

Materials for Clear Aligners—A Comprehensive Exploration of Characteristics and Innovations: A Scoping Review

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Abstract: Introduction: Transparent orthodontic aligners have revolutionized dentistry and orthodontics since the 1990s, offering advantages over traditional fixed appliances in terms of hygiene, comfort, and aesthetics. With the increasing demand for invisible orthodontic treatments, clear aligners have gained popularity, prompting research into materials to enhance their efficacy and performance. Materials and Methods: A scoping review was conducted using electronic databases (Pubmed, Medline, Cochrane Library, Embase, and Scopus) to identify studies on clear aligner materials published in the last decade. Selection criteria focused on studies specific to dental materials, excluding those unrelated to materials or clear aligners. Results: The review included 11 relevant studies evaluating 17 different clear aligner materials. Materials such as polyvinyl chloride derivatives, thermoplastic polyurethanes (TPU), and polyethylene terephthalate glycol (PETG) were commonly used. The studies assessed mechanical, physical, chemical, and optical properties, as well as thermoforming effects, stress decay, and surface characteristics. Discussion and Conclusions: Various materials exhibited distinct properties, with PETG materials offering transparency and flexibility, while TPU-based materials like Smart Track providing durability and elasticity. Thermoforming affected mechanical properties, with both PETG and TPU materials showing decreased efficacy post-thermoforming. Polymer blending improved mechanical properties, but variations existed among different brands and materials. Clear aligner materials exhibit diverse characteristics, influencing their suitability for orthodontic use. PETG-based materials offer transparency and flexibility, while TPU-based materials provide durability and elasticity. However, both materials undergo mechanical changes post-thermoforming, emphasizing the need for further research to optimize material performance for clinical use.

Keywords: orthodontics appliance; clear aligners; thermoplastic polymers; simulated oral environment; mechanical properties; physical properties; chemical properties



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1. Introduction

Since the 1990s, the development and diffusion of transparent orthodontic aligners has created a real revolution in the field of dentistry and orthodontics. These aligners are thin sequential aligners made of plastic material, removable, and personalized for each patient; each tray is programmed to perform a certain movement in order to replace the classic fixed orthodontics characterized by metal or ceramic brackets and wires [1,2]. This makes it possible to maintain better oral hygiene and often to overcome discomfort and aesthetic discomfort, two factors which, especially in the adult patient, do not encourage the start of orthodontic treatment [1,3,4].

The diffusion of clear aligners is rapidly expanding to overcome the disadvantages of conventional treatment, including, for example, lip discomfort and unattractive appearance.

Furthermore, the growing desire for “invisible” alternative treatments has contributed to the spread of mass-used clear aligners, a set of dental positioners based on precise impressions or digital scans of the patient’s teeth. The main advantages are the transparent appearance of the devices and the possibility of extracting them when eating while maintaining oral hygiene, together with greater comfort and ease of use. Treatment with clear aligners has a shorter duration and requires less chair time than traditional fixed appliances [5,6].

To date, it is estimated that more than seven million people worldwide have already been treated with this type of mask, a number that is constantly growing thanks to the progressive improvement of the product and technique. Creating aligners involves several complex steps, summarized as follows: intraoral scanning of the patient, creation of a dental model using 3D printing, and finally, thermoforming the aligners over the physical model [7]. Furthermore, recently, the development of 3D printing and biocompatible resins for the dental sector has led to the advent of a new generation of transparent orthodontic aligners, no longer made up of thermo-molded plastic material on the relative dental arch models but printed directly in transparent resin resulting in less material waste. In this situation of the rapid and constant development of the sector, it is therefore proposed to make the production of aligners evolve toward materials that can be increasingly effective and performing (Figure 1). The aim of this review is to identify the materials reported in the literature for thermoformed aligners, which are currently more widely used, and to evaluate their characteristics [2,7–9].

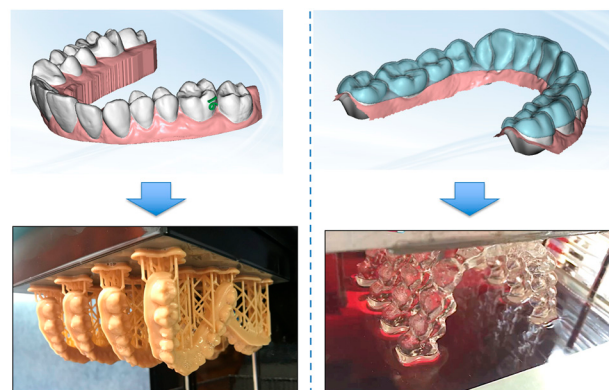


Figure 1. Generation of models and clear aligners using the CAD/CAM technique.

