

New 3D printed polymers in orthodontics: a scoping review



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Abstract

Aim The aim of this scoping review is to assess the application of new 3D printed polymeric materials in orthodontics, including polyamide-12 (PA-12) and Shape Memory Polymers (SMPs).

Methods A search for articles published until January 2023 was carried out using PubMed, Scopus, Web of Knowledge, Lilacs, Opengrey, Embase and Cochrane Library databases and by applying the search terms (orthodontic* OR paediatric* OR paedodontic*) AND ("3D printed" OR "three-dimensional printed") AND (polymer* OR material* OR resin* OR technopolymer*). Additional records were also screened through hand or electronic search. No restriction in terms of language or publication period was applied.

Results The initial search identified 281 records. After removing duplicates, 196 studies were screened based on title and abstract, and 103 full texts were assessed for eligibility. Nine articles were included in qualitative synthesis.

Conclusions Due to their mechanical, aesthetic and biocompatibility characteristics, PA12 and SMPs can be used in orthodontic practice. However, additional studies should be performed to evaluate the clinical efficiency of these recent materials.

KEYWORDS Digital orthodontic, 3D printing, polyamide, PA12, shape memory polymer, direct aligner

Introduction

The rapid advancements in digital technologies have completely changed the diagnostic and treatment modalities in dentistry, especially in paediatric and orthodontic fields [Paglia et al., 2022].

Focusing on the individualised needs of the children [Beretta et al., 2021, Tsolakis et al., 2022], the orthodontist or the technician may design a variety of appliances which can be 3D printed directly "in-office" or outsourced in specific labs [Tsolakis et al., 2022]. Starting from intra-oral scanning to 3D printing process, these customised appliances are fabricated by a fully digital workflow, without using a stone or proto-typed physical model as in the conventional manufacturing [Beretta M, 2017].

As previously reported in literature, this newly Computer Aided Design-Computer Aided Technofacturing (CAD-CAT) approach

represents the first step for a tailor-made orthodontics, leading to an increasing interest in new 3D printing materials [Beretta M, 2017, Beretta et al., 2021].

Generally, the 3D printed appliances can be fabricated using metal materials (such as cobaltium-chromium or titanium), or dental resins [Shahrubudin et al., 2019]. The metal-printed appliances are rigid and not flexible, requiring specific selective laser sintering (SLS) printers for metal printing [Tsolakis et al., 2022]. On the contrary, resin materials can be used to print appliances such as occlusal splints, trays for indirect bonding or surgical guide for mini-screw insertion, using stereolithography (SLA) printers [Tsolakis et al., 2022].

However, in the recent years the demand for metal-free orthodontic materials has been increasing, mainly due to aesthetic reasons or to the complications related to metal allergy and hypersensitivity [Maekawa et al., 2015]. Moreover, in children with special needs or with systemic diseases (autism, epilepsy or vascular problems) who undergo periodical magnetic resonance imaging (MRI) of the head district or are at high risk of emergency conditions, the metal interference with MRI may require the frequent removal of the orthodontic device, affecting the overall treatment [Beretta et al., 2021].

Actually, in the modern paediatric dentistry the use of new polymers, such as technopolymers or shape memory polymers, has been proposed as a viable alternative to conventional materials [Beretta et al., 2021, Tsolakis et al., 2022], offering to the clinicians the possibility of 3D printing customised, metal-free and "self-driving" appliances which may improve the treatment efficiency, the aesthetic and the collaboration of the younger patients [Paglia et al., 2022].

Among technopolymers, the Polyether-ether-ketone (PEEK) and the Polyamide 12 (PA12) have found to have ideal chemical-physical features that allow their use in orthodontics [Paglia et al., 2022].

As reported in literature, both these materials are biocompatible with excellent physical, mechanical and aesthetic properties [Beretta et al., 2021]. In particular, the polymer PA-12 is a linear, semi-crystalline, 3D-printable thermoplastic composite, with a thermal stability up to 185°C which allows its sterilisation before the clinical use [Paglia et al., 2022]. Beside PEEK, PA 12 is one of the most promising materials for orthodontic devices, given its higher flexural strength and modulus [Beretta et al., 2021].

