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Evaluation of chitosan quaternary ammonium salt-modified resin denture base material

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ABSTRACT

Chitosan quaternary ammonium salt displays good antioxidant and antibacterial characteristics and it shows appreciable solubility in water. When added to the traditional denture material to form a resin base, it could promote good oral health by improving the oral environment. In this study, chitosan quaternary ammonium salt was added to the denture material following two different methods. After three months of immersion in artificial saliva, the specimens were tested for tensile strength and were scanned by electron microscope. The murine fibroblast cytotoxicity and antibacterial properties were also tested. The result showed no significant differences in the tensile strength and in the proliferation of murine L929 fibroblast cells. The two structures of chitosan quaternary ammonium salt-modified denture material had different degrees of corrosion resistance and antimicrobial properties. These results indicate that chitosan quaternary ammonium salt-modified resin denture base material has the potential to become a new generation oral denture composite material.

1. Introduction

Chitin is a natural polymeric material; it is second only to cellulose. As the product of chitin deacetylation, chitosan is the only alkaline polysaccharide in nature [1]. Chitosan, as a new bioresource, possesses a number of unique properties, therefore, has extensive potential for applications in various fields. However, the lack of water solubility induced by chitosan's dense crystal structure greatly limits its usage. Once chitosan enters into an environment with a pH value greater than 6.5, this property disappears. The most common methods for the modification of chitosan include, but are not limited to, acylation, carboxymethylation, sulfhydrylation, quaternization, polyethylene glycol grafting [2]. When the chitosan molecule is converted to its quaternary ammonium salt, the number of positive charges can be increased, thereby greatly improving its water solubility [3,4]. Chitosan quaternary ammonium salt is a polycationic compound, characterized by good water solubility, flocculation, moisture absorption, and antibacterial properties with no cytotoxicity to cells. It can be applied in a wide number of fields. Graft copolymerization is an important method for chitosan modification. Currently, the derivatization of grafting copolymerization of chitosan is mainly performed at its 2-N and 6-C positions [5–8].

At present, during full denture and removable denture repair, the traditional material employed as the resin base support is poly (methyl methacrylate) (PMMA). Denture stays in the mouth for long periods of time, therefore, as the resin material ages, bacteria and fungi can adhere to its surface. Bacterial and fungal colonies are difficult to be completely removed, thus the instances of bacterial and fungal infections are increased (mainly the bacterial white beads infections) in the mucosal area under the denture support. The cases of denture disease and mouth inflammation caused by dentures are substantially high [9–12]. By adding antimicrobial agents to the denture base material, the oral environment can be greatly enhanced thereby improving the overall oral health.

PMMA and its modified products are widely used as a resin denture base. The modification of the resin denture base material has become a research hotspot. The main modification method is to add various materials into the resin denture base to improve its performance. For example, the addition of fiber and crystal whiskers can increase the mechanical property of the resin denture base material [13–15]. Ceramic nanoparticles and carbon nanotubes can induce toughened and reinforced denture base materials [16,17].

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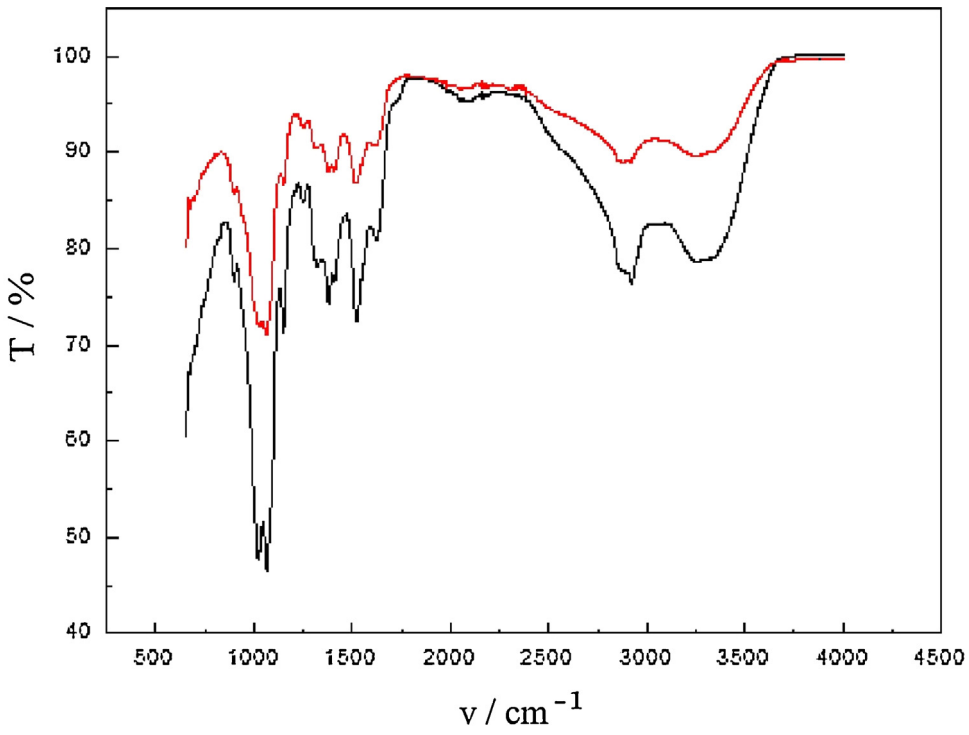

