Preparation and Tribological Properties of bionic materials with nacre shell structure

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Abstract—Ceramic materials have many advantages, such as high hardness, wear resistance, self lubrication in the process of friction, but there are also some inherent defects, such as brittle texture and poor toughness. By observing the microstructure of shell pearl layer, a kind of bionic composite ceramic with brick wall structure can greatly improve the natural defects of ceramic materials, and greatly expand the application range of ceramic materials. The tribological properties of materials are of great significance to the efficiency and service life of mechanical structures. Therefore, four kinds of ceramic composites with nacre shell structure with gradient concentration were prepared by freeze casting and standard polymerization, and the tribological properties of five materials were characterized. The experimental results show that when the loading load is large, the friction coefficient of material surface varies with the material With the increase of PMMA content, the friction coefficient of the material shows an upward trend.

1. INTRODUCTION
In the long process of evolution, through natural selection, many organisms have formed unique and effective "weapons" and materials, such as animal horns, scales and bone structures. Many mollusks are slow-moving and protect themselves with a calcareous shell. Through the study of the shell microstructure, it provides a blueprint for researchers to improve the performance of new materials\cite{1,2}.

Through the study of shell, it is found that the organic compounds represented by protein, glycoprotein and chitin account for about 0.1% - 5%, more calcite, aragonite, vaterite and amorphous CaCO$_3$, accounting for about 95% - 99.9%. Different kinds of shells have different components, but they all have similar brick wall hybrid structure\cite{3-10}. As a natural layered composite, the research on shell has attracted extensive attention of many scholars since its strength and toughness are far higher than any single component\cite{3}, making it an important direction for researchers to design new composite structures.

In the layered structure of nacre layer, the interfacial shear strength between CaCO$_3$ lamellae and organic matrix is very large. If relative displacement is to be generated, great pull-out work needs to be overcome\cite{11}. At the same time, due to the lamellar structure of the shell, when the crack passes through the organic ductile layer in the shell material, the crack will deflect and extend in a "bow" shape\cite{12-24}. At the same time, the organic ductile layer will also play a buffer role, which absorbs part of the energy and makes the material more difficult to be broken.
2. MATERIAL PREPARATION

In order to simulate the microstructure of nacre, many scholars have made great efforts. The pore structure of frozen tofu has inspired scholars. The ice crystals growing in the process of freezing squeeze the macromolecules around. When the water molecules are removed, the void structure is left. A large number of experiments show that the ceramic composite with shell like structure can be prepared by the ice template method [25-42].

The ceramic slurry consists of deionized water, α-Al2O3 powder with particle size less than 13nm, sodium citrate and polyvinyl alcohol. The above drugs are purchased from sigma Aldrich company.

The preparation process of the material is shown in Fig. 1. The solid phase composition other than water is 100wt%, including 97wt% Nano-Al2O3 powder, 2wt% sodium citrate and 1wt% polyvinyl alcohol. Five kinds of ceramic pastes with water content of 70wt%, 75wt%, 80wt%, 85wt% were prepared. After carefully weighing all ceramic slurry components, put them into alumina ball milling tank. After manual uniform mixing, put a proper amount of grinding ball into the ball mill, start the ball mill, turn off the machine for half an hour every two hours, and repeat 12 times. The Al2O3 powder in the slurry is not agglomerated or flocculent, the uniformity of the slurry is improved, and the slurry temperature is not too high.

When the grinding is completed, we take out the alumina grinding tank and put it to rest, and dissipate the heat generated in the grinding process until it recovers to the ambient temperature. Then we put the slurry evenly ground into the vacuum degassing chamber for 30min to remove the air mixed in the slurry during the grinding process, so as to prevent the pore defects of the ceramic framework made by mixing too much air in the slurry. The prepared ceramic slurry is directionally frozen to -30 °C at the speed of 6 ℃ / min, kept warm for 10min, and dried in a fully cooled freeze dryer for 24 hours. Under a high vacuum, the ice crystals in the frozen ceramic embryo will sublime, leaving the alumina ceramic green with lamellar structure.