Although the properties of PEEK polymer have been already investigated in a recent review [Paglia et al., 2022], a lack of knowledge about PA12 is still present in literature.

On the other side, the shape memory polymers (SMPs) are a class of smart materials which can alter their geometry according by external condition (such as heat and water), being able to recover their original shape [Shahrubudin et al., 2019]. SMPs are characterised by a low density, high elastic deformation and great chemical stability [Bichu et al., 2023]. Their adjustable physical properties, such as their relative transparency, have made SMPs suitable as a new material for 3D printing direct aligners with a self-shape recovery [Bruni et al., 2019]. Because of their ability to change their shape over the course of treatment, direct aligners aim to shorten treatment times and costs, because a single shape memory aligner might replace several conventional aligners [Elshazly et al., 2022]. In addition, reducing the number of plastic aligners per patient, the overall amount of used plastic can be reduced, according to the ethical responsibility to protect the environment [Elshazly et al., 2022].

Therefore, the aim of this review was to evaluate PA12 and SMPs and their use in orthodontics.

Materials and Methods

Literature Search

The present review was performed according to the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) statement [Dickson and Yeung, 2022].

The search for articles was carried out using the following electronic databases: MEDLINE via Pubmed, Scopus, Web of Knowledge, Lilacs, OpenGrey, Embase and Cochrane Library. The literary search included publications with no language restrictions up to January 2023.

Studies which featured the keywords (orthodontic* OR paediatric* OR paedodontic*) AND ("3D printed" OR "three-dimensional printed") AND (polymer* OR material* OR resin* OR techopolymer*) were identified. In addition, the reference and citation lists of the included articles and relevant reviews were manually searched.

All titles identified from the literature were screened and selected by two independent authors (A.C.; G.B.). Duplicate studies were eliminated. The abstracts were examined, and full texts were obtained if additional data were needed to fulfil the eligibility criteria. When appropriate, studies were excluded with reasons. Conflicts were resolved by discussion with a third author (M.B.).

Eligibility criteria

Because of the novelty of the topic, case reports, case series and in-vitro studies were also considered for the qualitative analysis. On the contrary, low-quality prospective studies, reviews, editorials, and conference abstracts were excluded.

Data extraction

After a first screening based on title and abstract, the full texts of all relevant articles were obtained. After full-text evaluation, the characteristics of the included studies were independently extracted by two authors (A.C.; G.B.). For further clarification, missing or unclear information was directly requested from the respective authors. The flow chart of the selection of eligible studies for this review is summarised in Figure 1.

Results

The initial search identified 157 records for Medline, 118 for Scopus, 107 for Web of Science, 0 for Lilacs and OpenGrey, 35

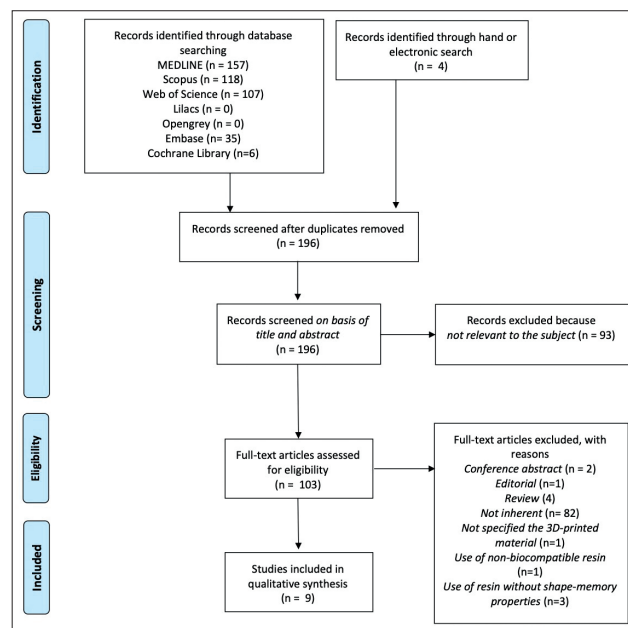


FIG. 1 Flow diagram of the included studies according to the PRISMA

for Embase, and 6 for Cochrane Library. In addition, four studies were identified through electronic search.

