ALIGNER MATERIALS AND THEIR PROPERTIES

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ABSTRACT:

Clear aligner therapy (CAT) has gained popularity due to its transparency, removability, and comfort, offering an effective solution for teeth realignment. The development of aligners has evolved significantly from single-layer plastics to advanced multilayer materials incorporating polymers like polyurethane, polyethylene terephthalate (PET), and polyethylene terephthalate glycol (PETG). The introduction of CAD/CAM technology and direct 3D printing has further enhanced aligner precision and efficacy. Aligner materials, including thermoplastic polyurethane (TPU) and polymer blends, are critical to their performance, influencing mechanical and clinical characteristics. Advanced materials like SmartTrack™ and 3D-printed photopolymers have improved elasticity and consistency. Bioactive materials and antimicrobial coatings are also being explored to mitigate microbial accumulation during treatment. Shape memory polymers (SMPs) represent a promising innovation, offering significant self-shape recovery and enhanced orthodontic force generation. The mechanical and thermal properties of these materials, along with their chemical resistance, are crucial for maintaining aligner effectiveness and patient comfort.

INTRODUCTION:

The recent upsurge in adults seeking orthodontic treatment has sparked a greater demand for appliances that offer enhanced aesthetics and comfort compared to traditional fixed braces. The limitations of conventional methods, combined with patients' growing preference for "invisible" alternatives, have propelled the popularity of transparent aligners. Clear aligner therapy (CAT) typically involves a series of transparent plastic trays that fit snugly over the teeth and to be worn by the patient all time except during meals and brushing. These trays are usually replaced sequentially every one to two weeks to facilitate planned orthodontic tooth movement.

The performance of clear aligners is directly affected by the composition of the material used in their fabrication. This composition, in turn, is shaped by the manufacturing process, which can be broadly categorized into two methods: the traditional approach involving vacuum thermoforming with thermoplastic material molded on physical models, and the alternative method of direct 3D printing without the need for intermediary physical models.[1]

This article aims to review the various materials used for manufacturing the clear aligners and the various properties of aligners such as mechanical, physical, therma, opticall and chemical properties.

MATERIALS USED FOR ALIGNERS

Thermoplastic polymers

They can be classified as amorphous and semicrystalline polymers based on their inherent molecular structure[1]

The polymers commonly employed in the production of commercial clear plastic orthodontic aligners include polyester, polyurethane or co-polyester, polyproplene, polycarbonate, ethylene vinyl acetate, and polyvinyl chloride, among others. Over time, clear aligner materials have progressed from single-layered plastics to second-generation polyurethane materials, and currently, third-generation multilayered materials are prevalent, often comprising both hard and soft layers. The soft layer allows for elastic deformation, facilitating comfortable fitting of the aligner, while the hard layer provides strength and durability[2]. Within the polyester category, polyethylene terephthalate (PET) and polyethylene terephthalate glycol (PETG) – a non-crystallizing amorphous copolymer of PET – are extensively utilized due to their outstanding mechanical and optical properties[3].

Polyethylene terephthalate (PET)

Combining ethylene glycol with terephthalic acid, polyethylene terephthalate (PET) exists in both amorphous and crystalline forms, with each form influencing its material properties. The amorphous structure of PET is transparent and offers superior ductility, while the crystalline structure is opaque and white, providing hardness, stiffness, and good strength[4]. PET can be rigid or semi-rigid depending on the processing methods used and demonstrates excellent mechanical properties, toughness, and resistance to various solvents[5].

Polyethylene terephthalate glycol (PETG)

PETG is a non-crystalline co-polyester composed of 1,4-cyclohexane two methanol (CHDM), ethylene glycol (EG), and terephthalic acid (TPA). It boasts excellent transparency, sufficient flow properties, and resistance to various solvents. These materials are exceptionally durable, possess high impact strength, and resist chemical changes, making them ideal for intricate designs. PETG represents an altered form of PET, transitioning it from a semi-crystalline to an amorphous state, enhancing transparency and aesthetics. With a glass-transition temperature (Tg) around 80°C, PETG offers better handling and glass-like features[6]. Its improved transparency, mechanical strength, and optical properties render PETG suitable for crafting clear aligners.

Thermoplastic polyurethane (TPU)

Primarily composed of di- and tri-isocyanates and polyols, thermoplastic polyurethane (TPU) is an extremely versatile polymer known for its excellent mechanical and elastomeric characteristics, chemical and abrasion resistance, adhesion properties, and ease of machining. Under load, TPU can change shape and recover its original form when the load is removed, owing to its flexibility. It also demonstrates high tear resistance and a broad range of resiliency[7].

