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Review

Polymeric materials and films in dentistry: An overview

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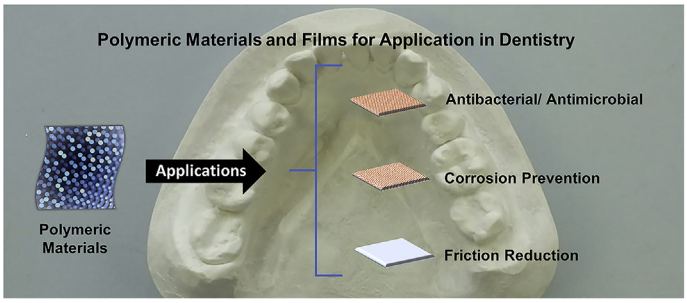
GRAPHICAL ABSTRACT



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ABSTRACT

The use of polymeric materials (PMs) and polymeric films (PMFs) has increased in medicine and dentistry. This increasing interest is attributed to not only the excellent surfaces of PMs and PMFs but also their desired mechanical and biological properties, low production cost, and ease in processing, allowing them to be tailored for a wide range of applications. Specifically, PMs and PMFs are used in dentistry for their antimicrobial, drug delivery properties; in preventive, restorative and regenerative therapies; and for corrosion and friction reduction. PMFs such as acrylic acid copolymers are used as a dental adhesive; polylactic acids are used for dental pulp and dentin regeneration, and bioactive polymers are used as advanced drug delivery systems. The objective of this article was to review the literatures on the latest advancements in the use of PMs and PMFs in medicine and dentistry. Published literature (1990–2017) on PMs and PMFs for use in medicine and dentistry was reviewed using MEDLINE/PubMed and ScienceDirect resources. Furthermore, this review also explores the diversity of latest PMs and PMFs that have been utilized in dental applications, and analyzes the benefits and limitations of PMs and PMFs. Most of the PMs and PMFs have shown to improve the biomechanical properties of dental materials, but in future, more clinical studies are needed to create better treatment guidelines for patients.

Introduction

Dental biomaterials have been extensively studied for many decades. Current advances in biomaterial science have led to the discovery of new materials for dental use and have broadened their

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use in preventive, restorative, and regenerative treatments [1,2]. A wide variety of these materials ranging from dental cements, resins, metals, and alloys to ceramic materials are used in dentistry. Metals and alloys commonly used in dentistry include titanium (Ti) and their alloys such as nickel-titanium (NiTi), stainless steel, cobalt-chrome alloys, nickel-chrome, gold-based alloys, or dental amalgam [3]. Despite the wide availability of biomaterials, no material has ideal physical, mechanical, biological, and surface characteristics [4]. Therefore, selecting a biocompatible material for dental use depends on numerous factors such as their corrosion behavior, mechanical properties, cost, availability, and esthetics [5].

The increased longevity of the population has raised the demands for improved dental material function and esthetics. Polymeric materials (PMs) are widely used in biomedical fields [6], and their use has increased due to their improved properties and wide applicability. Polymers play a major role in different aspects of dentistry, such as preventive, restorative, and regenerative therapies [7]. The use of PMs and polymeric films (PMFs) rather than traditional materials (such as dental amalgam and cements) used in dentistry is becoming more common due to their physical and mechanical properties and biological properties. Moreover, these materials can be used for dentin regeneration or as advanced drug delivery systems.

Polymers are high-molecular-mass macromolecules consisting of repeating structural units derived from their respective monomers. Polymers commonly used in dentistry are polyethylene (PE) [$-(CH_2-CH_2)-$], polymethyl methacrylate (PMMA) [$-\{CH_2--C(CH_3)-CO-OCH_3\}-$], polycarbonate (PC) [$-\{O-(CO)-O\}-$], polyethylene glycol (PEG) [$-\{CH_3(O)-CH_3(O)\}-$], polydimethylsiloxane [$-\{(CH_3)_2-Si-O\}-$], polyurethane (PUR) [$-(NH-COO)-$], polylactic acid (PLLA) [$-\{O-CH(CH_3)-O\}-$], poly(e-caprolactone) (PCL) [$-\{CO(CH_2)_5-O\}-$], polypyrrole (PPy) [$-\{C_4H_5-N\}-$], and hexamethyldisilazane (HMDC) [$-\{C_6H_{19}-N_5-Si_2\}-$], N-isopropylacrylamide [$-\{C_6H_{11}-NO)\}-$], N-tert-butylacrylamide [$-\{C_7H_{13}-NO)\}-$], and hydrogel [$-\{C_3H_3-NaO_2)\}-$] [6]. Although the mechanical properties of these biomaterials are dictated by their bulk properties, their tissue biomaterial interactions are governed by their surface properties which can be easily tailored to specific requirements [8]. Thus, polymer coatings may be used to increase the biocompatibility of a bulk material.

The increased use of engineering and nanotechnology in medicine and dentistry has led to the development of improved PMs for dental applications [9]. However, there exist no reports presenting an overview of the latest advancements in PMFs for dental applications. This review presents a brief overview of the approaches for using PMs for dental and medical applications. Here, we also present an update on PMs for use in dentistry covering their antimicrobial properties, drug delivery, and tissue regeneration and for reducing corrosion and friction. Available articles (from 1990 to 2017) on PMs and PMFs use in medicine and dentistry were reviewed using MEDLINE/PubMed and ScienceDirect resources.