2. Materials and Methods

For this review, an electronic search was performed through the PubMed, Medline, Cochrane Library, Embase, and Scopus databases; the search words were “Materials” and “Clear aligners”.

The following parameters were considered for the selection of the studies:

- Studies conducted in the last 10 years in English;
- Studies concerning only the dental field;
- Studies describing the currently used clear aligner materials and their characteristics;
- Articles for which the material of the aligner was not specified were excluded from the analysis.

A total of 737 articles were identified within the aforementioned search in the databases. From this selection, all the articles found were entered into EndnoteWeb® to eliminate duplicates. Finally, 720 articles were considered. After screening, based on the title and abstract, 128 studies were considered eligible.

These 128 articles were subsequently included in the Rayyan program to verify the relevance of the above inclusion and exclusion criteria established by two reviewers, who also took care of the data collection. Inclusion was confirmed by a third supervisor who intervened in the case of disagreement (Figure 2).

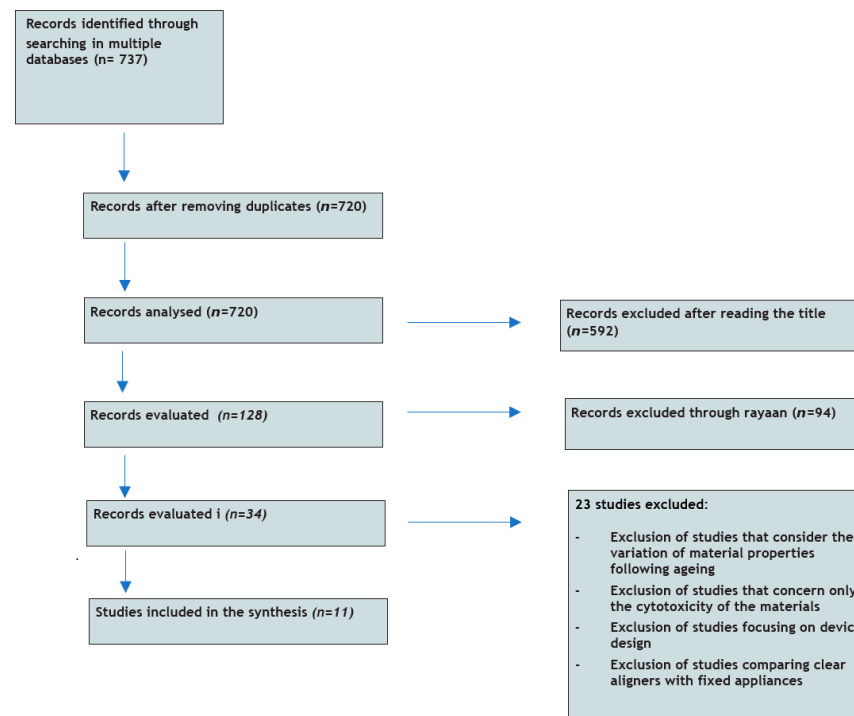


Figure 2. Literature search flowchart (PRISMA).

The following specific criteria based on study content served to determine the final inclusion of the studies.

Inclusion Criteria:

- Studies linking different types and materials of clear aligners;
- Studies that consider the mechanical, thermal, physical, chemical, viscoelastic, and optical properties of the materials.

Exclusion criteria:

- Studies that consider the variation of material properties following aging;
- Studies concerning only the cytotoxicity of the materials;
- Studies focusing on device design;
- Studies comparing clear aligners and fixed appliances.

The application of specific criteria led to the selection of 34 eligible studies, for which the full text was obtained and assessed. Finally, 23 articles were excluded because they did not match the previously established selection criteria, and 11 relevant articles were included. These studies evaluated 17 different clear aligner materials and their properties by comparing the different materials analyzed:

- Thermal, mechanical, physicochemical, and viscoelastic properties;
- Roughness and surface energy;
- Stability against intra-oral coloring agents, optical properties, and water absorption behavior;
- Structural variations (hardness and infrared spectroscopic analysis);
- Properties of absolute stress and stress decay.

3. Results

This review included 11 articles (Table 1) through a selection process depicted in Figure 2, and in Excel spreadsheet in supplementary materials.

Only three studies received external funding. The Lee et al. study [10] was funded by MOTIE (Ministry of Commerce, Industry and Energy of South Korea), the Golkhani

et al. [11] by the DEAL project in Germany, while the Kwok et al. [12] by the US Department of Orthodontic Discretionary Funds.

Almost all the included studies are in vitro, with the exception of the Alexandropoulos et al. comparative study [13].

Table 1. The 11 review articles that found to be eligible were considered for this scoping review.

