A Nan composite for invisible dental device with highly transparent and antibacterial

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Abstract. The thermoplastic polyurethane elastomer modified by nano-TiO₂ particles was synthesized by in-situ polymerization, and the composite film is used for invisible dental device. The effects of different contents of nano-TiO₂ on the transparency and mechanical properties of the composite film were investigated. The results show that the nano-TiO₂ treated with silane coupling agent is uniformly dispersed in the TPU matrix. Compared with the pure TPU, the addition of nano-TiO₂ makes the transparency decrease and mechanical properties improve significantly. The surface of the film was modified with dopamine and then connected with antimicrobial peptides. The results of antibacterial experiments show that the modified films have excellent antibacterial properties.

1. Introduction
Tooth deformity is one of the common diseases in society, which brings serious inconvenience to patients' lives. The correction of deformity mainly depends on wearing the appliance in the oral cavity, imposing appropriate "biological force" on the teeth, alveolar bone and jawbone, so as to achieve the purpose of deformity correction.

After decades of development, fixed orthodontic technology has been widely used. But the metal appliance cannot be removed from the teeth, long-term wearing is easy to lead to bacteria breeding, serious gingivitis and enamel demineralization. Meanwhile, the aesthetic problems caused by wearing metal appliance has not been solved. Nowadays, great breakthroughs have been made in the technology of invisible orthodontic treatment without brackets [1]. The invisible tooth appliance has a high degree of transparency and can achieve the "invisible" effect. It can be removed and worn without the limitation of time and space, and gradually occupies a dominant position in the field of appliance.

Thermoplastic polyurethane elastomer (TPU) is a kind of material between rubber and plastic [2]. It is a block polymer containing carbamate (-NCOO-) repeating group in the main chain. It is usually composed of soft segment in high elastic state and hard segment in crystal state [3-4]. There is thermodynamic incompatibility between the two chain segments, which will produce micro phase separation, with wear resistance, corrosion resistance and high transparency it is widely used in automobile manufacturing, building construction, synthetic leather and medical equipment [5-6]. But under the suitable temperature and humidity conditions, TPU materials are easy to cause the growth of
bacteria, which will cause serious medical accidents and economic losses [7-8]. How to improve the antibacterial property of polyurethane materials has become the research hotspot.

Since the formation of nano concept in 1980s, a lot of researches have been carried out on the properties, preparation methods and applications of nano materials. The main nano materials are nano calcium carbonate, nano silica, nano titanium dioxide and carbon nanotubes [9-12]. Nano-TiO$_2$ has special optical properties, good chemical stability, and excellent antibacterial properties [13-15]. It has been widely studied and used.

The existing invisible dental appliances use diphenylmethane diisocyanate (MDI) as the raw material. In the process of preparation, small molecular need to be added to prevent oxidation and yellowing. Small molecular will cause potential harm to human body and shorten the service life of dental appliances. In this study, isophorone diisocyanate (IPDI) was selected as the raw material, nano-TiO$_2$ was treated by silane coupling agent, TiO$_2$/TPU composite was prepared by in-situ polymerization, and antibacterial dental appliance with high transparency was prepared. Without changing the "invisibility" of dental appliances, it improves the antibacterial performance of dental appliances, increases their service life, reduces the cost, and provides a new direction for the development of invisible dental appliances.

2. Experiment

2.1. Materials
Tetrahydrofuran ether glycol (PTMG, Mn=1000), Jining Hongming Chemical Reagent Co., Ltd.; anatase nano titanium dioxide (TiO$_2$), Jiangsu Tianxing New Material Co., Ltd.; isophorone diisocyanate (IPDI), 1,4-butanediol (BDO), N, N-dimethylformamide (DMF), 3-aminopropyl triethoxysilane (KH-550), dibutyldilaurate tin (DBTDL), Aladdin Biochemical Technology Co., Ltd

2.2. Preparation
Weigh TiO$_2$ powder with electronic balance, add it into the beaker with DMF, add 0.01g silane coupling agent KH-550 dropwise, ultrasonic 1.5h, and make silane coupling agent graft to the surface of nanoparticles. Add PTMG to the four port flask with thermometer and stirrer, remove water for 2h under vacuum condition of 110℃, and then cool down to 80℃. Add the treated nano particle dispersion into a four port flask, add IPDI drop, add 1 drop of catalyst DBTDL drop, react at constant temperature for 3h at 90℃, and get the prepolymer. Then, the temperature is reduced to 70℃, chain extender BDO is added, the chain is extended for 30min, the product is poured into the preheated mold, vacuumized to no bubble, put into the oven at 110℃, and aged for 12h, the thermoplastic polyurethane elastomer modified by nano titanium dioxide is prepared. The preparation route were schematically presented in Figure 1 and 2.
2.3. Characterizations

In order to observe the dispersion of nano-TiO$_2$ in the TPU matrix, the samples were analyzed by SEM. The specimen was cooled in liquid nitrogen, brittle broken, and the section was treated with gold spray. SU-8100 scanning electron microscope was used to observe the dispersion of nano-TiO$_2$ in the TPU matrix.

