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# Chemical and mechanical characteristics of contemporary thermoplastic orthodontic materials

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*Aim:* The aim of the present study was to characterise the chemical and mechanical properties of contemporary thermoplastic orthodontic materials.

*Materials and methods:* Four thermoplastic materials were tested: Clear Aligner (Scheu-Dental), ACE and A+ (Dentsply), and Invisalign (Align Technology). Eight appliances were fabricated from each material and a small portion from each was analysed by ATR-FTIR spectroscopy. The appliances were cut and, following metallographic grinding and polishing, were subjected to instrumented indentation testing (IIT) employing a Vickers indenter. Martens Hardness (HM), Indentation Modulus ( $E_{IT}$ ), Elastic to Total Work Ratio (elastic index ( $\eta_{IT}$ )) and Indentation Creep ( $C_{IT}$ ) were determined according to ISO 14577-1. The mean values of the mechanical properties were statistically analysed by one way ANOVA and Tukey Kramer multiple comparison test at  $\alpha = 0.05$ .

*Results:* ATR-FTIR analysis identified that Invisalign was a polyurethane-based material, whereas the others were based on polyester, polyethylene glycol terephthalate (PETG). Invisalign showed higher hardness and modulus values, a slightly higher brittleness and lesser creep resistance compared with the PETG-based products.

*Conclusions:* The materials tested showed significant differences in their chemical structure and mechanical properties and therefore differences in their clinical behaviour are anticipated.

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## Introduction

Recent surveys<sup>1-3</sup> have shown that aesthetics is a major concern of patients wishing to receive orthodontic treatment. Therefore, lingual and aesthetic ceramic brackets as well as clear aligners have been introduced as alternative therapies to metallic brackets and wires.<sup>2,4</sup> Conventional metal brackets are aesthetically acceptable to only 55% of patients.<sup>2</sup> With regard to adult preferences of appliances, over 90% accept aesthetic appliances, with clear retainers accepted

as the appliance of choice for both adults and adolescents.

Although previous studies have indicated that treatment efficacy with clear aligners has varied from 41% to 59%,<sup>5,6</sup> orthodontic research is still attempting to improve this outcome by optimising associated parameters. Orthodontic forces exerted by clear aligners are of concern<sup>7-10</sup> because the forces are partially governed by the thickness and mechanical properties of the appliance's thermoplastic

material.<sup>10,11</sup> Previous studies have recorded significant force variation during clear aligner therapy, as an aligner with high initial force may be followed by an aligner with low force, resulting in inconsistent tooth movement.<sup>8</sup> As a result, changes in the mechanical properties of different systems or changes developed intra-orally during orthodontic treatment may have an impact on treatment outcome.<sup>11</sup> Clements et al.<sup>12</sup> demonstrated that stiffer aligner materials produced better results in tooth alignment following a two-week activation time. However, beyond the initial mechanical properties, intra-oral ageing during mechanotherapy resulted in an exponential deterioration of the material's viscoelasticity over time.<sup>13</sup> This resulted in compromised force delivery and treatment efficacy.

Although a clearer understanding of the material properties and the effects of material ageing may lead to better sequencing of tooth movement, the mechanical properties of contemporary thermoplastic materials used for the production of clear aligners remain unknown. Therefore, the aim of the present study was to characterise the chemical structure and mechanical properties of contemporary thermoplastic materials. The null hypothesis would state that there are no significant differences in the chemical structure, mechanical properties and molecular composition of commonly used materials.

## Materials and methods

### *Specimen preparation*

The study materials are listed in Table I. Eight thermoplastic sheets from each listed material were pressed over a dental stone model according to the manufacturer's instructions, employing the 'Essix Machine' for APL and CLA and the Ministar S (Scheu-Dental, Iserlohn, Germany) for ESA. Eight models for the same patient with no history of intra-oral exposure were used for the Invisalign group.