Classification of PMFs in dentistry

PMFs in dentistry can be classified according to their applications as detailed below:

Antimicrobial PMFs in dentistry

PMFs for preventing biofilm and dental caries development
PMFs for preventing tooth erosion
PMFs for drug delivery
PMFs in restorative dentistry
PMFs in prosthetic dentistry
PMFs in implantology
PMFs in periodontics

PMFs for reducing corrosion in dentistry
PMFs for reducing friction in dentistry

Antimicrobial PMFs in dentistry

Biofilms cause common dental diseases that involve microbes adhering to teeth or restorative materials [10]. Microbial adhesion is followed by bacterial growth and colonization, resulting in the formation of a compact biofilm matrix [11]. This matrix protects the underlying bacteria from the action of antibiotics and host defense mechanisms. The biofilm formed on teeth, prostheses, or implant-anchored restorations contains aciduric organisms such as *Streptococcus mutans* (*S. mutans)* and *lactobacilli* that secrete acid causing enamel and dentin demineralization Biofilm formation on dental implants can result in serious infection leading to dental implant failure. Adding different antibacterial agents such as, quaternary ammonium compounds [12], inorganic nanoparticles (NPs) [13,14], or fluoride varnish with natural products [15] into the dental materials prevents biofilm formation and bacterial growth. Dental varnishes containing fluoride with natural products including miswak, propolis, and chitosan have been shown to be an effective approach for caries prevention [15]. Newer techniques include the use of antibacterial polymer coatings for preventing bacterial growth on artificial tooth surfaces in other dental materials and dental composite kits increasing the restoration's longevity [16]. Examples of such antibacterial coatings include copolymers of acrylic acid, alkylmethacrylate and polydimethylsiloxane copolymers [1], pectin coated liposomes [17], and carbopol [2,18].

PMFs for preventing biofilm and dental caries development

Preventing bacterial biofilm formation is a major challenge in dentistry. Biofilms are collections of microbes that attach to hard tissue. These microbes produce excessive extracellular polymeric substances (EPS) that protect them from their environment and antibiotics, thereby making them antibiotic resistant [19]. Nanotechnology and polymeric nanomaterials have been used to prevent bacterial adhesion and biofilm formation [20,21]. The combination of nanoparticles (NPs) and antibiotics enhances antibiofilm activity. Preventing microbial adhesion and proliferation on dental material surfaces depends on interactions between synthetic polymeric biomaterials and tooth structure (Fig. 1) [19]. Polymer NPs help deliver drugs to the target site in entrapped or immobilized forms. In addition, NPs penetrate the biofilm structure, and release metal ions and antimicrobial compounds to destroy the biofilm and inhibits microbial colonization.

Fornell et al. [1] evaluated the anti-adhesive properties of polymers (acrylic acid, alkylmethacrylate, and polydimethylsiloxane copolymer) on plaque accumulation and enamel demineralization in low-caries adolescents. Their results showed that an anti-adhesive polymeric enamel coating used in conjunction with orthodontic appliances in adolescents with low caries cases had no clinical effects. However, their findings may be useful in high-risk caries cases, which should be investigated.

Bioadhesive nanosystems, such as liposomes, have been shown to be advantageous because they can reach sites inaccessible to other types of formulations, and can also be site-specifically targeted [22]. Nguyen et al. [17] found that pectin coated liposomes that formed naturally on tooth surfaces adsorbed the hydroxyapatite (HA) *in vitro* and acted as protective biofilms. The ability of pectin-coated liposomes to remain on enamel suggests their possible use as a protective coating on the teeth. In fact, the use of charged liposomes, either uncoated or coated using electrostatic deposition with polysaccharides (alginate, chitosan and pectin),