Authors	Year	Title	Journal
Se Yeon Lee, Hoon Kim, Hyun-Joong Kim, Chooryung J. Chung, Yoon Jeong Choi, Su-Jung Kim, Jung-Yul Cha	2022	Thermo-mechanical properties of 3D printed photocurable shape memory resin for clear aligners	Scientific reports
Fabienne Suter, Spiros Zinelis, Raffaello Patcas, Marc Schaetzle, Giorgio Eliades, Teodoro Eliades	2020	Roughness and wettability of aligner materials	Journal of orthodontics
Valeria Daniele, Ludovico Macera, Giuliana Taglieri, Loredana Spera, Giuseppe Marzo, Vincenzo Quinzi	2021	Color Stability, Chemico-Physical and Optical Features of the Most Common PETG and PU Based Orthodontic Aligners for Clear Aligner Therapy	Polymers
Bijan Golkhani, Anna Webber, Ludger Keilig, Susanne Reimann, Christoph Bourauel	2022	Variation of the modulus of elasticity of aligner foil sheet materials due to thermoforming	Journal of orofacial orthopedics
Aseel Alhendi, Rita Khounghanian, Raisuddin Ali, Saeed Ali Syed, Abdullazez Almudhi	2022	Structural Conformation Comparison of Different Clear Aligner Systems: An In Vitro Study	Dentistry journal
Luca Lombardo, Elisa Martines, Valentina Mazzanti, Angela Arreghini, Francesco Mollica, Giuseppe Siciliani	2017	Stress relaxation properties of four orthodontic aligner materials: A 24-h in vitro study	The angle orthodontist
Paolo Albertini, Valentina Mazzanti, Francesco Mollica, Federica Pellitteri, Mario Palone, Luca Lombardo	2022	Stress Relaxation Properties of Five Orthodontic Aligner Materials: A 14-Day In-Vitro Study	Bioengineering
Isabella Pratto, Mauro Carlo Agner Busato, Paulo Rodrigo Stival Bittencourt	2022	Thermal and mechanical characterization of thermoplastic orthodontic aligners discs after molding process	Journal of the Mechanical Behavior of Biomedical Materials
Francesco Tamburrino, Vincenzo D'Antò, Rosaria Bucci, Giulio Alessandri-Bonetti, Sandro Barone, Armando Viviano Razionale	2020	Mechanical Properties of Thermoplastic Polymers for Aligner Manufacturing: In Vitro Study	Dentistry Journal
Alexandros Alexandropoulos, Youssef S Al Jabbari, Spiros Zinelis, Theodore Elides	2015	Chemical and mechanical characteristics of contemporary thermoplastic orthodontic materials	Australian Orthodontic Journal
Man-Hin Kwok, Betina Porto, Shadi Mohebi, Lei Zhu, Mark Hans	2021	Physical and chemical properties of five different clear thermoplastic materials	Journal of Applied Polymer science

The most used materials are generally derivatives of polyvinyl chloride, thermoplastic polyurethanes (TPU), polyethylene terephthalate, polyethylene terephthalate glycol (PETG), polypropylene, polycarbonate, and copolyester. Among them, PETG is widely used for its excellent impact and tear strengths, barrier properties, chemical resistance, and transparency. In addition, TPU with greater elasticity is used by the most famous brands of aligner production to obtain more predictable orthodontic movements by applying light and constant forces. Multi-hybrid materials have also been developed to improve the physical properties of the single material [10,14].

3.1. Mechanical, Physical, and Chemical Properties

Three studies focused on the mechanical, physical, and chemical properties of different materials [10,12,13]. The properties of the materials are summarized in Table 2.

Table 2. Summary of the properties of the materials under investigation.

Materials	Properties
TC-85	High flexibility, wider elastic range, slight stress decay, shape memory properties, better adaptation post-usage, viscoelastic properties, geometric stability
Ca—medium, Essix-copopolyester (PETG), Erkodur (PETG)	Smooth surface structure before thermoforming, very rough structure after thermoforming
Duran (PETG)	Increase in yield stress after thermoforming, elastic modulus increases after thermoforming, smooth surface structure before thermoforming, very rough structure after thermoforming
Essix ACE (PETG)	High mechanical properties, maintains high force after thermoforming, high transparency, perceptible color change after 14 days in red wine and coffee, exhibits high tensile strength and Young's modulus
Zendura (PU)	Stiffest flexural modulus among tested materials, significant decrease in yield stress after thermoforming, increase in elastic modulus after thermoforming
SmartTrack (PU)	Higher hardness and modulus, slightly higher brittleness, lower creep resistance compared to PETG-based products
Essix C+ (PP-EPR)	Not soluble in any tested solvents, more crystalline characteristics, lower transparency, significant decrease in tensile strength and Young's modulus after heat treatment
F22 Aligner	Single layer material, high stiffness, rapid stress decay in the first 8 h, higher absolute stress values.
Erkoloc-Pro	Double layer material, lower stiffness, very constant stress release, but with lower absolute stress values.
Durasoft	Double layer material, lower stiffness, very constant stress release, but with lower absolute stress values.
F22 Evoflex	Maintained high stress rates over a 15-day period, highest final stress level with a constant stress release.
Eon (PU)	Hardness comparable to other PU-based aligners, smooth surface but with some irregularities and impurities
SureSmile (PU)	Hardness comparable to other PU-based aligners, irregularities and impurities found on surface
Clarity (PU)	Resistant and practically invisible material, hardness comparable to other PU-based aligners, some impurities and irregularities on surface