After eliminating duplicates and ineligible studies by title and abstract, a total of 103 full texts were screened. Finally, a total of nine papers were identified according to the eligibility criteria.

The characteristics of the studies are presented in Table 1. Of the 9 included studies, 8 articles analysed the in-vitro properties of 3D printed aligners with SMPs, while only one study was a case-report about PA12 appliance. Among the in-vitro studies, three articles compared the different characteristics between 3D printed aligners and conventional thermoformed aligners [Hertan et al., 2022, Koletsi et al., 2022, Lee et al., 2022].

Discussion

Due to the recent improvements of biomaterials and CAD-CAT technology, new polymers have been proposed as a promising alternative to conventional materials in orthodontics. The aim of this scoping review was to highlight the use of PA12 and SMPs to 3D print orthodontic appliances.

Polyamides (PAs), also known as "nylon", are thermoplastic polymers which can become highly elastic under controlled heating [Chuchulska and Zlatev, 2021], through the condensation between a diamine and a dibasic acid [Soygun et al., 2013]. These technopolymers had application in many fields, such as automotive, aerospace and medical industry [Scherer et al., 2020].

The recent interest of PA in medical sector is mainly due to its good biocompatibility with human tissue and to its good mechanical properties [Winnacker, 2017]. As reported in literature, polyamide was firstly introduced as denture base polymer since 1950s, instead of acrylic-resin materials [Soygun et al., 2013].

However, the advantages of PA and their composites have encouraged their use for biomedical implants, membranes, suture materials and orthodontic appliances [Winnacker, 2017, Beretta et al., 2021] (Figure 2-3).

Among its characteristics, there are mechanical strength, flexibility, toughness, and resistance while maintaining the ability to be modified [Winnacker, 2017]. Moreover, PA is less vulnerable to chemical modifications and relatively inert in comparison to many other polymers [Winnacker, 2017]. In medical application,

No.	Authors	Year	Study Design	Orthodontic Appliances	Material of 3DP	Type of 3DP	3D Printer	Properties
1	Zinelis et al.	2022	In-vitro	DA	Tera Harz TC-85DAW resin, Graphy	G1. LCD G2. LCD G3. DLP G4. LCD G5. DLP	G1. Karv LP 550 (Shinwon Dental, Seoul, Korea); G2. L120 (Dazz 3D, Shenzhen, China); G3. MiiCraft 125 (MiiCraft, Jena, Germany); G4. Slash 2 (Uniz, San Diego, CA, US); G5. Pro 95 (SprintRay, Los Angeles, CA)	Mechanical properties of DA are dependent on the 3D printer used
2	Willi et al.	2022	In-vitro	DA	Tera Harz TC-85A resin, Graphy	DLP	Sprinray Pro 55 3D printer (Sprinray, Los Angeles, CA, USA)	Potential concerns about the amount of the UDMA monomers released by DA
3	Pratsinis et al.	2022	In-vitro	DA	Tera Harz TC-85A resin, Graphy	DLP	Sprinray Pro 55 3D printer (Sprinray, Los Angeles, CA, USA)	DA are not cytotoxic
4	Lee et al.	2022	In-vitro	DA	Tera Harz TC-85 resin, Graphy	DLP	Uniz 4K printer, Uniz, USA	DA has clinical advantages compared to TFA (PETG) due to their geometric stability at high temperatures and to their shape memory properties
5	Koletsis et al.	2022	In-vitro	DA	Tera Harz TC-85DAC, Graphy	DLP	Moonray S100 printer (Sprinray, Los Angeles, CA, USA)	Intra-oral exposure and function induce significant changes in surface roughness properties of DA (such as TFA aligners)
6	Hertan et al.	2022	In-vitro	DA	Tera Harz TC-85DAC, Graphy	DLP	Sprint Ray Pro95 (Sprinray, Los Angeles, CA, USA)	Forces delivered by aligners in the vertical dimension by DA are more consistent and of lower magnitude than those of TFA aligners.
7	Elshazly et al.	2022	In-vitro	DA	ClearX v.1.1 (Kline-Europe, Dusseldorf, Germany)	DLP	Asiga Max (SCHEU-DENTAL GmbH, Iserlohn, Germany)	Release of orthodontic forces after a suitable thermal stimulus within the oral temperature range
8	Can et al.	2022	In-vivo	DA	Tera Harz TC-85DAC, Graphy	DLP	Moonray S100 printer (Sprinray, Los Angeles, CA, USA).	No significant changes of mechanical properties after one week of intra-oral use
9	Beretta et al.	2021	Case-report	Zero-expander	Polyamide-12 (or PEEK)	Multi-jet fusion	HP Jet Fusion printer (HP inc.)	Metal-free techopolymers are efficient and comfortable