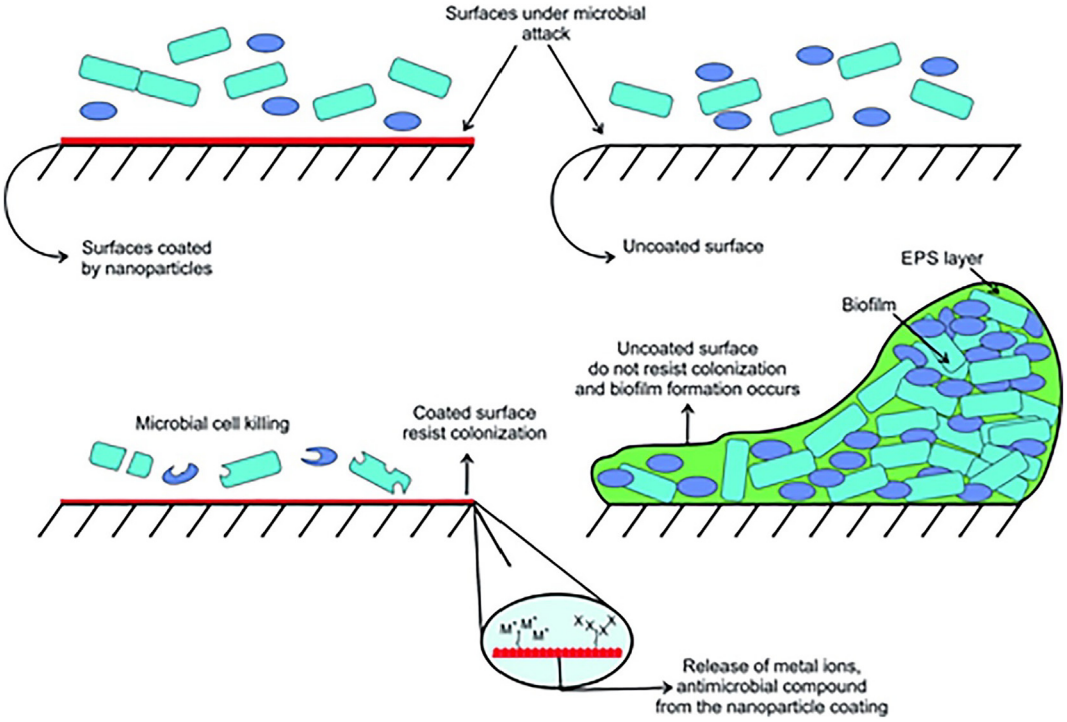

Fig. 1. Prevention of biofilm formation by an antimicrobial polymeric film on the tooth surface. (Reproduced from Qayyuma and Khan [19] with permission from The Royal Society of Chemistry).

as bioadhesive systems for the oral cavity was investigated through an *in vitro* study (Fig. 2) [23]. It was found that the liposome surface charge was highly important for their stability in saliva and for bioadhesion. The negatively charged liposomes were the most stable in artificial saliva, and the stability of the positively charged liposomes in the film was improved using a negatively charged polysaccharide [23].

PMFs for preventing tooth erosion

Soft drinks with low pH causes tooth erosion and dental caries. Erosive enamel demineralization results in surface softening and roughening [24]. Various polymeric films have been tried for physically protecting the teeth against erosion by preventing the direct contact of acidic environment in the oral cavity with the teeth [24–27]. Beyer et al. [25] studied the ability of a polymer modified citric acid solution of propylene glycol alginate to reduce tooth erosion. They found a layer, consisting of two opposing gradients of hydroxyapatite (HA) particles and polymer molecules, helped to reduce the erosion on dental enamel surfaces. The polymers (propylene glycol alginate, highly esterified pectin and gum arabic) adsorbed on the teeth forming a protective layer on the enamel and dentin that reduced the erosive effects of acid [26].

Chitosan is a natural polymer derived from the deacetylation of chitin. Carvalho and Lussii [24] studied the preventive effects of a fluoride-, stannous- and chitosan-(F/Sn/chitosan-) containing toothpaste on enamel erosion and abrasion. They found that the toothpaste containing F/Sn/chitosan showed promising results in reducing tooth surface loss from erosion and abrasion. Chitosan, due to the presence of a cationic amino group, has a high positive zeta-potential and readily adsorbs onto materials such as enamel of strong negative zeta potential [28] through electrostatic forces [29]. The preventive potential of chitosan against erosion and enamel demineralization is attributed to its ability to form a protective multilayer on the tooth surface in the presence of mucin

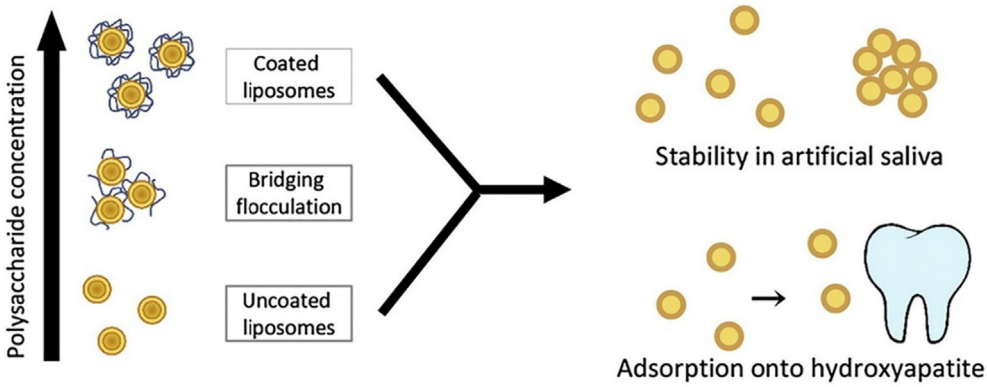

Fig. 2. Pectin-coated liposomes that formed on tooth surfaces used as bioadhesive systems in the oral cavity. (Reproduced from Pistone et al. [23] with permission from Elsevier).

from saliva [30]. This layer-by-layer build-up on the dental enamel is acid resistant, and it provides a better protection against erosive attacks. In addition, tin (Sn) has a protective effect due to the formation of amorphous deposits on the enamel surface, and the incorporation of Sn into the eroded enamel and dentin [31].