### *ATR-FTIR spectroscopy*

A sample piece (approximately 5 × 5 mm) was cut from each aligner and removed from the labial surface of the central incisors. The chemical composition of the material was investigated by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The eight specimens of each group were

Table I. Brand name, manufacturer and code for the materials tested.

Brand name	Manufacturer	Code
A+	Dentsply Raintree Essix Sarasota, FL, USA	APL
Clear Aligner	SCHEU-DENTAL GmbH, Iserlohn, Germany	CLA
Essix ACE Plastic	Dentsply Raintree Essix Sarasota, FL, USA	ESA
Invisalign	Align Technology, San Jose, CA, USA	INV

placed against the diamond reflective elements of a single reflection ATR accessory equipped with SnSe lenses (Golden Gate, Specac Inc., Smyrna, GA, USA). The buccal surface was pressed with a sapphire anvil to achieve firm contact with the diamond crystal. Spectra were acquired using an FTIR spectrometer (Spectrum GX, Perkin-Elmer Corp, Bacon, UK) operated under the parameters of 4000–650 cm<sup>-1</sup> range, 4 cm<sup>-1</sup> resolution and 20 scans co-addition. All spectra were subjected to ATR and baseline corrections. The depth of analysis was estimated at 2 μm at 1000 cm<sup>-1</sup>.

### *Instrumented indentation testing (IIT)*

Additional samples were cut from the labial surface of the central incisors of each aligner and embedded in cold-cure acrylic resin (VersoCit-2, Struers, Ballerup, Denmark). The specimens were ground with SiC water coolant papers up to 4000 grit and polished with a diamond suspension (DiaPro, Struers) employing a grinding/polishing machine (Dap-V, Struers). All specimens were subjected to instrumented indentation testing (IIT), using a universal hardness testing machine (ZHU0.2/S2.5, Zwick Roell, Ulm, Germany) equipped with a Vickers indenter. Three force-indentation depth curves were generated from each specimen under a 4.9 N load and a 2 second contact period for the evaluation of Martens Hardness (HM), indentation modulus ( $E_{IT}$ ), elastic index ( $\eta_{IT}$ ) (defined as the elastic to total work ratio) and a 120 second contact period for indentation creep ( $C_{IT}$ ). The latter is defined as the percentage increase in indentation depth under constant loading over a given period. All properties were measured according to the international standard ISO 14577-1, 2002<sup>14</sup> and the mean values of three measurements were used to characterise the specimen.

### Statistical analysis

The results of HM,  $E_{IT}$ ,  $\eta_{IT}$  and  $C_{IT}$  were statistically analysed by one way ANOVA and Tukey Kramer post hoc multiple comparison tests employing material type as a discriminating variable. The level of significance was set at  $\alpha = 0.05$ .

### Results

Figure 1 illustrates representative ATR-FTIR spectra from all materials tested. The Invisalign identified characteristic molecular bands of OH ( $3380\text{ cm}^{-1}$ ), NH ( $3313\text{ cm}^{-1}$ ), aromatic C-H ( $3047, 1605, 1597, 812, 766\text{ cm}^{-1}$ ), C-H ( $2928, 2853, 1413, 915\text{ cm}^{-1}$ ), C=O ( $1728, 1308\text{ cm}^{-1}$ ), amide I (C=O of NCO,  $1698\text{ cm}^{-1}$ ), amide II (N-H and C=O of NCO,  $1518\text{ cm}^{-1}$ ), C-O ( $1214$  and  $1205\text{ cm}^{-1}$ ) and C-O-C ( $1100-1060\text{ cm}^{-1}$ ). The remaining three materials demonstrated identical spectra (Figure 1) with characteristic bands of CH ( $2928, 2853, 1413, 1010, 716\text{ cm}^{-1}$ ), C=O ( $1724\text{ cm}^{-1}$ ), Aromatic CH ( $1505\text{ cm}^{-1}$ ) and C-C-O- ( $1246, 1083\text{ cm}^{-1}$ ).

