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PREPARATION OF FUNCTIONAL AIR FILTER MATERIAL BASED ON BIODEGRADABLE FIBERS AND NANO TITANIUM DIOXIDE

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Silk fibers and cotton fibers were pretreated and mixed in a certain proportion to prepare filter materials by wet forming process, and nano-TiO_2 was immobilized on the filter materials by filtration method. Pore size structure, filtration performance and strength of the filter materials were investigated by using Pore Size Meter, Field Emission Scanning Electron Microscope (FESEM), Automated Filter Tester and Burst Tester, and antibacterial activity of the filter materials were tested by disk diffusion method. Results show that air filter material containing 10% cotton fibers is relatively high in both burst index and filter efficiency. Nano-TiO_2 particles are mainly distributed on the surface of the filter materials, and filter material loading 6% nano-TiO_2 has good antibacterial activity, relatively high burst index and filter efficiency.

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Keywords: Silk, Cotton, Nano titanium dioxide, Air filter material, Antibacterial activity

1. Introduction

With the rapid development of economy and urbanization, human activities have an increasing impact on the environment, and air pollution problems such as dust, automobile exhaust, fog and haze are becoming more and more serious. Large amounts of fine particulate matters (PMs), especially particles smaller than 2.5 microns in diameter (PM2.5), bacteria and viruses have posed a great threat to human health [1-4]. Air filtration is an important way to control air pollutant level in certain areas and achieve air purification. High-efficiency air filter material is the development trend, and filter materials with high temperature resistance, corrosion resistance, antistatic, antibacterial activity, water repellent, oil repellent, flame retardancy and other special functions have been the research hotspot in the field of air filter materials in recent years. Nanometer materials and techniques are key to preparing functional air filter materials [5, 6].

Conventional air filter materials mainly include nonwoven made from polymer fibers such as polyacrylonitrile (PAN) and poly (vinyl alcohol) (PVA), polytetrafluoroethylene (PTFE) membrane and glass fibers materials [7, 8]. They are incapable of capturing fine particles and removing toxic and harmful ingredients due to the micro-sized fiber diameter [9, 10]. They are non-renewable resources and non-biodegradable materials, and environmental pollution would be caused during their preparation process and waste disposal. Silk is a natural macromolecular protein derived from silkworm which is an antioxidant, antibacterial and UV resistant. The diameter of silk fiber is only a few microns, one tenth to one fifth of that of wood fibers (the diameter of wood fiber is about 15~40 µm), and it has high specific surface area and flexibility. Silk fiber is similar to plant fibers, which can be fibrillated by refining and can be cross-linked and blended with other macromolecular materials to produce porous filter materials with improved properties. However, high cost and poor fiber strength limit its widespread use [11-15]. Cotton is an abundant, renewable and biodegradable fiber resource, cotton fiber is very long and is about 20 µm in diameter, so it is high in strength and is commonly used as filter materials to adsorb and intercept fine particles.

Nano titanium dioxide (nano-TiO_2) photocatalytic materials are the most promising filter materials for eliminating harmful gases. The immobilization technology of nano-TiO_2 includes: a

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thin film of nano-TiO_2 is attached to the surface of glass fiber, activated carbon fiber and other fibers; nano-TiO_2 is immobilized on fibers by the mechanism of filtration; deposition of titanium dioxide aerosol particle on fibers, and so on [16-18].

In order to give full play to the advantages of silk fiber and cotton fiber and overcome their disadvantages, in this study, silk fibers and cotton fibers were pretreated chemically and mechanically and mixed in a certain proportion to prepare sheet material, then nano-TiO_2 particles were immobilized on the sheet to prepare filter material with photocatalytic function. The structure and properties of the filter material were investigated by pore size analysis, scanning electronic microscope (SEM), burst test, filter test and bacteriostatic test.

2. Experimental

2.1. Materials

Silk was supplied by a filature of Zhejiang province and cotton pulp board was supplied by Hangzhou Special Paper Co. Ltd. Nano titanium dioxide powder (crystalline form: anatase, size: 6 nm, specific surface area: 200 m^2/g) was provided by Hangzhou Wan Jing New Material Co. Ltd. Polyethylene oxide (PEO) was obtained from Shanghai Zhanhe industrial Co. Ltd and Na_2CO_3 (AR) was purchased from market. Growth media and strains were provided by microbiology lab of Zhejiang University of Science & Technology.