Carbopol, a high-molecular-weight acrylic acid polymer, has been used as a thickening agent in many formulations such as gels, suspensions, and emulsions. It also prevents or controls the enamel demineralization causing no deleterious effects on the tooth [18]. A carbopol film combined with sodium fluoride has demonstrated an improved protective effect against tooth demineralization [2].

Gracia et al. [27] studied the effect of pre-treating sound human enamel with a water-soluble combination polymer system (TriHydra™) on *in vitro* erosion by citric acid. This system comprised 0.20% carboxymethylcellulose (CMC), 0.010% xanthan gum, and 0.75% copovidone, alone or in combination with fluoride. They found that the combination polymer system had an anti-erosion effect. The polymer/F admixture significantly reduced surface roughness; however, bulk tissue loss reduction was not significantly different compared with either treatment alone. This was because the combination polymer system employed as an admixture with F conferred significantly greater suppression of enamel surface etching (as shown from surface roughness) compared with either treatment alone. There was no specific interaction between the F ions because CMC and xanthan gum are anionic polysaccharides and copovidone is a non-ionic copolymer. These polymers transport F to the enamel surface.

Studies have been conducted on the efficacy of toothpastes and topical creams containing casein phosphopeptide-amorphous calcium phosphate (CPP-ACP) with fluoride in preventing erosive tooth wear from acidic beverages or solutions [32–34]. A randomized controlled trial was conducted by Maden et al. [32] to investigate the effect of acidulated phosphate F (APF) gel and CPP-ACP on the dental erosion in primary teeth. They found that artificial saliva, CPP-ACP, and 1.23% APF treatments reduced erosive enamel loss produced by carbonated drinks in primary teeth. The 1.23% APF gel showed the highest protective effect against erosive enamel loss.

PMFs for drug delivery

Drug delivery via the oral mucosa can occur through keratinized mucosa (gingival and hard palate), and nonkeratinized mucosa (sublingual and buccal) [35]. The bioadhesive formulations protect fragile drugs and improve the retention time of active substances ranging from days to months improving the efficacy of the treatments resulting in patient comfort and compliance [35]. There have been advances in drug formulations and drug delivery strategies using various polymers and NPs to prevent biofilm formation [17,36–40].

Drug-loaded polymeric nanocapsules prepared with different biodegradable polymers, such as chitosan, alginate, gelatin, and methacrylic acid have exhibited potential use as drug delivery systems [36]. The use of nanocapsules as carriers allows for targeted drug delivery, controlled/sustained release drug delivery systems, transdermal drug delivery systems, and improved drug stability and bioavailability. Furthermore, Lococo et al. [40] investigated the use of submicron size (<250 nm) argan oil-based nanoemulsions as drug carriers that demonstrated, negative zeta potential (between −40 and −50 mV) and drug-encapsulation efficiency (higher than 85%), indicating good physical stability and good performance as drug carriers. The polymer microsphere-based systems used for delivery included molecules ranging from smaller molecules to peptides; and macromolecular drugs such as proteins, oligonucleotides and DNA [41]. The mucus or cell-specific bioadhesive polymers that allow for cytoadhesion and bioinvasion provide unprecedented opportunities for targeting drugs to specific cells or intracellular compartments. Similarly, the use of multi-walled carbon nanotube-coated Ti alloy for drug delivery significantly inhibited biofilm formation for up to 5 days [37]. Hence, this coated alloy may be effective against the pathogenic biofilm on endoprostheses, such as the knee joint, hip, and teeth. The NPs incorporated with polyethylene glycol (PEG), or subjected to 'PEGylation' improved the efficiency of drug and gene delivery to target cells and tissues [38]. Such NPs-PEGs protect the NPs surface from aggregation, opsonization, and phagocytosis prolonging systemic circulation time. In addition, Carbopol can be used as an adjuvant for bioadhesive drug delivery systems [2].

For dental drug delivery, different pectin (LM-, HM- and AM-pectin)-coated liposomes were effective because they adsorb on HA and the dental enamel [17]. Their ability to be retained on enamel surfaces suggests using these pectin molecules as a protective coating for teeth. In addition, polymers such as polycarbonate micelles have also been investigated for controlled drug release applications [39].

Polycarbonate, a naturally transparent amorphous thermoplastic that has good heat resistance, high toughness and impact strength, can be combined with polyethylene glycol (PEG) and antimicrobial agents for controlled drug release applications. Amphotericin B (AmB) [9], an antifungal agent can be mixed with polymer micelle in films (Ambicelles) for controlled AmB release and minimize systemic toxicity [39,42–44]. Wang et al. [39] assembled phenylboronic acid-functionalized polycarbonate (PBC)/PEG and urea functionalized polycarbonate (PUC)/PEG diblock copolymers incorporated with AmB. They found that these polymer micelle films were promising AmB carriers with comparable antifungal activity, however, disadvantages of AmB include poor water solubility and nephrotoxicity at high concentrations [44]. Chen et al. [44] developed a novel self-assembling mixed polymeric micelle delivery system based on lecithin and combined with amphiphilic polymers, d-alpha tocopheryl PEG succinate, and 1,2-distearoyl-sn-glycero-3-phosphoethanolamine-N-methoxy(poly(ethylene glycol)-2000 (DSPE-PEG2K) (Fig. 3). These polymers demonstrated increased bioavailability and a synergistic anticancer effect. The disadvantage of Ambicelles is that they are unstable when they are stored for a long period.