According to the study by Alexandropoulos et al., the Smart Track (PU) material showed higher hardness and modulus values, slightly higher brittleness, and lower creep resistance than PETG-based products perhaps due to the different chemical composition. For this study, we analyzed Clear Aligner (PETG), ACE and A+ (PETG), and Smart Track (PU) [13,15].

With regards to the chemical properties, Kwok et al. considered five different materials: Smart Track (ST), Zendura, Essix Ace (Ace), Essix C+ (C+), and Tru-Tain DX30-25 (DX30). C+ was not soluble in any of the solvents tested; it shows better chemical resistance due to the polypropylene/ethylene-propylene rubber (PP-EPR) blend. Ace and DX30 were soluble in chloroform. The results suggest that the core of ST, Ace, and DX30 are PETG- or PCT-type thermoplastics, while Zendura is TPU. C+ exhibits more crystalline characteristics, which is consistent with its lower transparency. The flexural moduli values of all five aligners are between 0.9 and 1.7 GPa, with Zendura being the stiffest [12,16].

Lee et al. published an article testing a new material for making transparent aligners, namely TC-85. The results indicate that TC-85 can consistently apply a light force to the teeth due to its flexibility and viscoelastic properties. Additionally, it is expected that the strength decay induced by repeated insertion of the clear aligners will be reduced and a constant orthodontic strength will be maintained. Furthermore, its geometric stability at high temperatures and shape memory properties provide benefits for clinical application. The production of aligners with TC-85 therefore makes hygiene management and disinfection possible [10].

Finally, regarding stress relaxation and sliding, TC-85 has greater flexibility and better adaptation after being used in the oral cavity [10].

3.2. Mechanical and Physicochemical Properties after Thermoforming

Three studies dealt with testing the mechanical and physicochemical properties following thermoforming; one of these additionally tested the materials following preservation in artificial saliva [11].

Golkhani et al. considered the following materials: Duran Plus (PETG), Zendura (PU), Essix ACE, and Essix PLUSTM (PETG). At a distance from the substrate of 8 mm and a displacement of 0.25 mm, Essix[®] PLUSTM, with the thickest thickness untreated, showed the highest forces, followed by Duran Plu, Essix ACE, and Zendura. Thermoforming drastically reduced thickness and forces in bending tests. Young's modulus decreased significantly, especially for Essix PLUSTM [11].

Pratto et al. instead analyzed ACE Plastic 0.35 Essix Clear Aligner–Dentsply Sirona–PETG, C Plastic + Essix Clear Aligner–Dentsply Sirona, Crystal Plastic 0.75–Bio-Art–PETG, and Crystal Plastic–Bio-Art[®]–PETG. In particular, heat treatment at 200 °C did not affect the chemical structure of the polymer chains for all systems studied. However, the C+ sample showed macromolecule relaxation. A decrease in tensile strength and Young's modulus was also found [17,18].

Infrared spectroscopy analysis showed no changes in the chemical structure of the samples after thermal processing. However, differences in the region attributed to the crystalline phase were found in the polypropylene aligner. Differential scanning calorimetry analysis for the same sample showed a decrease in the crystallinity fraction. In the tensile tests evaluated, tensile strength and Young's modulus showed higher values for aligners containing 100% PETG [17].

Tamburrino et al. considered three thermoplastic polymers commonly used to fabricate clear aligners, namely Duran (PETG), Biolon (PET), and Zendura (TPU), following thermoforming and storage in artificial saliva and considering their combination on mechanical properties. The results showed that thermoforming did not lead to a significant reduction in yield stress, except for Zendura which showed a decrease of approximately 30%. After thermoforming, however, an increase in the elastic modulus of Duran and Zendura was observed. The same increase was noted for the yield stress of Duran. For the test in artificial saliva, the elastic modulus generally decreased. A decrease in yield stress, on the other hand, was significant for Zendura [19,20].

