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Short communication

Organosilicate based superhydrophilic nanofilm with enhanced durability for dentistry application

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ABSTRACT

The present work presents a layer-by-layer assembled nano-film with enhanced stability onto mouthguards for the first time. To obtain high thermal and mechanical durability of modified mouthguards, the silicon-based material, silsesquioxane and silica nanoparticle matrix (SiSQ), was introduced into nanofilms. Moreover, with the help of hydrogen-bonding interactions between SiSQ and a bio-compatible building block of branched polyethyleneimine (BPEI), $(BPEI/SiSQ)_n$ nanofilms were successfully prepared. Anti-bacterial property of treated mouthguards is expected to be shown in terms of film superhydrophilicity. Above all, this organosilicate-based superhydrophilic nano-film with biocompatibility and enhanced durability is of great significance, which can be applied to other biomedical platforms.

Introduction

Thermoplastic polymer sheets have been widely applied in the field of dentistry for fabricating splints, mouthguards, mandibular advancing devices, tooth aligners, orthodontic retainers, and bleaching trays [1,2]. Removable appliances composed of thermoplastic polymer sheets are gaining popularity, in terms of their excellent esthetic characteristics (invisible), formability, cost-effectiveness, and ease of use [1,3,4]. Several types of materials, such as polyethylene, polycarbonate, polypropylene, and polyethylene terephthalate glycol-modified (PETG), are currently being used for preparing thermoplastic vacuum-formed appliances (VFAs). They typically show high viscoelasticity and are sensitive to temperature, humidity, time elapsed after elastic deformation, and manufacturing processes [5]. Surface roughness increases due to adsorption of integuments at the stagnation site and localized calcification of the biofilm developed during intraoral service. Water absorption, hydrolytic degradation, and repeated load cycling cause changes in the force delivery properties and mechanical strength. The poor wear resistance and durability along the incisal and occlusal surfaces are usually exhibited, thanks in large part to vulnerable materials [3,6,7]. The increased surface roughness and occlusal wear of these materials result in cracks and subsequent fracture. Thus, frequent replacement of these appliances becomes a big problem for patients.

To overcome these issues, fabrication of multilayer appliances has been attempted to improve the mechanical properties [8,9]. However, delamination between layers occurs frequently and the increased material thickness causes discomfort. It has been recommended that the optimal mouthguard thickness should not exceed 4 mm [10]. Kataoka et al. also reported that the additional intermediate titanium layer in the anterior area of a mouthguard may not have a beneficial effect on impact absorption and dissipation [11]. Another approach is polymer blending, which has been accepted as an efficient way to integrate diverse polymer properties. Recent progress has suggested various polymer combinations to improve the mechanical properties of polymers, such as PETG/PET(polyethylene terephthalate), PETG/LCP(liquid crystal polyester), PC(polycarbonate)/ABS(acrylonitrile butadiene styrene), PC/PP(polypropylene), TPU(thermoplastic polyurethane)/PP, and PETG/PC/TPU [12–16]. However, in some cases, the resultant materials were opaque and had lower rebound resilience.

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Nanofilms onto removable intraoral appliances can be site-specific surface modification. Each appliance surface requires different types of modifications to realize specific properties, such as high anticaries efficacy, wear resistance, and water resistance. Moreover, high nano-film thickness is not required, which is of importance for patients' convenience.

Thus, superhydrophilic and biocompatible nanofilms with enhanced durability onto thermoplastic mouthguards were prepared for the first time, while the biofunctionalization of titanium was ever tried for dental implants in previous research [17,18]. Particularly, organosilicate-based material can serve as a unique building block of the layer-by-layer assembled nanofilms [19–21]. The silica nanoparticles have a high yield strength and rigidity, resulting in excellent mechanical properties of the nanocoating [22]. Then they were dispersed into the polymeric silsesquioxane matrix fabricated by a simple sol–gel reaction, leading to a relatively uniform coating. The covalent bondings between particle and polymeric silsesquioxane matrix that are generated by additional hydrolysis and condensation reactions enhance the physical strength of the nanofilms [23]. During coating assembly, biocompatible branched polyethyleneimine (BPEI) was typically selected as another component of multilayers [24]. Therefore, multifunctional $(BPEI/SiSQ)_n$ (n = number of bilayers) nanofilms onto mouthguards were prepared by hydrogen bonding-based layer-by-layer assembly, which is a unique method for fabricating nanofilms [25–27]. In addition, considering the nanoscale films and low refractive index of polymeric silsesquioxane, as-prepared nanofilms also exhibit high transmittance, which will not show serious adverse effects in the oral cavity environment.

