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Fabrication of superhydrophobic coating for preventing microleakage in a dental composite restoration

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ABSTRACT

Superhydrophobic coatings were successfully fabricated by photo-crosslinked polyurethane (PU) and organic fluoro group-functionalized SiO_2 nanoparticles (F-SiO_2 NPs), and were introduced for preventing microleakage in a dental composite restoration. The F-SiO_2 NPs possessed low surface energy and the PU can not only improve the mechanical stability but also promote F-SiO_2 NPs to form multiscale structure, which could facilitate the properties of the as-prepared superhydrophobic coating by synergetic effect. The morphology and properties of the resulted superhydrophobic coatings with different PU/F-SiO_2 ratios were studied using ^{1}H NMR spectrum, fourier transform infrared spectra, scanning electron microscopy, atomic force microscopy and UV–vis spectrophotometry. The results showed that the superhydrophobic coatings with low PU/F-SiO_2 ratio (1:3) possessed excellent hierarchical papillae structure with trapped air pockets, high contact angle (160.1°), low sliding angle (<1°) and good transparency. Additionally, MTT experiments results certified the prominent cell viability and biocompatibility for clinical application. Based on its fantastically superhydrophobic property, the as-prepared superhydrophobic coatings effectively prevented water permeation in resin composite restoration evaluation. This research may provide an effective method to solve the problem of microleakage and will efficiently increase the success rate of dental composite restorations.

1. Introduction

Composite resins, composed of organic resin matrix material, surface treated inorganic filler and initiator, have been widely used in dental clinical restoration for about 50 years because of their esthetic results, minimally invasive treatment, favorable adhesive and environment-friendly properties etc. [1,2]. However, almost all composite resin materials suffer a certain degree of marginal microleakage [2], which easily leads to water permeation, bacterial growth, sensitivity, recurrent caries, discoloration of the restoration margins etc., seriously reducing the durability of the restoration [3–5].

The microleakage at the tooth-restoration interface is usually caused by the residual stresses due to polymerization shrinkage of the composite resin during the light curing process [6]. Up to now, researchers have devoted extensive efforts to develop new dental resin composites with lower polymerization shrinkage and lower water sorption. There are some reports on reducing the polymerized volumetric shrinkage to <1% [7,8], which can temporarily avoid the emergence of the interfacial gap at the beginning of tooth-restoration. However, due to the different thermal expansion coefficients between the cured resin composite and dental tissues, the gap will still arise after undergoing a series of repetitive expansions and contractions with the change of temperature in the oral environment. Therefore, it is necessary to explore some other methods to solve the microleakage problem completely.

On the other hand, the character of the surface between the adhesive and tooth structure is another influencing factor for microleakage. The present dental adhesive materials applied in dental composite restoration are mainly composed of 2-hydroxyethyl methacrylate (HEMA), ethyl alcohol/acetone and bisphenol A glycerolate dimethacrylate (Bis-GMA). Among them, HEMA can infiltrate into the dentin tubules funneled by the etching agent and form resin tags after curing [4], which could effectively enhance the bonding strength between the resin composite and dental tissues. Unfortunately, on account of the water absorption character of HEMA, water is prone to permeate into the dental resin composite completely through the dental adhesive materials by forming water blisters and "water trees" [9,10], thus leading to the microleakage problem and the failure of dental restorations.

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Superhydrophobic surfaces possessing high contact angles (CAs, typically above 150°) and low sliding angle (SAs) for water and other aqueous solutions [11–16], have been intensively studied and received a great deal of attention for their applications in a wide variety of areas, such as anti-fouling, self-cleaning surfaces and so on [17–20]. On basis of this, in order to prevent the microleakage caused by the resin composite polymerization shrinkage or adhesive (component HEMA) water infiltration, we introduced the superhydrophobic coating on the surface of cavities, as shown in Fig. 1. Since low surface energy and roughness with dual structure are two key factors for superhydrophobic property [21,22], the superhydrophobic coating we designed were comprised of F-SiO_2 NPs and PU, in which F-SiO_2 NPs can provide low surface energy to achieve hydrophobicity, and PU can not only enhance superhydrophobic coating strength but also promote the formation of hierarchical structure with increased roughness by single SiO_2 NPs aggregation. Additionally, the CAs and SAs, cytotoxicity, transparency and the preventing microleakage effect of the superhydrophobic surfaces were tested.

2. Experimental section

2.1. Materials

Silica NPs (SiO_2 NPs, 30 nm diameter), tetraethyl orthosilicate (TEOS), 3-Methacryloxypropyltrimethoxysilane (KH570), ethanol, trimethoxy (1H,1H,2H,2H-heptadecafluorodecyl) silane (FAS), acetic acid (HAc), isophorone diisocyanate (IPDI), 2-Hydroxyethyl methacrylate (HEMA), Dibutyltin dilaurate (DBTDL), camphorquinone (CQ), ethyl-4-dimethylaminobenzoate (4-EDMAB) and methylene blue were purchased from Aladdin. Polyester diol 2000 was purchased from Yantai Wanhua Chemical Group Co., Ltd. (Shandong, China). Resin composite Valux Plus (3M ESPE) was used for dental composite restoration in this research. MC3T3-E1 pre-osteoblast cell lines from mice were purchased from the Chinese Academy of Sciences Cell Bank (Shanghai, China).