Figure 2a depicts representative force indentation depth curves for all materials tested. The shift towards higher

indentation depth indicates a softer material. Figure 2b presents representative indentation depth-time curves under constant loading from all materials tested. The indentation depth increased and reached a maximum value after 60 to 80 seconds. The results of the mechanical properties tested are presented in Table II. APL and CAL showed intermediate HM values while  $E_{IT}$  was significantly different from all tested materials. APL and ESA depicted intermediated  $\eta_{IT}$  while INV demonstrated significantly higher  $C_{IT}$  values.

### Discussion

Based on the experimental results of the present study, the null hypothesis is rejected, as significant differences were identified in the chemical structure and mechanical properties of the materials tested.

The ATR-FTIR analysis showed that INV is made of a polyurethane-based material, a finding that is in accordance with previous studies.<sup>15</sup> However, the three other materials (APL, ESA and CLA) showed identical spectra which matched that of polyethylene glycol terephthalate (PETG), a material that has been extensively used for orthodontic retainers.<sup>16-18</sup>

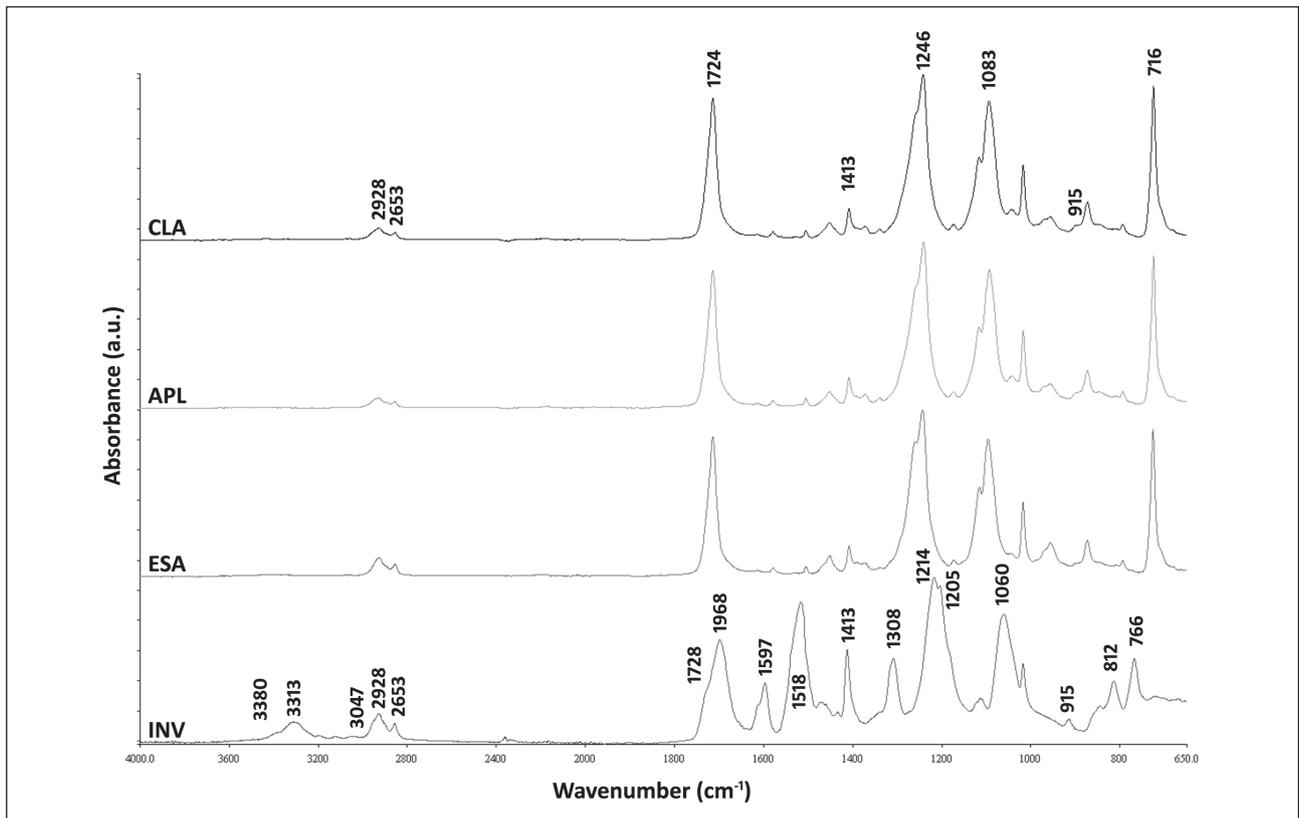


Figure 1. Representative ATR-FTIR spectra of the materials tested.

In general, determining mechanical properties by conventional testing requires bulky specimens of specific dimensions.