Experimental

Synthesis of silica nanoparticle and polymeric silsesquioxane matrix (SiSQ)

To 9.56 g EtOH solvent, 1.33 g tetraethyl orthosilicate (TEOS, >99.0%, M_w = 208.33) and 0.015 g 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane (PFAS, M_w = 610.38) were dispersed, stirring for 20 min. Then, acid catalyst (1.14 g of pH 2 water, adjusted by HCl) was added into the solution. After 3.5 h hydrolysis and condensation reaction at room temperature, the polymeric silsesquioxane solution (SQ) was prepared. To prepare the SiSQ solution, 1 ml of LUDOX® TMA colloidal silica (34 wt% suspension in H_2O) and 0.5 ml SQ solution were mixed by a vortex mixer for 5 min.

Preparation of $(BPEI/SiSQ)_n$ nanofilms

The silicon wafer and polyethylene terephthalate glycol-modified substrate (PETG, Thermoforming foil Track A; Forestadent, Pforzheim, Germany) were cleaned by deionized-water and EtOH for 5 min each, finally dried by a N_2 stream. Then they were dipped into 1 mg/ml branched polyethyleneimine (BPEI, $M_w \sim 25{,}000$, dissolved in EtOH) solution for 10 min and washed three times with deionized water for 2, 1, and 1 min, respectively. After that, the substrates were immersed into the SiSQ solution (0.4614 g SiSQ solution in 60 ml EtOH) for 10 min and washed with deionized water three times, dried by the N_2 stream at last. The whole process is defined as one cycle or bilayer of the LbL films. And repeated process was carried out for a few times to fabricate final $(BPEI/SiSQ)_n$ nanofilms.

Mechanical test

Ten dumbbell-shaped specimens were prepared from PETG thermoplastic polymer sheets (Fig. S1). The thickness of each specimen is 0.8 mm, and five of them were coated with $(BPEI/SiSQ)_{20}$ films. The tensile strength test was performed using a universal mechanical testing instrument, Instron 3367 (Instron Co., Canton, MA, USA) with a loadcell of 3 kN. The ultimate tensile strength and maximum tensile load with a loading rate of 1.5 mm/min were measured at RT. The mechanical test was analyzed by using Bluehill® Lite version 2.0 software (Instron Co.). The obtained data were expressed as the mean ± S.E.. The Mann–Whitney U-test was used to compare the tensile strength dataset. P-values <0.05 were considered statistically significant.

Cell culture

Human periodontal ligament (PDL) cells were obtained from healthy patients who underwent surgical extractions at the Department of Oral and Maxillofacial Surgery. The cells were cultured in alpha minimal essential medium (α-MEM, Gibco, Carlsbad, CA, USA) supplemented with 10% fetal bovine serum (FBS), and 1% penicillin and streptomycin. The PDL cells of the 3rd to 5th passage were used in this study.

Attachment assay

PETG sheets (control), BPEI spin-coated film, SQ spin-coated film (thickness: 100 nm), and SiSQ spin-coated film (thickness: 400 nm) were fabricated to be circular in shape with a 0.9-cm diameter. After UV sterilization, each test sample was added to a 48-well plate, and 1 ml of cell suspension at an initial density of 5×10^4 cells/ml was added to each well. All samples were prepared in triplicates. At 72 h after cell seeding, test samples were rinsed with phosphate-buffered saline to wash out any unattached cells and then fixed with 10% buffered formalin solution for 1 d at room temperature. After washing with distilled water, the cells attached on the test samples were stained with hematoxylin for 10 min, as previously described [28]. The number of attached cells included in a unit area of 0.025 mm^2 (five areas on each sample) was counted under an optical microscope equipped with an ocular-micrometer. For comparison between groups, the Kruskal–Wallis test was used. P-values <0.05 were considered statistically significant.

Inflammatory cytokine assay

Circular sample disks based on PETG sheets and $(BPEI/SiSQ)_{50}$ with a 0.9-cm diameter were placed on a well of a 6-well plate, and cells were seeded at 1×10^6 cells/well. After 48 h incubation, 700 μl/well of cell culture supernates was collected and centrifuged at 20,000 rpm at 4 °C for 10 min. A cytokine assay was immediately performed according to the manufacturer's protocol (Proteome Profiler™ Human Cytokine Array, R&D Systems, Inc., MN, USA). Briefly, biotinylated detection antibodies were added to each prepared sample, and the sample/antibody mixture was incubated overnight with nitrocellulose membranes: 36 different anti-cytokine antibodies were spotted in duplicate (shown in Table S1). After washing out unbound material, streptavidin-horseradish peroxidase and chemiluminescent detection reagents were sequentially added. The cytokine blot images were obtained using the ChemiDoc gel documentation system (Bio-Rad, Hercules, CA, USA). And positive signals in cytokine assay serve as the standard to calibrate the difference among samples.

Results and discussion

Characterization of $(BPEI/SiSQ)_n$ multilayer

As we mentioned above, $(BPEI/SiSQ)_n$ multilayer films were assembled by layer-by-layer method based on hydrogen bonding interaction. Specifically, amine groups in BPEI act as hydrogen