3.3. Properties of Absolute Stress and Stress Decay

Lombardo et al. and Albertini et al. analyzed absolute stress and stress decay properties in five materials: F22 Evoflex, F22 Aligner, Durasoft, Erkoloc-Pro, and Duran [21,22].

Lombardo et al. analyzed four of these materials: F22 Aligner (PU) and Duran PETG (monolayer materials), Erkoloc-Pro and Durasoft (multilayer materials). All polymers analyzed experienced significant stress decay over a 24-h time period. This was the greatest during the first 8 h, reaching a plateau that remained constant. Monolayer materials showed higher values for both absolute stress and stress decay rate. The bilayer materials, on the other hand, showed a very constant stress release, but with absolute values up to four times lower than the single-layer samples tested [21].

Albertini et al. analyzed F22 Evoflex in addition to the previous study. The yield strength, deformation, and especially, the stiffness of each material were found to be similar in the single-layer samples, while the double-layer samples showed much lower and similar stiffness values to each other [22–24].

F22 Evoflex and Erkoloc-Pro maintained the highest stress rates over the 15-day period. Duran and Durasoft had the lowest final stress values and the lowest percentage of normalized stress. All the materials we tested showed rapid stress decay during the first few hours of application, before reaching a plateau phase. The F22 Evoflex material exhibited the highest final stress level, with a relatively constant stress release over an entire 15-day period [22,25].

3.4. Surface Roughness and Energy before and after Thermoforming

Surface roughness and energy were evaluated in the article by Suter et al. which tested the following materials: CA-medium, Essix-copolyester (PETG), Duran (PETG), and Erkodur (PETG) [26].

Microscopic and profilametric analyses revealed a smooth surface structure of the materials but a very rough structure after thermoforming, with insignificant differences within each state. Significant differences were found in the surface energy parameters [26,27]. Stability toward intra-oral coloring agents, physicochemical and optical properties, and water absorption behavior were also considered.

Daniele et al. considered Essix ACE Plastic (PETG), Erkodur (PETG), Ghost Aligner (PETG), Zendura FLX (PU), and Smart Track (PU) for various properties [28].

The results obtained show that the clear aligners consist of PETG, semi-rigid PU, a blend of PU, and PETG, with different degrees of crystallinity affecting the transparency of each aligner. In particular, PETG-based materials reveal the highest properties in terms of transparency. After 14 days of immersion in red wine and coffee, the PETG- and PU-based aligners reveal a perceptible color change. These results are particularly marked for Smart Track, which shows variations toward other colors probably due to the thermoforming process which has led to the formation of a rough surface which traps impurities [28–30].

3.5. Structural Variations by Hardness and Infrared Spectroscopic Analysis

Alhendi et al. analyzed the structural variations via infrared spectroscopic and hardness analysis on the following materials: Eon (PU), SureSmile (PU), Clarity (PU), and Smart Track (PU) [31].

No statistically significant differences were observed between the included systems with regards to hardness. Some structural variations were noted in the Smart Track material which had a more homogeneous architecture. The four materials had comparable levels of hardness. Slight differences in molecular composition were found, but all systems had the similarity of being made up of a polyurethane-based material. Carbon and oxygen were the primary elements, as they were found in all clear aligners studied. SEM analysis revealed that Smart Track had a smoother surface than the other three systems [31].

4. Discussion

The development of new materials has significantly improved the characteristics of clear aligners. However, the vast majority of these are produced with the conventional thermoforming method during which the shrinkage and expansion of the material affects the orthodontic strength and the fit of the aligners to the teeth [10].

Polymer blending is an effective method for improving the mechanical properties of polymers. Polymers exist in amorphous, crystalline, and liquid crystalline forms. In the first case, the structure of the polymer is disordered, while in the second case, it is organized and regular. From a structural point of view, the crystalline domains act as a reinforcing grid, thus improving the performance of the polymer in a wide range of temperatures. These are known as semi-crystalline polymers because they retain amorphous regions in their structure [32].

Exceed30 (EX30) was the polymer material used to make Invisalign® aligners from 2001 to early 2013. It was a medical-grade polymer made up of polyurethane methylene diphenyldiisocyanate 1,6-hexanediol [32]. From the first quarter of 2013, EX30 was replaced by a new polymer called Smart Track (LD30), a multilayer aromatic thermoplastic polyurethane/copolyester. LD30 denotes increased flexibility providing gentle and constant force, reducing pain, duration, pressure upon insertion, and long-term clinical action. It also features better adaptability and adhesion to the dental arch improving comfort and ease of use [32].