<sup>13,17,18</sup> Testing of the various mechanical properties of orthodontic appliances can be a complex and difficult task if the devices are tested directly, because the material specimens should geometrically correspond to the actual conditions of use. This is to simulate functional loading effects and to include the influence of the thermoforming process in the material mechanical properties.<sup>17</sup> Moreover, since Invisalign is manufactured and delivered exclusively as an orthodontic appliance, the procurement of a large specimen is unlikely. Nevertheless, the limitations can be overcome by IIT, in which a variety of mechanical properties can be derived from a single hardness measurement by evaluating the applied force against the indentation depth during a loading-unloading cycle.<sup>11,14</sup>

According to the results of the mechanical testing (Table II), INV showed significantly higher values compared with the other tested materials for Hardness, Modulus and Elastic Index but lower Creep Resistance. This finding can be ascribed to the different chemical structure between the materials.

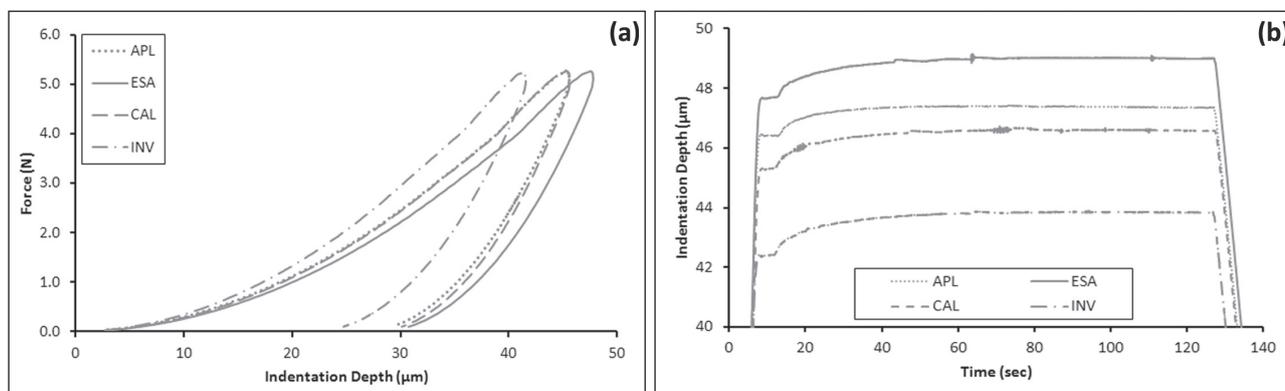
Significant differences were also identified between APL, ESA and CLA, which are all made of PETG. These differences might be attributed to two factors, one of which is a different molecular weight of the various PETGS polymers, undetected by ATR-FTIR, and the second of which is the thermoforming effect on the mechanical properties. Thermoforming may influence the molecular orientation, mean molecular weight and residual stresses due to rapid cooling of the thermoplastic materials on the stone models.<sup>17</sup> However, the contribution of all factors requires further analysis, which was considered to be beyond the scope of this study.