3DP=3D-printing; G=group; SLA= Stereolithography; LCD= Liquid Crystal Display; DLP=Digital Light Processing; DA=Direct Printed Aligners; TFA=thermoformed aligners; UDMA=urethane dimethacrylate

TAB. 1 Characteristics of the included studies

another advantage of PA is its ability of preventing bacterial transmission, as previously reported [Winnacker, 2017].

Among disadvantages, there are a discoloration tendency and a high water absorption that initially led this material not suitable for common use [Winnacker, 2017]. In fact, considering the complex environment of the oral cavity, the color stability and the physical and mechanical properties of PA could be severely

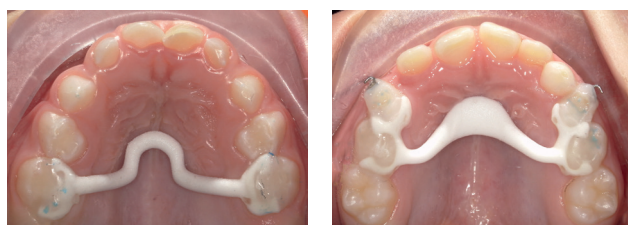


FIG. 2 ZeroExpander in PA12, made with digital set up and bonded by adhesive technique and bioactive materials on second deciduous molars, in a 4-year-old child

FIG. 3 Nance space maintainer in PA12, bonded by adhesive technique and bioactive materials on first and second deciduous molars, with bonded vestibular hooks for postero-anterior orthopedic traction, in a 7,5-year-old child

affected by oral humidity, saliva and foods and liquids, as well as by pH levels, bacteria and enzymes [Stewart and Finer, 2019].

First generation of PA materials (such as aliphatic PA 6 and PA 6,6) exhibited lower properties in terms of deformation, water sorption, and fatigue resistance during cyclic heat change and mechanical loads. This class of materials was characterised by hydrophilic amide bonds on the main chains, which makes them inclined to water absorption [Chuchulska and Zlatev, 2021].

On the contrary, in the later PA generations (including PA12) the water sorption and its associated mechanical and dimensional shortcomings were reduced through amide group concentration control [Chuchulska and Zlatev, 2021].

As reported in literature, PA12 is commonly used in powder bed fusion processes resulting in devices of good mechanical properties [Scherer et al., 2020]. In addition to stereolithography, powder-based techniques are considered among the most important ones in additive manufacturing [Scherer et al., 2020, Tsolakis et al., 2022].

In 2016, a new technology called multi-jet fusion was commercially introduced by the company HP, requiring specific outsourced printers which use PA12 powder [Scherer et al., 2020]. Among the advantages of this process, there are the recyclability and the reusability of the PA12 powder, reducing environmental impact [Scherer et al., 2020].

Despite the potential of PA12, in literature the clinical appli-

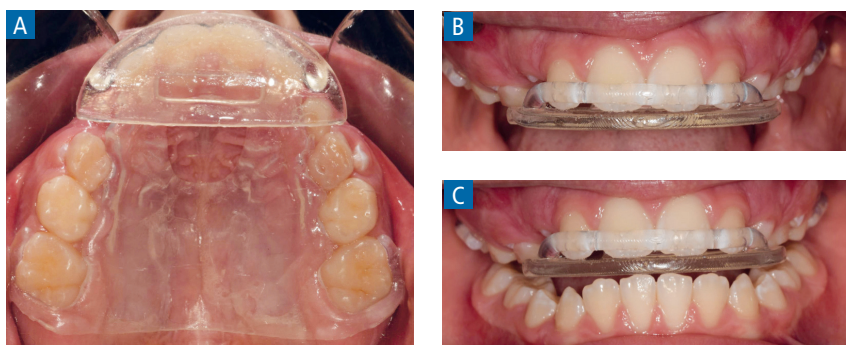


FIG. 4 Functional removable appliance (Cervera-type), made with digital setup and 3D printed with Graphy resin