Fig. 1. IR spectrum of crude chitosan (red) and co-polymerization of MMA and chitosan (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Antimicrobial agents enhance the antimicrobial property of the resin denture base material [18]. Chitosan quaternary ammonium salt derived from quaternization of chitosan shows antioxidant and antibacterial properties with no cytotoxicity to cells, therefore it has been applied in various fields. However, the effect of chitosan quaternary ammonium salt addition into the resin denture base material in terms of its antibacterial and antioxidant performances has not yet been reported.

The antioxidant property of chitosan and its derivatives mainly comes from the presence of a large numbers of hydroxyl groups in the chitosan quaternary ammonium salt. The hydroxyl radical can form very stable macromolecular free radicals with the active hydrogen atoms on the hydroxyl and amino groups, exhibiting and promoting the antioxidant property in the chitosan quaternary ammonium salt. Wan et al. [19] examined the antioxidant property of three chitosan quaternary ammonium salts with different degrees of substitutions on the amino group. The results indicated that when 33.9% of the amino groups were substituted in the chitosan quaternary ammonium salt molecule, the maximum clearance rate of OH• was 40.2%, and the maximum inhibition rate of $^{\bullet}O_2^-$ was 65.6%. In addition, it was also found that the clearance rate of the two quaternary ammonium salt products decreased with increasing degrees of substitutions, which provides a foundation for expanding the applications of chitosan. With an increasing degree of substitution of the quaternary ammonium salts, fewer amino groups remain in chitosan, resulting in a decreased clearance rate of $^{\bullet}O_2^-$ and OH• [19]. Xing et al. [20] studied the relationship between the molecular weight of chitosan quaternary ammonium salt and its antioxidant activity. They found that the quaternized chitosan with lower molecular weight had a higher clearance capacity of $^{\bullet}O^{2-}$ and OH• and higher reducing power compared with the quaternized chitosan with higher molecular weight, with specific concentration-dependent tendencies [20,21].

In this study, chitosan quaternary ammonium salt was added to the denture powder in two ways: (1) added directly to the denture base material in different proportions; (2) grafted with the methyl methacrylate monomer and polymerized. The grafted copolymer denture material was then precipitated from the solution, and aggregated with the denture water to form the resin denture base. The antibacterial, antioxidant, and cytotoxic properties of the two chitosan quaternary ammonium salt modified resin denture base materials were tested. These tests on these materials have not yet been reported.

2. Materials and methods

2.1. Material preparation

The co-polymerization of MMA and chitosan, as well as the FT-IR spectra, purity and grafting degree of the polymer, have been previously reported [22–25]. As shown in Fig. 1, the two FT-IR spectra represent the chitosan polymers before (red) and after (black) grafting with MMA 4 h under 80 °C. We followed their work to create our polymers, which are expected to have similar properties. The cuboid mold of the specimen was 50 mm in length, 30 mm in width and 2–3 mm thick. The traditional resin denture base formation material had two components: the Denture Water (Heraeus Kulzer), containing methyl methacrylate (MMA) monomer and trace amount of the cross-linking agent, inhibitor and UV absorber, and the Denture Powder (Heraeus Kulzer), containing PMMA. The first formulation, referred to as Material 1 in this investigation, was prepared by adding varying amount of the chitosan quaternary ammonium salt (Guangzhou Namgyal Technology Co., Ltd.) directly to the Denture Powder, then the Denture Water was added according to the denture material manufacture's instruction and the mixture was incubated at 68–74 °C for 90 min and then boiled for 30 min for curing. The final concentrations of the chitosan quaternary ammonium salt in Material 1 were 0.50 mg/mL, 1.0 mg/mL, 2 mg/mL, and 3 mg/mL. The second formulation, referred to as Material 2, was prepared by adding varying amount of chitosan quaternary ammonium salt to the Denture Water, allowing the chitosan quaternary ammonium salt and the MMA monomer to