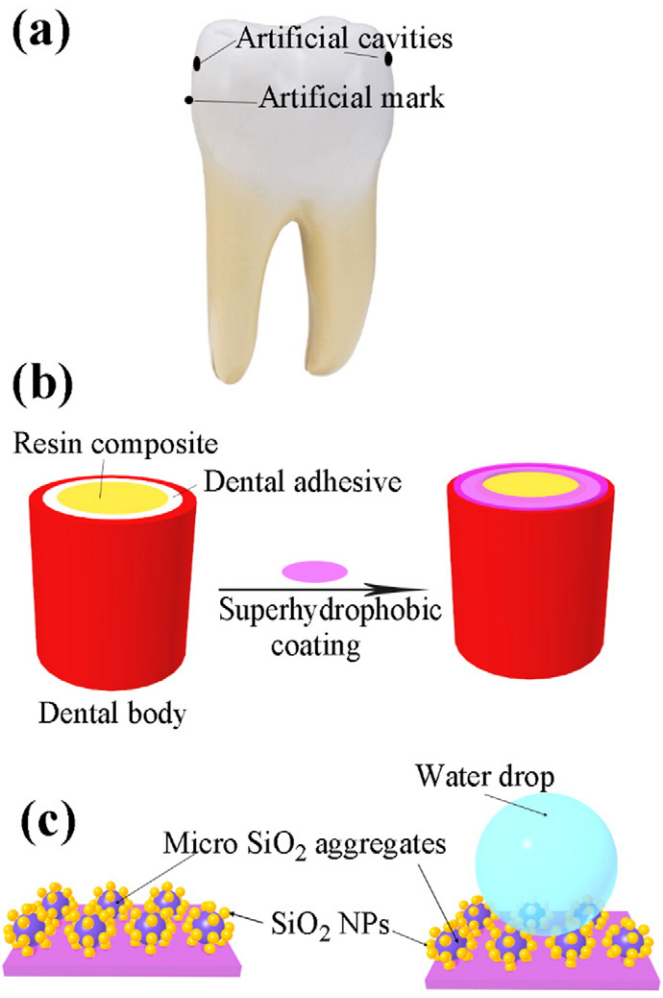

Fig. 1. (a) Schematic model of the microleakage evaluation specimen; (b) structure of artificial restoring cavity with superhydrophobic coating; (c) Cassie-Baxter and superhydrophobicity model of superhydrophobic coating.

2.2. Fabrication of superhydrophobic surface

2.2.1. Synthesis of PU

As shown in Fig. 2, firstly, Polyester diol 2000 (20 g, 0.01 mol), DBTDL catalyst (0.06 g, 3‰,) and a certain amount of anhydrous tetrahydrofuran (THF) were mixed and preheated to 70 °C for 5 min. Then IPDI (4.44 g, 0.02 mol) was added under stirring (500 rpm) and kept constant for 4 h under nitrogen atmosphere. When hydroxyl group could not be observed by IR-spectroscopy, HEMA (2.6 g, 0.02 mol) was added, then the reaction system was stirred and heated for 3 h [23]. After the reaction was completed, the cooling solution was added into petroleum ether and white solid formed. This step was repeated three times and then was dried in a vacuum to obtain the PU (23.66 g, 87.5%). In the subsequent process of solution preparation, the synthesized PU was diluted with acetone to the 10%wt solution.

2.2.2. Modification of SiO_2 NPs

In order to obtain the double bond-containing and fluorinated SiO_2 NPs (F-SiO_2 NPs), SiO_2 NPs (0.2 g) were dispersed in ethanol (10 g). Then KH570 (0.3 g), TEOS (0.3 g) and FAS (0.4 g) were added into the solution. Subsequently, H_2O (30 μL) and HAc (30 μL) were injected and the mixture reacted at room temperature for 10 h.

2.2.3. Preparation of superhydrophobic solution

10%wt PU acetone solution and the modified SiO_2 ethanol solution were mixed uniformly to form PU/F-SiO_2 NPs with different ratios (shown in Table 1). After adding 1% CQ and EDMAB initiator into the solution, the PU/F-SiO_2 NPs mixture were immediately spray-coated on the substrates (wafer, glass or resin matrix surface) and cured by the blue light to prepared the PU/F-SiO_2 superhydrophobic coating.

2.3. Characterization

^{1}H NMR spectrum was recorded on a Bruker AVANCE NMR spectrometer using Dimethyl Sulphoxide (DMSO) as standard. Fourier transform infrared (FTIR) spectra were performed by using a BRUKER VERTEX 80 V in a range of 4000–400 cm^{-1}. The morphologies of the samples were examined with scanning electron microscopy (SEM, JEOL FESEM 6700F) and atomic force microscopy (AFM, AVENER SPA300) in tapping mode. Contact angles were measured via a contact angle meter (Dataphysics OCA20). The droplet size of the liquid was controlled to be 5 μL. The optical transparency of the coated glasses substrates were measured with UV–vis spectrophotometry (UV-3600).

2.4. Cytotoxicity evaluation: cell culture and MTT assay

The MTT assay was applied for measuring the cytotoxicity of the superhydrophobic coatings. By using 3M resin composite as substrate (cylinder with diameter of 4 mm and the thickness of 2 mm), the superhydrophobic coating was coated on the surface of the 3M resin composite and then 3 M resin composite was light-cured. Blank group (without 3M resin substrate and superhydrophobic coating) and control group (without superhydrophobic coating) were prepared separately for comparison. Three specimens were prepared for each group. These specimens were separately put into 6-well culture plates. Fetal