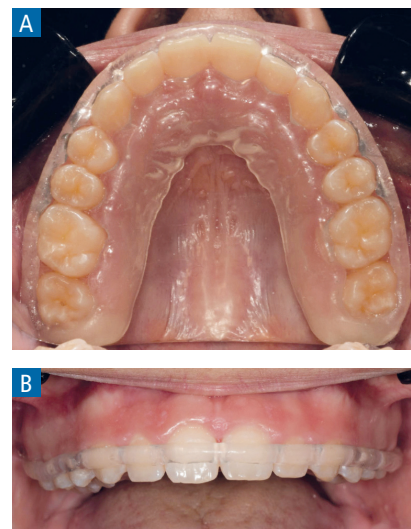


FIG. 5 Upper Hawley retainer, made with digital setup and 3D printed with Graphy resinretainer, made with digital setup and 3D printed with Graphy resin

cations of PA12 are currently limited to the manufacturing of a palatal expander (Zero Expander), which results effective in paediatric orthodontic treatment of palatal transverse deficiency, not requiring patient and parental compliance. Through a fully digital process, a pre-programmed expander can be designed on the virtually expanded maxillary arch, and then 3D printed using PA12 powder, to obtain a metal-free appliance [Beretta et al., 2021]. After its placement in contraction on teeth, the shape memory properties of PA12 enable the expander to reach its original dimension, exerting an expansion force like a pre-activated Quad-Helix, in a controlled and comfortable way [Beretta et al., 2021].

SMPs are a sub-group of smart shape memory materials which can switch from a temporary to their permanent shape, changing their macroscopic form in a predefined way in response to a suitable stimulus [Bichu et al., 2023].

The shape memory mechanism of SMPs is based on two key characteristics: a stable polymer network structure which determines the original shape, and a reversible switching polymer that enables the material to change into a modified or temporary shape [Huang et al., 2010, Elshazly et al., 2021].

In fact, SMPs are characterised by the shape memory effect (SME), which is the ability of materials to be deformed and fixed in a temporary or inactive form (programming), which remains stable until exposed to a proper stimulus (recovering) [Bruni et al., 2019]. Upon recovering the original shape, the material can be programmed again [Bruni et al., 2019]. The SME is not an inherent property of the material, but rather a combination of a specific polymer network structure of the material with a specially designed processing and programming method [Huang et al., 2010].

The underlying mechanism for the SME is due to a two-domain system, in which one domain is hard/elastic at room temperature maintaining dimensional stability, and the second one is soft/ductile or stiff depending on the applied stimulus [Bichu et al., 2023]. The first segment represents the elastic domain (or shape-fixing component), while the second one is the transition segment (or shape switching component) [Bruni et al., 2019].

The shape-memory effect has been appealing for its potential adoption in medicine and dentistry since its discovery in metal alloys, such as nickel-titanium [Bruni et al., 2019].

As compared with its metallic counterpart, the advantages of the polymeric SMPs are a significant elastic deformation, transparency, low density, low cost, tailorable physical properties, chemical stability and biocompatibility [Li et al., 1997, Bruni et al., 2019].

In particular, thermoresponsive SMPs may have high potential as a new orthodontic material, having a new capacity to recover their original shape after being deformed, upon specific thermal

initiation [Elshazly et al., 2021] (Figure 4-5).

In response to the thermal stimulus, there is reversible activation or deactivation of polymer-chain motion in the switching segments, according to the threshold of transition temperature (generally the glass transition) [Nakasima et al., 1991]. Therefore, the stimuli-responsive effects on the molecular level are converted into macroscopic movement. In fact, upon reaching this temperature, the elastic property of SMP allows it to return from the altered to its original shape, and this shape recovery produce orthodontic forces resulting in tooth movement [Bichu et al., 2023].