In order to explore the influence of nano-TiO$_2$ content on the transparency of composite materials, the transmittance of samples was measured by 754N ultraviolet spectrophotometer (Shanghai aopler Instrument Co., Ltd.), and the scanning wavelength was 300-1000nm.

In order to explore the mechanical properties of composite materials, the shore hardness of samples was measured by LX-D type shore hardness tester. (Wenzhou Haibao Instrument Co., Ltd.)

The surface of the film was modified with dopamine and then connected with antimicrobial peptides. Staphylococcus aureus was selected as experimental strain. It is observed that the growth of bacteria by Confocal laser scanning microscope.

3. Results and discussion

![SEM spectra of TiO$_2$/TPU: pure TPU (a) 0.1wt% TiO$_2$/TPU (b)](image)

Figure 3. SEM spectra of TiO$_2$/TPU: pure TPU (a) 0.1wt% TiO$_2$/TPU (b)

Fig.3 is the SEM spectra of composite materials with different nano-TiO$_2$ content. It can be seen that when the content of nano-TiO$_2$ is 0.1wt%, nano-TiO$_2$ is well dispersed in the TPU matrix, which
indicates that the well dispersed nano-TiO$_2$/TPU composite is successfully prepared. After the surface treatment of nano-TiO$_2$ by silane coupling agent, the surface of nano-TiO$_2$ is wrapped by coupling agent, which can reduce the surface energy and is not easy to agglomerate; Meanwhile, the coupling agent with amino group is used to connect the surface of nano-TiO$_2$ with amino group, which can react with isocyanate and chain extender, so that nano-TiO$_2$ can be evenly dispersed in composite materials.

Figure 4. UV Transmittance of TiO$_2$/TPU

Fig.4 is the UV transmittance diagram of composite materials with different nano-TiO$_2$ content. It can be seen from the figure that with the increase of wavelength, the transmissivity gradually increases, and the growth slows down from the 400nm wavelength, and tends to be stable gradually. The transmissivity of 400-800nm band is selected as the experimental result, and the average value is calculated. The average transmittance of b c and d samples was 92%, 86% and 82%. The transmissivity of the invisible dental appliance is more than 85%. The first two samples meet the requirements of "invisible" dental appliance. With the increase of the content of nano-TiO$_2$, the transmissivity of the sample decreases gradually, which results in the higher crystallinity of TPU, the more serious scattering of visible light, the lower transmissivity of the sample and the worse transparency.

Figure 5. HS of TiO$_2$/TPU

Fig.5 is the hardness diagram of samples with different nano-TiO$_2$ content. It can be seen from the figure that with the increase of nano-TiO$_2$ content, the hardness of the sample increases significantly.
Compared with pure TPU, when the content of nano-TiO$_2$ is 0.1wt%, the shore hardness of the sample is 48D, which is 12% higher than that of pure TPU. Therefore, the addition of nano-TiO$_2$ improves the hardness and mechanical properties of TPU. The reason is that the addition of nano-TiO$_2$ increases the content of hard segment in the TPU matrix, the number and energy of hydrogen bond, and the intermolecular interaction, which leads to the increase of hardness. When food enters the mouth, it needs to be chewed by teeth before swallowing. This process requires a lot of shear stress. The improvement of the hardness of the appliance can improve the orthodontic force, protect the enamel and increase the service life of the appliance.

Figure 6. Antibacterial effects of TiO$_2$/TPU against S. aureus: TiO$_2$/TPU (a) peptide-TiO$_2$/TPU (b)

Fig.6 is the bacterial growth diagram of the anti S. aureus test of TiO$_2$/TPU composite. Cells with a compromised membrane that are considered to be dead or dying will stain red, whereas cells with an intact membrane will stain green. It can be seen that the film modified by antimicrobial peptides show excellent antibacterial properties.

Antimicrobial peptides act on the cell membrane, forming ion channels across the membrane, destroying the integrity of the membrane, causing leakage of cell contents, and killing cells. Antimicrobial peptides can inhibit the formation of bacterial cell wall, make bacteria unable to maintain normal cell morphology and growth blocked, and make cell wall perforation, eventually leading to bacterial death.

4. Conclusion
Nano-TiO$_2$/TPU composites were successfully prepared by in situ polymerization, and the composite films for orthodontic treatment were also prepared. The results show that the nano-TiO$_2$ treated by silane coupling agent is well dispersed in the TPU matrix and does not agglomerate. Compared with pure TPU, adding nano-TiO$_2$ did not significantly reduce the high transparency and improve the mechanical properties of the composite. The results of antibacterial experiments show that the film modified by antimicrobial peptides can significantly inhibit the growth of S. aureus and has excellent antibacterial properties. When the content of nano-TiO$_2$ is 0.1wt%, the nano-TiO$_2$/TPU composite has high transparency and excellent antibacterial, which can be used in the field of orthodontics.

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