Align Technology is considered the leader in the clear aligner market, producing the world's most advanced clear aligner system (Invisalign®). Meanwhile, Eon® Holdings designs and manufactures clear removable aligners with a special form of polyurethane.

Then, 3M™ launched its own clear aligner system called Clarity®, made up of a resistant and practically invisible material. Finally, the SureSmile® aligners were designed by Dentsply-Sirona; these are manufactured from Essix plastic, which is a thermoformed polyurethane material [31,33]. While most clear aligners are polyurethane thermoset polymer products, there is some variation among different companies. These differences are attributed to processing variations in manufacturing techniques incorporating various additives and dimensional characteristics [31].

The creation work begins through a virtual software with the use of plaster impressions or digital 3D intra-oral scanners. For each individual aligner in the set, a physical 3D model is required, either by 3D printing, stereolithography, or casting. Next, the aligners are fabricated by modelling the clear material on the 3D model of the patient's teeth and finally cut [5,34] (Figure 3).

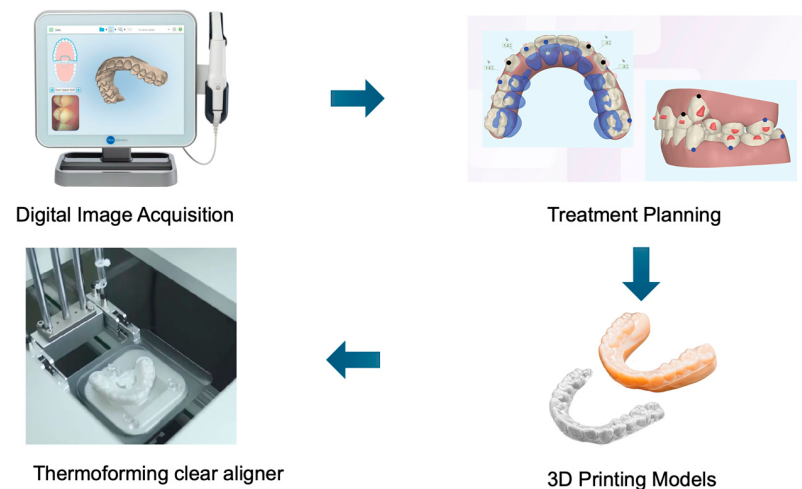


Figure 3. Digital orthodontic workflow of 3D-printed aligners.

All tested materials showed good mechanical, chemical, physical, thermo-mechanical, viscoelastic, stress decay, and structural characteristics. The materials were also tested following thermoforming and reported a reduction in properties [13,35].

Specifically, the analysis of the mechanical and chemical properties highlighted, according to the study by Alexandropoulos, that there are two differences between the PETG materials: the first is due to the different molecular weight, while the second is due to the influence of thermoforming on the mechanical properties. However, these data need further analysis [13]. The high hardness values in Smart Track indicate better wear resistance in clinical conditions, while the high moduli of elasticity indicate an increased force delivery capacity in orthodontic devices, however causing greater fragility. The lower resistance to sliding also means that, under constant occlusal forces, it is more likely to deform [13]. Despite the differences noted, there is no clinical evidence of a different influence on treatment or intra-oral behavior. Future controlled clinical studies are therefore also needed to determine the wear resistance and in vivo deterioration of materials [13].

As already mentioned in the results of Kwok et al., the study instead analyzed the physical and chemical properties of five transparent thermoplastic materials. Most of them are amorphous polymers, such that the transparency of the materials decreases when their structure changes from amorphous to crystalline [12]. We can therefore divide these materials into three main groups. The first group is based on PETG or PCT, comprising ST (PCT), Ace (PETG), and DX30 (PETG). The second group consists of ST (TPU) and Zendura (TPU). Finally, the third group consists of C+ (PP-EPR). PETG and PCT normally exhibit excellent clarity as they have an amorphous structure (Figure 4); this aspect is important to guarantee an acceptable aesthetic result for the patient [12]. As for the flexion modules, Zendura is a TPU material without any soft segments. The flexural modulus of Ace is

higher than that of DX30. However, as mentioned in the results, the flexural modulus of ST was between Ace and DX30 [12].