SMPs may exhibit many temporary shapes due to a wide temperature range for shape recovery [Huang et al., 2010; Bichu et al., 2023]. Moreover, many of SMPs have a transition temperature near the body temperature, therefore the intraoral temperature may act as an initiator [Edelmann et al., 2020; Elshazly et al., 2022].

Shape memory polyurethane resins are composed of polar and non-polar molecules that can separate into microdomains of hard and soft segments [Bichu et al., 2023]. By combining these two properties, the material is able to achieve high strength from the hard segments and high toughness from the soft ones, making it easier to create long-lasting orthodontic aligners that can move teeth over an extended period of time with significant shape recovery forces [Bichu et al., 2023, Li et al., 1997].

In addition to the aesthetic and functional advantages of their intrinsic characteristics, polyurethane resin is also durable against stain deposits, therefore aligner can remain clear in the intra-oral environment for a longer period of time [Bichu et al., 2023].

As confirmed by the articles included in the present review, so far the main use of SMPs has been direct printing of aligners, as a suitable clinical alternative to conventional thermoplastic material [Bichu et al., 2023, Jindal et al., 2019]. The 3D printing of SMPs (also called 4D printing) is based on additive manufacturing through SLA technology [Tsolakis et al., 2022].

Compared to thermoforming procedures or 3D printing subtractive process, the use of SMPs to 3D print direct aligners seems to offer several practical advantages, such as improved accuracy, ease of production, shorter supply chains, significantly shorter lead times, and lower costs of raw materials and of processing workflow [Peeters et al., 2019, Bichu et al., 2023, Jindal et al., 2019].

A reported in the included studies, two biocompatible SMPs have been proposed in literature for 3D printing of clear aligners:

ClearX v.1.1 [Elshazly et al., 2022] and TC-85 [Can et al., 2022, Hertan et al., 2022, Koletsi et al., 2022, Lee et al., 2022, Pratsinis et al., 2022, Willi et al., 2022, Zinelis et al., 2022].

Using ClearX resin, Elshazly et al. [2022] reported that SMP aligner is able to release biocompatible orthodontic forces after a suitable thermal stimulus within the oral temperature range. However, this 4D technology was patented by K Line Europa, requiring the involvement of a third company [Elshazly et al., 2022].

On the contrary, TC-85 resin is the first commercially available material for 3D printing of clear aligners [Hartshorne and Wertheimer, 2022]. Introduced by Korean Graphy Inc company, TC-85 is a biocompatible photocurable free-aromatic resin [Can et al., 2022, Pratsinis et al., 2022]. Although the specific chemical structure of this material is covered by patent, the material is an aliphatic vinyl ester-urethane polymer, possibly cross-linked with methacrylate functionalisation [Lee et al., 2022, Can et al., 2022, Willi et al., 2022].

As reported by previous studies, direct aligner printed using TC-85 showed an enhanced accuracy and surface quality, overcoming the current limitations of thermoformed aligners [Hertan et al., 2022, Koletsi et al., 2022, Lee et al., 2022]. Moreover, their geometric stability at high temperatures and their shape memory properties led to clinical advantages, such as the release of constant and light forces during their intra-oral use and the feasibility of disinfection at high temperature [Can et al., 2022, Hertan et al., 2022, Lee et al., 2022].

Moreover, depending on patient's need, SMPs aligners may be designed with tailored features (such as customisable intra-aligner thickness or pressure points) and may be 3D printed in laboratories or directly in-office (without the involvement of aligner companies) [Huang et al., 2010], because SLA printers can be installed in orthodontic office due to their reduced size, affordable cost and ease to use [Tsolakis et al., 2022, Can et al., 2022].

Therefore, the use of new polymers for 3D printing technology seems to be the future trend to manufacture most of the orthodontic appliances, ensuring excellent mechanical properties throughout all orthodontic treatment.

Conclusion

Advancement in orthodontic materials is influencing the clinical practice. The search for efficient polymers and cost-effective techniques to reduce treatment time and patient's compliance is making significant progress.

PA12 and SMPs are new materials for 3D printing customised, metal-free and fully digital orthodontic appliances, which broaden the outlook towards a tailor-made orthodontics.

However, further clinical studies should be performed to assess the efficiency of these polymers compared to conventional orthodontic materials.

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