PMFs in restorative dentistry

Because of the high complexity of the tooth organic substrate, collagen and dentin proteins, it is difficult to achieve the optimal interaction between polymers and dentin [45]. Thus, the disadvantages of composite restorations include polymerization shrinkage, secondary caries, and restorative material fracture [46,47]. In addition, many restorative materials, including resins and composites accumulate more biofilm than other restorative materials, such as amalgam and dental restorative cements [48,49].

Resin composite restorations are technique sensitive, and achieving good isolation is very important [50]. Saliva contamination during restoration curing disrupts the bonding of the composite restoration with the tooth structure [51,52]. In addition, composites may degrade in the oral cavity. Biofilm formation contributes to the formation of an environment that is more prone to composite degradation, reducing the composite restoration lifespan. Cariogenic bacteria can degrade composites, thereby increasing the surface roughness. Increased roughness and subsequent increased bacterial accumulation may facilitate the development of secondary caries around composites, which is the most common reason for composite restoration failure [53]. Lee et al. [54] investigated using a dopamine-methacrylate, 2-methoxyetheyl acrylate as a dental adhesive. They found that the catechol-functionalized methacrylate random copolymer containing Fe^{3+} improved the bond strength of dental adhesives to an artificial saliva contaminated dentin surface. The catechol groups undergo polymerization,

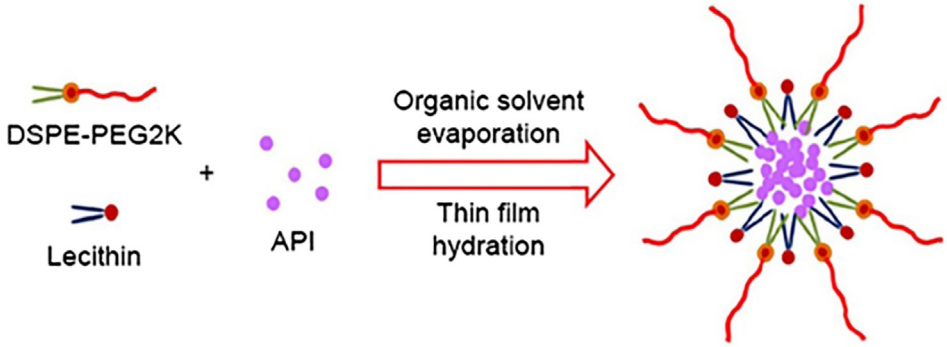

Fig. 3. Polymeric micelles mixed with amphotericin B. DSPE-PEG2K: 1,2-disteroyl-sn-glycerol-3-phosphoethanolamine-N-methoxy(poly(ethylene glycol)-2000; API: Active Pharmaceutical Ingredients. (Reproduced from Chen et al. [44] under the creative commons attribution - noncommercial (unported, v3.0) license from Dove Medical Press Ltd.)

which immobilize proteins on substrate surfaces. The catechol-functionalized polymer can function as a dental adhesive for wet dentin surfaces, potentially eliminating the complications associated with saliva contamination. The authors suggested that this polymeric film may reduce dental restoration failure due to saliva contamination [54]. In addition, the polymer adhesives could be used for dental implant coatings, where good biocompatibility and good cell adhesion are required.

It has been shown that some dental cements are antibacterial [55–57]. Târcă et al. [55] evaluated the surface antibacterial properties of glass ionomer cements (GIC) and compomers. The materials with bioactive features inhibited the growth of *S. mutans* in the bacterial biofilm on coronal restoration surfaces. Yengopal and Mickenautsch [56] studied the caries-preventive effect of resin-modified GIC (RM-GIC) compared with resin composites. Their results showed either no difference between the materials or indicated that RM-GIC had a superior caries preventive effect.

Feroz et al. [57] found that ZOE and zinc polycarboxylate (ZPC) cement showed antibacterial activity against *S. mutans* and *Lactobacilli* as determined by the agar diffusion test. However, each cement showed some antibacterial activity in a direct-contact test. Hence, the antibacterial activity varied according to the methods used. Long-term clinical trials using specific methods and techniques are necessary to determine the antimicrobial effects of dental materials.

Various anti-bacterial polymeric coatings such as acrylic acid, alkylmethacrylate, and polydimethylsiloxane copolymer [1], Carbopol [2], N-halaminebased polymer additive [58], and Ti oxide-chitosan/ heparin multilayers [59] have been used to prevent biofilm formation and to increase restoration longevity (25).

PMFs in prosthetic dentistry

Polymethyl methacrylate (PMMA) is widely used as biomedical material to make various types of prostheses in medicine and dentistry [60]. PMMA is a strong, tough, lightweight material with good impact strength compared with glass and polystyrene, and its environmental stability is superior to most other plastics such as PE and polystyrene [61]. However, PMMA has certain disadvantages; it swells and dissolves in many organic solvents and chemicals due to its easily hydrolyzable esters groups [62].