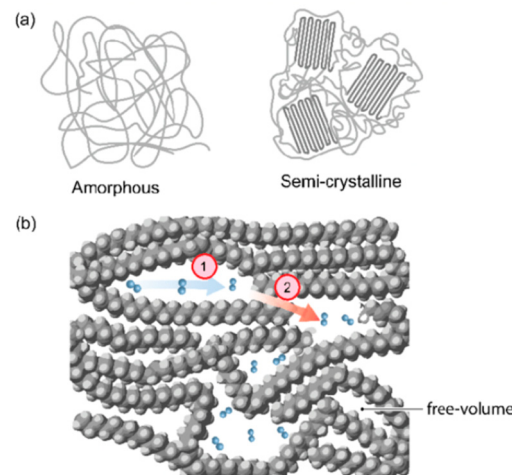


Figure 4. (a) Polymer chain arrangement in amorphous and semi-crystalline polymers. (b) The microscopic mechanism of gas dissolution and diffusion in an amorphous polymer. The unoccupied space in between polymer electronic clouds is considered as free volume.

Normally, we would prefer a material with high and stable moduli. This means that it can provide a high enough force to the teeth even with a thinner, more invisible aligner. However, the high stiffness could cause problems when a patient transitions to a new set of aligners (the aligner may not fit as well) [12].

A new material (TC-85) was then compared with the PETG materials in the Lee et al. study for the analysis of thermo-mechanical and viscoelastic properties. It was found that conventional thermoplastics show thickness changes after thermoforming depending on size and shape [10]. In clinical practice, since the clear aligners are produced using dental models with variability in anatomical structures, irregular thicknesses can occur. Since the thickness of the aligners affects the orthodontic force applied to the teeth, the uneven thickness of clear aligners makes it difficult for clinicians to predict performance and treatment outcomes [10,36]. The yield strength and elastic modulus were higher in PETG than in TC-85, while the elastic range was wider in TC-85 than in PETG. Thanks to the greater flexibility and the wider elastic range of the TC-85 aligners, it is possible to perform more tooth movements without permanent deformations [10,37].

Furthermore, TC-85 showed a slight stress decay, while it was faster for PETG [3].

Thanks to the shape memory property (bending test) of the TC-85, the aligners can consistently apply orthodontic forces to the teeth under normal temperature conditions without force decay caused by deformation. However, further studies such as voltage testing are needed in the future [10,38]. In the Lee et al. study, only one type of thermoplastic material, PETG, was compared as a control. Therefore, it is difficult to conclude that TC-85 is superior to all conventional materials [10].

Golkhani highlighted material thickness reduction and geometry modification following thermoforming by altering an aligner's ability to transmit controlled forces and moments onto a tooth and decreasing mechanical properties. This decrease can be attributed to partial changes from the amorphous to the crystalline structure of the material during thermoforming, where the crystalline phase could affect the elastic properties of the material. Both PETG and PU materials were tested [11]. Moreover, it was then possible to observe a decrease in the Young's modulus for all thermoformed materials [11].

Pratto et al. showed a change in mechanical properties after heat treatment. Taking into account that the luminaires are heat-molded to obtain the desired shape, the order proposed in this study to use these marks is C+, ACE 035, Crystal 0.75, and Crystal 1.0, suggesting that manufacturers should indicate these values after thermal processing [17,18].

Tamburrino et al. evaluated the effect of the thermoforming process, preservation in artificial saliva, and their combination on the mechanical properties of three thermoplastic polymers [19]. Considering the clinical aspects, the absorption of liquids could also affect the size of the aligner by modifying the adaptation to the patient's arch. This aspect combined with the change in the mechanical properties of thermoplastic materials could lead to a potential loss of effectiveness [19,20].

Ideally, an aligner should apply a gentle, consistent force over time. To be effective, the ideal material should therefore be stiff enough with a high yield strength. None of the four materials tested in the Lombardo et al. demonstrated all these characteristics. The thickness of the aligner material has a great influence on the force it develops; however, the tested materials are not all of the same thickness and therefore not the same [21].

Through the bending test, it was shown that the single-layer materials (F22 Aligner and Duran) were more than four times stiffer than their double-layer counterparts (Erkoloc Pro and Durasoft). This feature should be calculated as some aligners may not be able to exert enough force to drive the teeth into their programmed positions. Stress decay tests showed in all samples that this was very rapid during the first 8 h of application, subsequently tending to decrease to a plateau. This indicates that the performance of an aligner should be evaluated not only upon insertion, but also after 15–20 h. There were, in fact, notable differences in how the materials performed over the 24-h test period [21,24,39–41].

Lombardo et al.'s research work has some limitations. It is an *in vitro* analysis that evaluates the behavior of different materials before the thermoforming phase where the samples are not the same. Furthermore, these characteristics can change during the treatment period due to the physical, chemical, and masticatory stress that can occur in the oral cavity [21,23]. Albertini et al. demonstrated rapid stress decay in all materials during the first hours of application before reaching a plateau phase (Figure 5). The limitations are congruent with Lombardo et al.'s [22,41–44].