2.2. Preparation of functional air filter material

Silk fibers were cut into 5 mm in length and were degummed using 0.5 % Na_2CO_3 water solution at 100 ^oC for 60 min [15, 19]. The degummed silk and cotton fibers were respectively disintegrated in a Valley beater and refined in a PFI refiner to obtain silk fibers with beating degree of 65 ^oSR and cotton fibers with beating degree of 52 ^oSR. Two kinds of fibers were mixed in a certain proportion and diluted to a fiber suspension of 0.02 % consistency. 0.1 % PEO solution was added to the fiber suspension to improve fiber dispersion and avoid fiber flocculation. Filter material with basis weight of 60 g/m^2 was prepared on a Canadian standard sheet former and a rotary drum dryer.

A certain amount of nano-TiO_2 powder was dispersed to a dilute starch solution using ultrasonic dispersion method. The prepared sheet was placed in a Buchner funnel and the well dispersed nano-TiO_2 suspension was poured into the funnel, nano-TiO_2 was retained on the filter material through the mechanisms of filtration and adsorption. After filtering, the sheet was dried in an air dry oven to obtain functional filter material.

2.3. Characterization

Pore size of the prepared filter material was measured using Pore Size Meter PSM165 (TOPAS company, Germany).The morphology of the filter material was observed by Field Emission Scanning Electron Microscope (FESEM)-SIRION-100 (FEI company, USA). The filtration performance of the filter material were determined by TSI-8310 Automated Filter Tester (USA), and the aerosol particles used in the test were sodium chloride (NaCl), with a particle size of 0.3 µm, at a flow rate of 32 l/min and a flow velocity of 5.3 cm/s. The burst strength of the filter material was measured using PNBSM-160 Burst Tester (PNSHAR, China).

Beef extract peptone medium was used as the medium for bacteria. A proper dose of strains were inoculated to a culture plate and was amplified by bacteria culture. The disk diffusion method was used for antibacterial testing. The prepared sheet was punched into small disks with a diameter of 6 mm using hole puncher， and the disks were dried and stored for later use after high pressure sterilization. Strains were dispersed to a suspension of 10 mg/ml with 0.9 % saline, and 0.2 ml strain suspension was pipetted spread out on a culture medium evenly. The disks were placed face up on the surface of culture medium, and then was placed in an incubator at 37℃ for 24 h. Finally, the diameter of inhibition zone was measured with a pair of calipers.

3. Results and discussion

3.1. Effect of cotton fiber content on the structure and properties of filter material

Fig.1 shows that pure silk filter material has an average pore size of 1.01µm, which is smaller than that of filter materials containing cotton fibers. The average pore size of filter materials increase with the increase of cotton fiber content. Silk fiber filter materials have denser structure and smaller pore size due to two primary reasons: silk fiber has smaller diameter than cotton fiber and is easy to obtain compact filter structure. In addition, the beating degree of silk fiber is 65 ^{o}SR, that is, there are a large amount of microfibrils raised from the surface of silk fiber after its being refined, and higher external fibrillation of silk fibers make them have larger contact area and more joint points as they form filter material. Filter materials containing more cotton fiber have more pores and larger average pore size due to the larger diameter of cotton fiber. The average pore size of the filter material presents a slow upward tread when the addition of cotton fiber is lower than 15%, however, it increases rapidly when cotton fiber content exceeds 15%. In order to obtain high filter efficiency, the cotton fiber content should not be higher than 15%.

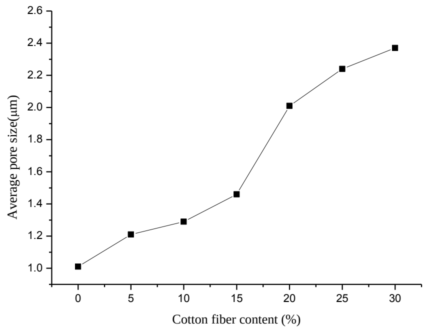


Fig.1. Effect of cotton fiber content on the pore size of filter material

Fig.2 shows that filter material with pure silk fibers has the burst index of 1.12 kPa.m^{2}.g^{-1}, which is the lowest one. The polypeptide chain molecule of silk fiber has polar amino group and hydroxyl group, which can form hydrogen bond between fibers and improve the fiber-to-fiber bonding strength during wet forming process, so as to give physical strength to the filter material. However, silk fiber itself is very thin and low in strength, which limits the strength improvement of silk fiber filter material, so the filter material is easily broken by air pressure during filter process. With the increase of cotton fiber content, the burst index of the filter materials are improved, and the burst index of the filter material increases to 2.34 kPa.m^{2}.g^{-1}, more than twice that of pure silk filter material, as the cotton fiber content reaches 10%. In addition to forming hydrogen bonds between fibers, cotton fiber itself is strong, so the addition of cotton fiber can effectively improve the strength of filter material and ensure its safe use.