Reducing biofilm formation on dental materials, such as denture base, is a key to oral health. Various additives such as zirconium oxide nanoparticles (ZrO_2-NPs) [63], Yamani henna power [64], silver nanoparticles (Ag-NPs) [65] or platinum nanoparticles (Pt-NPs) [66] have been incorporated into PMMA to reduce bacterial or fungal colonization. The addition of ZrO_2-NPs to cold-cured PMMA reduced *C. albicans* adhesion to denture bases and cold-cured removable prosthesis [63]. Li et al. [65] found that *C. albicans* biofilm bioactivity dose-dependently decreased with increasing Ag-NP concentration and exhibited anti-adhesion activity at a high concentration (5%). The antibacterial activity after adding Pt-NPs to PMMA was investigated by Nam [66] who reported that the Pt-NPs-modified PMMA showed a significant anti-adherent effect rather than a bactericidal effect above 50 mg/L Pt-NPs compared with control.

Various polymeric films have been used as antimicrobials on prostheses to prevent biofilm development. Shibata et al. [67] investigated the effect of a phospholipid polymer, poly(2-methacryloyloxyethyl phosphorylcholine-co-n-butyl methacrylate) (PMB), on PMMA in preventing biofilm formation. The PMB polymeric film inhibited sucrose-dependent *S. mutans* biofilm formation on PMMA denture base, indicating that this biocompatible PMB polymer film may reduce biofilm formation on PMMA surfaces.

Polymers have been used to fabricate nanosilver nanocomposites with better properties and enhanced antibacterial activity [68]. Travan et al. [69] developed an antimicrobial nanocomposite using lactose-modified chitosan incorporated with Ag-NPs for the heat polymerized PMMA that is used in dentistry. Their *in vitro* results showed that the nanocomposite effectively killed both gram+ and gram− strains, but was not cytotoxic to osteoblast-like cell-lines, primary human fibroblasts or adipose-derived stem cells.

The polymer graphene, which has been described as the "thinnest material in the universe", has attracted attention in various fields, including dentistry, because it has dramatically improved mechanical properties [70]. Graphene, discovered in 2004 [71], is an allotrope of carbon with a one-atom-thick planar sheet of sp^2 bonded carbon atoms that are densely packed in a honeycomb crystal lattice [9,72]. Methods of fabricating graphene sheets with improved properties have been explored [73]. Graphene oxide (GO) materials are widely studied for fabricating various nanocomposites of different polymer matrixes for different applications [9,74]. Graphene can be reduced and functionalized with other polymers to produce antimicrobial nanocomposites. Nam et al. [75] evaluated an antimicrobial nanocomposite composed of reduced graphene oxide using antimicrobial agents and catechol derivative conjugated to PEG-grafted poly (dimethylaminoethyl methacrylate). In addition, Ag-NPs deposited onto functionalized hybrid graphene demonstrated increased antimicrobial activity against *Staphylococcus aureus* and *Escherichia coli* compared with that against control. Biocompatible antimicrobial graphene and Ag-NP polymer may have good potential to produce an antimicrobial surface on dental biomaterials such as a dental prosthesis.

PMFs in implantology

The osseointegration of cpTi/Ti alloy implants used for dental, craniofacial and orthopedic purposes is related to their composition and surface roughness. Rough surfaced implants increase osseointegration and biomechanical stability [76]. Implant surface treatment methods include Ti plasma-spraying, grit-blasting, acid-etching, anodization and calcium phosphate coatings [77]. A favorable environment is necessary for implant osseointegration. The reduced oxygen concentration from the poor vasculature at the implant surface interface promotes a buildup of host-cell-related electrons as free radicals and proton acid that can encourage infection and inflammation causing implant failure [78,79]. To provide a favorable environment for osseointegration and overcoming the problems associated with Ti implants, surface modifications can be performed using high-strength fiber-reinforced and complex fillers/additives including hydroxyapatite or antimicrobial incorporation via thermoset polymers, which cure at low temperatures [78]. The polymer/carbon-fiber-reinforced composite produced successful osseointegration. Thermoset polymer matrix and carbon fibers generate covalent bonds providing strong bone structure support with excellent osseointegration [80].

Researchers are also focusing on developing bioactive coatings on dental implants to enhance osseointegration by interactions between proteins, cells and tissues, and implant surfaces [76]. The local release of bone stimulating or resorptive drugs in the peri-implant region may result in long-term dental implant success. Biomimetic coated Ti surfaces with nano-hydroxyapatite (n-HA) and poly(lactic-co-glycolic acid) (PLGA)/collagen nanofibers have been studied for dental and bone implant surfaces to enhance osseointegration [81]. This coating enhanced initial cell adhesion, cell proliferation, differentiation and mineralization on the implant surface.