Transfer the freeze-dried ceramic green body to the muffle furnace for high-temperature sintering, make the ceramic sintered at 1650℃ for 4 hours, and then cool to room temperature to obtain the lamellar alumina porous ceramic required for the test [43,44].

First, put a proper amount of methyl methacrylate monomer into a small beaker, add an appropriate amount of azodiisobutyronitrile as the initiator, and stir at 70 ℃ for 30-40 minutes until methyl methacrylate becomes an oil like viscous liquid. The preformed porous ceramic skeleton is immersed in the prepolymerized MMA. Then put the prepolymerized sample into the vacuum chamber, adjust the vacuum degree of the vacuum chamber to -1bar, and remove the gas under low pressure for 10 minutes. Put the prepolymerized material after degassing into the mold and keep it in the electric constant temperature drying oven at 40 ℃ for 24 hours; cool and demould. The preparation process is shown in Fig. 1.

The surface of the sample is treated by a grinding and polishing machine, and the material is polished in water for 10 minutes by 320, 800, 1500 and 3000 mesh metallographic sandpaper in the order of coarse to fine. Then on the polishing pad, the polished sample surface is polished with diamond suspension polishing solution for 10 minutes. After polishing, deionized water, petroleum ether and anhydrous ethanol were used as cleaning agent to clean the material for 10 minutes respectively, in order to remove the impurities such as abrasive paper and diamond polishing liquid adhered to the surface of composite material during the surface treatment process, which affected the characterization of test material.
Figure 1. Preparation route of composite ceramics.

The different solid content in the ceramic slurry will affect the microstructure of the porous ceramic body, as shown in Fig. 2. The porous ceramics with 70, 75, 80, 85 wt% water content prepared by freeze casting technology have the structure of connecting pores, and the pores are parallel to each other, and the pore distribution is relatively uniform. With the increase of water content, the pore size increases gradually. The pore sizes of the composites with water content of 15, 20, 25 and 30 wt% were 8.18, 15.9, 20.5, 27.3 μm, respectively, and the thickness of ceramic lamellae was 6.67, 26.2, 19, 15, 22.9 μm.
EDX analysis results of layered ceramic composites are shown in Figure 3. The results show that after the porous ceramic body is filled with polymer PMMA, the ceramic interface and polymer interface combine well, forming a relatively complete layered structure. In Fig. 3 (A), the peak value of Al element in the red box area is the highest, accompanied by a large number of O elements, indicating that this area is the base material Al₂O₃. In Fig. 3 (B), the peak value of C element in the red box area is the highest, accompanied by a large number of O elements, indicating that the area is filled phase PMMA.
3. FRICTION EXPERIMENT

In this paper, the alumina ceramic ball with a diameter of 2mm is used as the upper sample and the composite material is used as the lower sample. The loading loads are 1N, 2N, 3N, 4N and 5N respectively. The test bench for friction test is shown in Fig. 4. The friction coefficients of different materials under different loads are shown in Fig. 5.
Figure 5. Friction coefficient of materials under different loads.

As shown in Fig. 5, the friction coefficient of the laminated composite with the reinforcement phase of 80wt% is relatively stable and the change is not obvious under five different loads. The friction coefficient of composite materials with 70 wt% and 75 wt% reinforcements decreased with the increase of load, while that of composite materials with 85 wt% reinforcements increased with the increase of load. When the load is 1N, the friction coefficient of the composite surface with 85wt% of the reinforced phase material is the smallest, and the friction coefficient of the composite surface with 80wt% of the reinforced phase material is the largest. When the applied load increases gradually, this characteristic changes obviously. When the applied load exceeds 2n, the friction coefficient of the material surface increases with the content of the reinforced phase on the material surface when the same load is applied Rise. This is because when the surface of the material is applied with a large load, the reinforcing phase material PMMA on the surface of the material is more vulnerable to damage than Al₂O₃, which leads to the rough surface of the material. But at the same time, the broken Al₂O₃ material will be scattered in the grinding ditch to achieve particle lubrication. When the PMMA content in the material is low, the lubrication effect of the broken Al₂O₃ material is the main body, and when the PMMA content in the material is high, the influence of the unsmooth surface on the friction characteristics of the material surface is the main body. Space considerations.

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