The mechanical properties of the test materials may have different clinical implications. The HM of the materials was found to be within the range of 80 to 160 N/mm<sup>2</sup> as reported in previous studies.<sup>11,19</sup> However, the HM method was preferred rather than the traditional Vickers hardness test to eliminate the material rebound effect that occurs around the indentation and distorts a measured hardness value. Since HM is measured automatically during testing, it does not incur the limitations of indentation size effects.<sup>20</sup> Hardness is indicative of wear resistance and

**Table II.** Mean values and standard deviations in parentheses of Martens Hardness (HM), Indentation modulus ( $E_{IT}$ ), elastic index ( $\eta_{IT}$ ), and indentation creep ( $C_{IT}$ ) of materials tested.

Material	HM (N/mm <sup>2</sup> )	$E_{IT}$ (GPa)	$\eta_{IT}$ (%)	$C_{IT}$ (%)
APL	100.0 (0.7) <sup>a</sup>	2256 (40) <sup>a</sup>	35.9 (0.6) <sup>a</sup>	2.2 (0.3) <sup>a</sup>
ESA	91.8 (0.8) <sup>b</sup>	2112 (16) <sup>b</sup>	35.7 (0.2) <sup>a</sup>	2.6 (0.4) <sup>a</sup>
CAL	100.6 (0.6) <sup>a</sup>	2374 (4) <sup>c</sup>	34.0 (0.1) <sup>b</sup>	2.7 (0.5) <sup>a</sup>
INV	117.8 (1.1) <sup>c</sup>	2467 (19) <sup>d</sup>	40.8 (0.2) <sup>c</sup>	3.7 (0.3) <sup>b</sup>

Similar superscripts indicate mean values with no statistically significant differences ( $p > 0.05$ ).



**Figure 2.** (a) Representative force-indentation depth curves for all materials tested. The increase in indentation depth denotes a softer material. (b) Representative indentation creep curves for all materials tested showing the indentation depth as a function of time. In all cases the application of a constant load resulted in increasing indentation depth.

therefore INV was expected to demonstrate better wear resistance under clinical conditions. Previous studies have reported that PETG materials have higher wear resistance compared with polypropylene materials<sup>16</sup> but there is no similar comparison between PETG and PU based materials. The results of indentation moduli were found in accordance with the previous data<sup>11</sup> and ranged between 1500 and 2700 MPa.

A higher modulus of elasticity is a desirable property as it increases the force delivery capacity of appliances under constant strain. Alternatively, appliances made of materials of higher modulus of elasticity can provide the same forces from thinner dimensions.<sup>11</sup> The higher elastic index of INV denotes a slightly more brittle material compared with the other test materials, while the higher indentation creep of INV implies that under constant occlusal forces exerted by the opposing dentition, INV is more likely to deform and therefore attenuate the applied orthodontic forces.

In summary of the findings of the present study, INV showed a preferred combination of higher hardness and modulus but less creep resistance. Despite the statistically significant differences identified between the materials tested, there was no clinical evidence to indicate that differences in the material mechanical properties would have a significant influence on treatment outcome or the intra-oral behaviour of the thermoplastic materials. This assessment requires further evaluation by controlled clinical studies in order to select the optimal material. In addition, a controlled clinical study might also provide useful information to determine the optimal wear resistant period, as the in vivo deterioration of the material mechanical properties occurs.

## Conclusions

The contemporary thermoplastic materials tested were made of polyurethane (Invisalign) and polyethylene glycol terephthalate glycol (A+, Clear Aligner, Essix ACE Plastic).

Invisalign showed the highest elastic modulus and hardness but inferior creep resistance compared with the polyethylene glycol terephthalate materials. Significant differences were found in the mechanical properties between the appliances made of polyethylene glycol terephthalate, but their effect on clinical outcome should be further investigated.

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