The use of antibiotic-containing nanofiber-based polymeric films on dental implants has been investigated to minimize implant loss, especially in periodontally compromised patients. Bioactive polymers such as hydrogels, hydroxypropyl methylcellulose (HPMC), poly(lactic/glycolic acid) and poly(ε-caprolactone), have been used for the sustained release of antimicrobial drugs such as metronidazole, ciprofloxacin, and minocycline [82–85]. Polylactic acid (PLLA), a popular low-cost biodegradable polymer has excellent biocompatibility and good mechanical properties (particularly tensile Young's modulus, tensile strength, and flexural strength) compared with polyethylene and polysulfide [86,87]. PLLA has wide applications in medical sciences and is used in a range of devices, including degradable sutures, drug releasing micro-particles, nano-particles, and porous scaffolds for cellular applications [88]. Shahi et al. [89] used a tetracycline hydrochloride PLLA, poly(e-caprolactone), and gelatin polymer solution to synthesize tetracycline-containing fibers. These fibers inhibited the growth and biofilm formation of peri-implantitis associated pathogen such as *Fusobacterium nucleatum, Porphyromonas gingivalis, Prevotella intermedia* (42,43) and *Aggregatibacter actinomycetemcomitans* [85]. They suggested that tetracycline-containing fibers have potential to use as an antibacterial film on dental implants. However, the elongation at break and impact strength of PLLA are lower than that of polyethylene, polyethylene terephthalate and polyamide (PA), and PLLAS's poor toughness limits its use in applications requiring plastic deformation at higher stress levels; this requirement has stimulated investigation on toughening PLLA [90,91].

PMFs in periodontics

Inhibiting biofilm formation on tooth enamel is an important technique for preventing dental and periodontal diseases. The *2-methacryloyloxyethyl phosphorylcholine* (MPC) is a polymer that is water-soluble, biocompatible and has good hemocompatibility. MPC reduced the retention of human pathogenic microorganisms [92]. Kang et al. [93] immobilized MPC on the tooth surface to prevent oral bacterial adhesion. The synthesized MPC-ran-2-methacryloyloxyethyl phosphate (PMP) copolymer with zwitterionic and Ca^{2+} binding moieties formed a highly effective biofilm inhibiting surface on the HA of the tooth surface. It showed that HA surfaces coated with a copolymer containing 50% MPC (PMP50) reduced protein adsorption and subsequent cell adhesion and *S. mutans* adhesion compared with other polymer combinations. Thus, highly stable anti-adsorptive and anti-bacterial PMP films can be used in dentistry and medicine. However, a disadvantage of MPC is its complicated synthesis resulting in high production cost, which limits their wide applicability [94].

PMFs for reducing corrosion in dentistry

Corrosion is a diffusion interfacial electron-transfer process that occurs on the surface of metals, and metal corrosion is an important factor in biocompatibility. The Ni released from NiTi and stainless steel orthodontic wires is a known allergen. The oral signs and symptoms resulting from Ni released from orthodontic appliances include gingival hyperplasia, stomatitis, angular cheilitis, perioral rash, erythema multiforme, burning sensation, and loss of taste [95,96]. Another common metal used in dentistry is Ti and its alloys. Although, uncommon, it was found that Ti could generate dark staining of the tissues around the implant [97]. Soft tissue inflammation with black extracellular deposits and Ti particles within histocytes and foreign body giant cells resulting from the rough surfaces of Ti alloy medical prostheses or those that have loosened have been observed. This has led to concerns about the long-term metabolic, oncogenic, and immunological effects of Ti particles [97,98]. It was found that after placing single threaded screw implants into sheep mandibles, the Ti levels were below 400 ppb [99]. In addition, despite the tendency of Ti alloy mini-implants to release Ti ions, the amounts of Ti ions detected were significantly lower than the average intake of Ti through food and drink, and the levels did not reach toxic concentrations [100]. These findings suggest that although Ti can be released, the levels are not biologically meaningful. It is known that Ti ions are responsible for monocyte infiltration in the oral cavity by elevating the sensitivity of gingival epithelial cells to microorganisms [101]. Although, Ti at levels of 5–9 ppm may be involved in cytotoxicity, inflammation, and necrosis at >13 ppm at the interfaces of dental implants and gingival tissue [101], currently there are no clinical reports about Ti toxicity.

Biocompatible modified polymeric films have been coated on NiTi alloy wires to increase corrosion resistance and improve mechanical properties [102–104]. Polymeric films that can be used as coatings over NiTi, stainless steel wire and other materials to prevent corrosion are Pyy/HA nanocomposite [103], PUR [105], polyamide [106], polyetheretherketone [107], polytetrafluoroethylene [108], graphene oxide/HA [109], hexamethyldisilazane [110], and fullerene like-tungsten disulfide nanoparticles [111]. Another advantage of these films as a coating is that processing defects in non-coated rectangular wires can be eliminated after coating them with polymer. However, a disadvantage of these polymer coatings is that after a long-term use, the coatings may become rough or detach from the metal wire (Fig. 4) [112]. Hence, the polymer coating on metal should be evaluated for long-term use, and the polymer should be strong and stable.