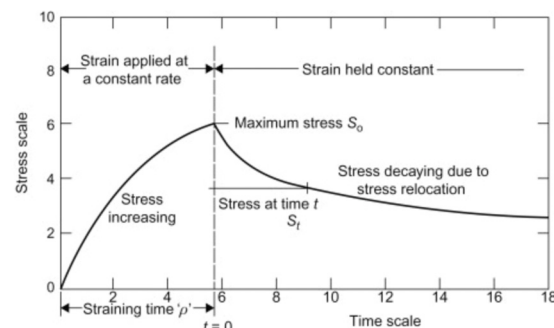


Figure 5. Stress relaxation.

Other properties such as roughness and surface energy have been described in the Suter et al. study using PETG-based materials. The materials showed low surface roughness values as these interfere with the wetting phenomena due to saliva. The roughness results after thermoforming were much higher [26]. The total bond work provides the retention capacity of the intra-oral biofilm. Thus, differences in this parameter can be hypothesized to have a clinical impact for pellicle formation. The tested materials showed the following differences: CAM showed the highest values, followed by COP and the DUR and ERK group [26]. To conclude, in the absence of statistically significant differences in the roughness parameters of the received and thermoformed materials, the differences recorded in the surface energy parameters can control biofilm formation and plaque development on the aligners [26–32,45,46].

Daniele et al. dealt with the study of color, physicochemical properties, and water absorption of PU- and PETG-based materials [28]. Investigations on water absorption provide indications of the interaction with the external aqueous environment and of their ability to maintain their characteristics during use, preventing mechanical degradation phenomena. The penetration of water molecules into the oral environment can lead to

modifications of the aligner from a physio-chemical point of view, causing phenomena of mechanical degradation and swelling. For these reasons, an ideal orthodontic clear aligner must have low water absorption properties, the worst performance being given by the PU-based aligner [28–30].

Alhendi et al. evaluated the structural differences of PU-based clear aligner systems versus Smart Track [31]. Hardness is the mechanical property of the resistance of a material to a certain load. This property can be influenced by factors such as the thickness, the thermoforming, the structure of the polymer, and the polymerization process [31,47].

FTIR (presence of contaminants) analysis revealed comparable spectral profiles on the surfaces of the included samples [31,32]. Smart Track has a smoother and less defective surface, while the other three materials showed a similar architecture with impurities, irregularities, and particles on their surfaces. SureSmile is the most porous of the four systems [31]. The two main elements highlighted are oxygen and carbon. Other elements such as nitrogen in Smart Track and fluorine in Eon and SureSmile have also been found. Sodium and chlorine resulted, however, related to immersion in artificial saliva. A considerable amount of mercury has been identified only in the Eon, this can cause adverse biological effects, so further investigations are needed [31,32].

5. Conclusions

Different characteristics emerged based on the various studies analyzed.

The Smart Track (PU) material was hard, wear-resistant, elastic but more brittle, and with lower sliding resistance than PETG-based devices, while compared to PU devices, it was smoother and less bumpy.

The PETG materials were then more transparent, flexible, and therefore thinner than the PU materials, even the roughness was low.

Stress decay was also tested, which was rapid for both PETG and PU devices in the first 8 h of application, subsequently tending to decrease to a plateau.

After thermoforming, both PETG and PU materials decreased the mechanical properties (Table 3).

Table 3. Summary of the properties of PETG and PU.

Property	PETG (e.g., Duran, Essix Ace, Essix Plus, Biolon)	PU (e.g., Zendura, SmartTrack, Eon, SureSmile, Clarity)
Elastic Modulus	Generally higher, decreases significantly after thermoforming	Higher hardness and modulus values
Tensile Strength	High, but decreases after heat treatment and immersion in artificial saliva	Maintains strength, but may show slight decrease after thermoforming
Flexibility	Less flexible compared to PU	More elastic, allowing for predictable orthodontic movements
Transparency	High, can be affected by crystallinity (e.g., Essix C+ is less transparent)	High transparency, practical invisibility
Stress Decay	Rapid stress decay, especially in the first few hours	Rapid initial stress decay but reaches a plateau over time
Chemical Resistance	Good, but varies (e.g., Essix C+ has higher chemical resistance)	Generally good, with specific formulations possibly affecting resistance
Surface Characteristics	Smooth but can exhibit impurities after thermoforming	Smooth but may show irregularities and impurities
Yield Stress	Generally higher but decreases significantly after thermoforming	Slightly lower, decreases about 30% after thermoforming
Applications	Widely used in orthodontics for clear aligners and retainers	Used for aligners requiring more elasticity and flexibility

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app14156533/s1>, Excel spreadsheet.

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