Polymer blends

Enhancing the mechanical properties of the polymers can be achieved through blending different types, such as polyester, polyurethane, and polypropylene. These blends are commonly used in commercial clear aligner manufacturing[8]. The ratio of polymer blending significantly impacts the characteristics of the blend. For example, blending PETG/polycarbonate (PC)/TPU at a ratio of 70/10/20 resulted in superior mechanical properties compared to other blending ratios, providing adequate and sustainable orthodontic forces compared to other commercial products[9]. Similarly, a blend of PETG/PC2858 at a 70/30 ratio showed the optimal combination of tensile strength, impact strength, and elongation at break[10].

3D printed aligner materials

Direct 3D printing offers several advantages over thermoforming processes, including avoiding adverse effects such as changes in mechanical, dimensional, and aesthetic properties of the material. It provides superior geometric accuracy, precision, fit, efficacy, mechanical resistance, and reproducibility[11]. Materials commonly used for 3D printing in orthodontics include acrylonitrile-butadiene-styrene plastic, stereolithography materials (epoxy resins), polylactic acid, polyamide (nylon), glass-filled polyamide, silver, steel, titanium, photopolymers, wax, and polycarbonates.

Graphy introduced Tera Harz TC-85, a photopolymer material designed to address the limitations of thermoforming sheet-type aligners. The Tera Harz direct aligner can be 3D printed directly with a 3D printer. TC-85 is a biocompatible photopolymer available in clear and white colors. TC-85DAC (clear) offers full transparency, while TC-85DAW (white) provides durability and aesthetics.

Bioactive materials used with clear aligners

Microbial accumulation poses a common challenge during orthodontic treatment, with studies indicating heightened levels of major oral pathogens like Streptococcus mutans and Porphyromonas gingivalis. Efforts have been made to enhance the antimicrobial properties of orthodontic appliances, leading to increased research on the application of nanoantibacterial materials in orthodontics[12]. Since aligners cover the teeth and gingiva for most of the day, there's an elevated risk of bacterial growth, potentially leading to tooth and adjacent tissue damage.

Zhang et al., in their initial study, applied a coating of 4,6-diamino-2-pyrimidinethiol-modified gold nanoparticles (AuDAPT) onto clear aligners. This coating demonstrated antibacterial properties against a suspension of P. gingivalis, affecting the surrounding region of the materials.

It also slowed down the formation of biofilm and exhibited favorable compatibility with biological systems[13].

SHAPE MEMORY POLYMERS

The shape memory effect in Shape Memory Polymers (SMPs) relies on a two-domain system with distinct glass transition temperatures. One domain is hard and elastic at room temperature, while the other is soft and ductile. Thermal stimuli trigger a reversible activation and deactivation of polymer-chain motion in these switching segments, occurring above and below a specified temperature known as the transition temperature. This temperature can be either the glass transition temperature or the melting temperature[14]. When the transition temperature is reached, the deformed SMP displays elastic properties, allowing it to recover its original shape. This shape recovery generates forces capable of producing orthodontic tooth movement. They possess several advantageous characteristics including low density, significant elastic deformation, high chemical stability, and the ability to be programmed with adjustable physical properties. They are also relatively transparent, making them ideal candidates for novel clear aligner materials

PROPERTIES OF ALIGNERS:

An ideal aligner material should exhibit high resilience, low hardness, sufficient elasticity, adequate resistance to varied stress and distortion, excellent transparency, low cytotoxicity, and high biocompatibility

MECHANICAL AND PHYSICAL PROPERTIES

Thermoplastic materials return to its original size and shape upon removal of applied stress when stress is proportional to strain. However, beyond the yield strength of a material, strain is no longer proportional to stress, and the material behaves plastically rather than elastically. Clear aligners benefit from thermoplastic materials with higher yield strength, ultimate tensile strength, and toughness[15]. When subjected to long-term forces, thermoplastic materials may exhibit viscoelastic properties, showing a time-dependent relationship between stress and strain. Clear aligner materials demonstrate viscoelastic behavior, absorbing shock, vibrations, and force to deform and generate necessary forces for tooth movement. Over time, the material's deflection increases under constant loads, termed stress relaxation, which affects the force exerted by the aligner on the teeth. Stress relaxation is crucial in determining aligner efficiency, as the force delivered may decrease exponentially over time, indicating material fatigue.

Lombardo et al. examined the mechanical characteristics and stress relaxation of four aligner materials, finding differences in stress resistance and relaxation rates between single-layer and multi-layer materials. Monolayer materials showed higher initial stress values and faster relaxation rates compared to multilayer materials. Clinical use of aligners involves both short-term and long-term forces, affecting stress relaxation over time due to the aligner's viscoelastic nature[16]. Factors such as material composition, oral cavity temperature, force magnitude, and aligner thickness influence stress relaxation. Selection of aligner thickness should consider stress values within biological limits, with polyether compounds offering greater toughness and moisture resistance compared to polyester urethanes, albeit with lower abrasion resistance.