The effect of graphene on preventing corrosion has been investigated [113–115]. Graphene coatings protected metal surfaces, especially of Ni materials, from corrosive environments [114]. These investigators observed that graphene provided effective resistance against water corrosion. Moreover, a conductive

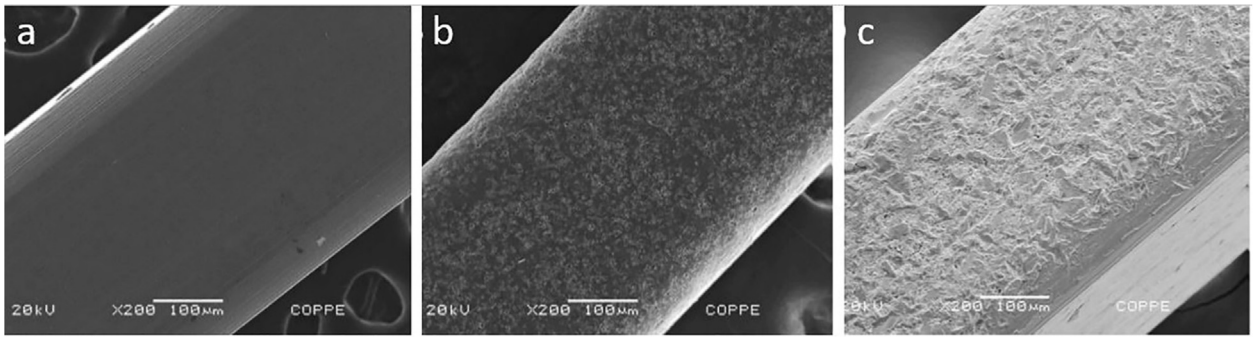

Fig. 4. SEM images of stainless steel orthodontic arch wire: (a) uncoated wire, (b) polymer coated wire, and (c) Coated wire showing rough surface and lost coating layer after use [112]. (Reproduced with permission from The E. H. Angle Education and Research Foundation).

biocompatible polymer 3,4-ethylenedioxythiphene and GO composite coating effectively reduced the corrosion of Mg-based medical implants [115]. Singh et al. [116] demonstrated that a graphene reinforced composite coating highly reduced copper corrosion. The corrosion inhibiting effect of graphene suggests that it could be coated on arch wires used in orthodontics, metal files and reamers used in endodontics, or metal prostheses [113,114,117].

PMFs for reducing friction in dentistry

Frictional force is an important consideration in dentistry, especially in orthodontic treatment because it results in the loss of applied force. Orthodontic arch wires that can deliver light forces over time would be useful to clinicians during the initial alignment phase of fixed appliance treatment [118]. Bravo et al. [119] compared the coefficient of friction of polyamide (PA) coated and uncoated NiTi wires. They found that the wear rates and the dynamic friction coefficients of PA wires were lower than those of uncoated wires. The PA coating seals the NiTi surface preventing corrosion and nickel ion release. The average decrease in Ni ion release due to this coating is approximately 85%.

Graphene film coatings have been used for lubrication and reducing friction. The tribiologic properties of GO were investigated by adding GO monolayer sheets to water-based lubricants that were applied to a sintered tungsten carbide ball and stainless steel flat plate [120]. Adding GO particles in water improved lubrication and provided a very low friction coefficient of approximately 0.05 with no obvious surface wear after 60,000 cycles of friction testing. Similar results were found by Berman et al. [121] who used a graphene coating, and Lin et al. [122] who used a graphene platelet coating to reduce friction. Thus, graphene could be used to reduce the friction of dental biomaterials such the metal-based prostheses used in dentistry [120].

Hydrogels comprise a group of PMs, the hydrophilic structure of which renders them capable of holding large amounts of water in their 3D networks [123]. Their properties include biodegradation, and chemical and biological response to stimuli [124]. However, hydrogels have disadvantages such as higher water absorption capacity and high stability, which is not favorable when degradation is desired. In addition, single component hydrogels have low mechanical strength, and recent studies have used composite or hybrid hydrogel membranes to increase the hydrogel strength [125]. Hydrogels have also been used in biomedical technology, tissue engineering, NiTi implants, and orthodontics because these polymers are viscoelastic and permeable, and their mechanical properties mimic those of many natural tissues [126–132]. Osaheni et al. [126] blended poly-vinyl alcohol with various amounts of zwitterionic polymer film, poly([2-(methacryloyloxy)ethyl] dimethyl-(3-sulfopropyl) ammonium hydroxide), demonstrating that biocompatible zwitterionic polymers reduced friction up to 80%. This material is useful in dentistry for reducing the friction and wear of dental biomaterials [133]. However, hydrogels must be used carefully because the resulting network cannot be reshaped and/or resized. The polymer is no longer soluble in solvents and melting degrades the polymer once crosslinking occurs [134].

Conclusions and future perspectives

The mechanical properties of biomaterials are dictated by their bulk properties, whereas, tissue-biomaterial interactions are governed by their surface properties. The surface modification of biomaterials can be achieved by polymer coating. Despite the availability of numerous biomaterials with suitable bulk properties, it is rare to find an ideal biomaterial that possesses excellent surface characteristics and is biocompatible for clinical applications. Based on the principles and knowledge of materials science, the benefits and limitations of these dental materials should be analyzed before deciding to use them clinically. The increased investigation into the use of PMFs has provided a novel set of therapeutic strategies for dental applications. Although most of the PMFs are not regularly used clinically, their use has shown to improve the biomechanical properties of dental materials that may translate into new treatment alternatives for patients in the future.

Conflict of interest

The authors declare no conflict of interest.

Compliance with Ethics requirements

This review article does not contain any studies with human or animal subjects.

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