 tjedna. Iako se oba troslojna sastoje od PETG-a u vanjskom sloju te od PU-a u unutarnjem sloju, kretanje *wagging* glikolnih CH2 grupa u transkonformaciji čimbenik je koji pridonosi različitom modulu elastičnosti između materijala Zendura FLX i CA Pro.

Sukob interesa

Autori nisu bili u sukobu interesa.

Doprinos autora: **S. M.** – nadzor projekta; **L. Š., K. S. i S. M** – konceptualizacija i metodologija; **A. J., S. M.** – validacija; **L. Š., I. B.** – istraživanje; **L. Š., I. B.** – formalna analiza; **L. Š.** – upravljanje podatcima; **L. Š., S. M.** – pisanje teksta, izvorni nacrt; **A. J., K. S., I. B.** – pisanje teksta recenziranje i uređivanje; Svi autori odobrili su konačnu verziju teksta.

Sažetak
Cilj: Za optimizaciju uspjeha terapijom alignerima, ključno je razumijevanje kako se njihova mehanička svojstva mijenjaju tijekom vremena. **Materijali i metode:** Uzorci četiriju različitih tvrtki, uključujući Duran+, CA® Pro, Zendura A i Zendura FLX, proizvedeni su za ispitivanje materijala termoplastičnih ortodontskih alignera (TOA) u dimenzijama 4 mm x 10 mm. Dvadeset četiri uzorka svakog proizvođača podijeljena su u tri skupine: G1– termoformirani, G2 – termoformirani i 500 puta podvrgnuti termociklusima (simulira 7 dana) i G3 – termoformirani i 1000 puta podvrgnuti termociklusima (simulira 14 dana). Za procjenu učinka starenja na TOA-u korištene su mjerenje hrapavosti površine, modul elastičnosti pri savijanju i spektrofotometrija. **Rezultati:** Poslije 1000 termociklusa, Duran+ imao je najveći modul elastičnosti i statistički se razlikovao od svih drugih skupina. Usporedba unutar skupine pokazala je da se samo elastični modul Durana+ značajno promijenio poslije 1000 termociklusa u usporedbi s kontrolnom skupinom. Vrijednosti hrapavosti površine (Ra) nisu se statistički razlikovale među uzorcima ili mjerama termociklusnih skupina. Promjena kemijskih svojstava nije bila značajna ni u jednom slučaju. **Zaključak:** Jednoslojni PETG (Duran+) nije pokazao stabilnost poslije starenja *in vitro*, što sugerira da kliničari trebaju biti svjesni promjene mehaničkih svojstava pri korištenju jednoslojnoga PETG-a (Duran+) u režimu od 2 tjedna.

Zaprimljen: 25. listopada 2023.
Prihvaćen: 1. prosinca 2023.

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MeSH pojmovi: ortodontske naprave; ispitivanje materijala
Autorske ključne riječi: aligneri, ortodontska naprava, mehanička svojstva, kemija

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