Top of Form

THERMAL PROPERTIES

Thermoplastic materials are typically linear or slightly branched polymers held together by strong intramolecular covalent bonds and weak intermolecular Van der Waals forces. These bonds melt at elevated temperatures, causing the polymers to flow, and solidify into new shapes upon cooling. Thermoplastics do not undergo further chemical changes with temperature alterations, allowing for repeated softening and hardening cycles. In their solid state, thermoplastics used for clear aligners are semi-crystalline, with amorphous polymer strands dispersed between crystalline polymers. Crystalline polymers are more transparent with defined melting points and glass transition temperatures[16].

During the thermoforming process, aligner materials must adapt or conform to dental models effectively. Studies have shown that polyurethane material exhibits superior adaptation ability at around 110°C compared to other materials. Thermoforming alters the transparency, hardness, and thickness of aligner materials. Research by Ryu et al. demonstrated reduced transparency post-thermoforming, particularly in copolyester-based and PETG-based aligner materials. Although hardness remained relatively unchanged, solubility in water increased for some materials. Essix A+ and Essix ACE samples showed higher surface hardness post-thermoforming[17].

Top of Form

Optical properties, colour stability and clear aligner transparency

Aligner materials should possess excellent light transmittance, ideally transmitting at least 80% of visible light for optimal clarity. Amorphous thermoplastic polymers are preferred for clear aligner fabrication due to their high translucency, unlike crystalline polymers, which are opaque and less aesthetically pleasing. Polymers such as polyurethane, polyester, polyvinyl chloride, polysulfone, and polycarbonate exhibit optical properties suitable for commercial aligner production[18]. Numerous studies have assessed the color stability and transparency of clear aligners when exposed to coloring agents and saliva. Results show minimal color changes after short-term exposure to coloring agents, but prolonged exposure, especially to coffee and black tea, can significantly alter the color of aligner materials. Certain materials, such as SmartTrack™, display more pronounced color changes compared to others. Polyurethane-based Invisalign aligners are particularly susceptible to pigment absorption and exhibit poorer color stability compared to polycarboxylate and PETG-based aligners[19]. Overall, aligners rated as clearer are considered more attractive, and minimizing the visibility of the appliance is crucial for societal acceptance.

Chemical resistance properties, the influence of the oral environment and clear aligner aging

Clear aligners are continuously exposed to saliva, various enzymes, temperature variations in the oral cavity, and sporadic exposure to beverages other than water, all of which can impact the chemical composition of their thermoplastic polymers. Certain polyesters like polycarbonates and polyamides may undergo irreversible hydrolysis, leading to degradation of their polymer structure. Therefore, it is preferable for aligner polymers to resist hydrolysis and water degradation[15].

Aligners are subjected to continuous and intermittent forces associated with normal oral functions such as chewing, speaking, swallowing, as well as parafunctional activities like teeth clenching and grinding. To maintain clinical performance, aligner materials must be durable and possess high wear resistance to withstand these stresses[15]. Instances of microcracks, delaminated areas, calcified biofilm deposits, and loss of transparency have been reported in aligners used for two weeks. Intraoral hygroscopic expansion can alter aligner fit and orthodontic forces exerted.

Studies simulating temperature variations in the oral environment have shown variations in hardness, thickness, and flexural modulus of aligners made from PETG sheets. Mechanical properties of thermoplastic materials decrease with gradual temperature changes, with polyurethane polymers demonstrating excellent shape memory. In vivo studies have found small reductions in aligner thickness over time but deemed these changes insignificant for clinical performance, indicating that PETG demonstrates adequate stability in the oral environment[20].

FUTURE INNOVATIONS:

In the future, aligners might integrate monitoring systems such as a chip capable of alerting users if they haven't worn the aligner for the prescribed duration. This notification could be delivered through a smartphone or by employing other inventive methods. These systems would help guarantee that patients stick to their treatment schedules, ultimately resulting in improved treatment outcomes.

Another significant area of innovation involves the advancement of novel biocompatible materials for aligners. Efforts in research are concentrated on crafting materials that not only enhance the efficiency of teeth movement but also provide superior comfort and usability. Potential future materials may showcase attributes like enhanced transparency, increased durability, and the capability to dispense therapeutic agents, thereby fostering oral health throughout the treatment process.

CONCLUSION:

Dental aligners have revolutionized the field of orthodontics, offering patients a discreet, comfortable, and effective alternative to traditional braces. With their customizable design and removable nature, aligners provide individuals with greater flexibility and convenience throughout their treatment journey. Moreover, their ability to address various orthodontic issues, from mild to moderate malocclusions, underscores their versatility and efficacy.Looking ahead, it is apparent that dental aligners will continue to play a pivotal role in orthodontic practice, with ongoing research and innovation driving further improvements in treatment protocols and aligner design.

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