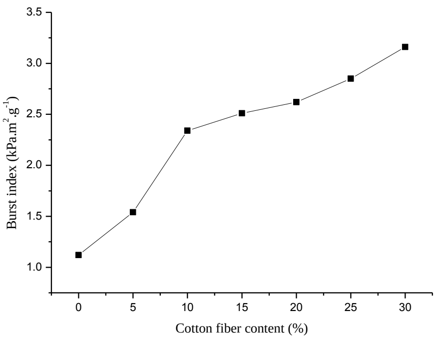


Fig.2. Effect of cotton fiber content on the burst index of filter material

Filter efficiency and filtration resistance are the most important factors for filter materials. A good filter should have high filter efficiency and low pressure drop [9]. It can be seen from Fig.3 that pure silk fiber filter material has the highest filter efficiency and filtration resistance among all the samples, 95.8% and 30.3 mmH_2O, respectively. Filtration and air resistance of porous filter materials occur through the microporous channel inside materials, and the filtration efficiency of materials rely on the micropore size. Pore size of pure silk filter material is very small, so there will be a high resistance and low penetration rate when NaCl aerosol particles pass through. Average pore size of the filter materials increase with the increase of cotton fiber content, so the penetration rate increases and the filter efficiency and filtration resistance decrease. When the cotton fiber content increase to 10%, the filter efficiency and filtration resistance of the filter material are 95.0% and 24.6 mmH_2O, respectively. Continuing to increase the content of cotton fibers will result in a significant decrease in filter efficiency and filtration resistance.

Considering the filter efficiency, filtration resistance and burst index of the filter materials, filter material containing 10% cotton fiber can meet the requirements of air filter materials well and 10% cotton fiber content is an appropriate proportion for the preparation of air filter materials.

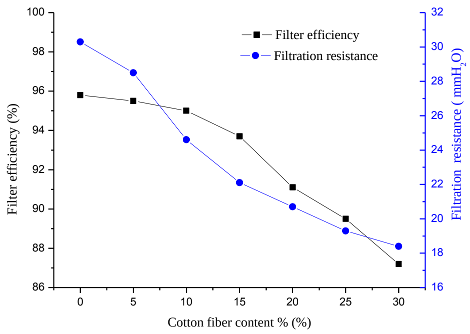


Fig.3. Effect of cotton fiber content on the filtration performance of filter material

3.2. Effect of nano-TiO_2 on the structure and properties of the filter material

Filter materials containing 90% silk fiber and 10% cotton fiber were prepared and different dosage of nano-TiO_2 was immobilized on them to investigate the effect of nano-TiO_2 on the structure and properties of the filter materials.

Fig.4 shows that the inhibition zone diameter of the filter materials increase with the increase of nano-TiO_2 dosage. The inhibition zone diameter of filter material with no nano-TiO_2 is 6.0 mm, and it increases to 12.5 mm when nano-TiO_2 dosage reaches 6%. In the antibacterial activity test using disk diffusion method, the larger the inhibition zone diameter, the better the antibacterial activity. The filter material loading more nano-TiO_2 has larger inhibition zone diameter, that is, it has better antibacterial activity. Because nano-TiO_2 is a semiconductor photocatalyst which can sterilize and decompose organics, and it can react with cell directly or indirectly and kill bacteria after being excited by ultraviolet light [20].

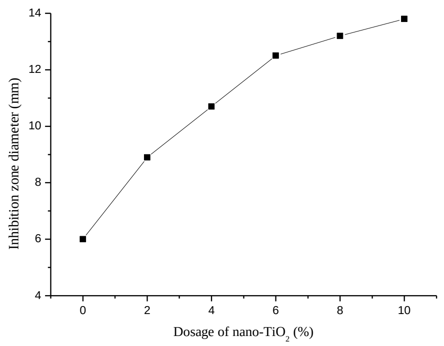


Fig.4. Effect of nano-TiO_2 dosage on the antibacterial activity of filter material

Fig.5 shows that the burst index of filter materials decrease with the increase of nano-TiO_2 dosage since the existence of nano-TiO_2 particles affects the hydrogen bonding between fibers and results in the decrease in strength of filter material. The change in burst index is not very significant when the dosage of nano-TiO_2 is less than 6%. However, the burst index of filter material shows a dramatic drop when the dosage of nano-TiO_2 exceeds 6%. The strength of filter material must be taken into consideration when giving special functions to it.

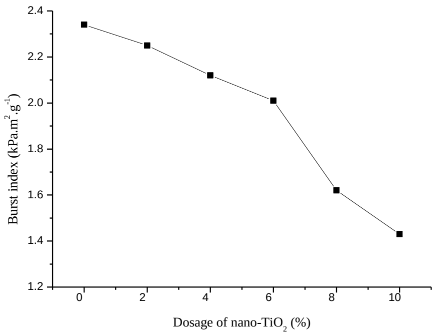


Fig.5. Effect of nano-TiO_2 dosage on the burst index of filter material

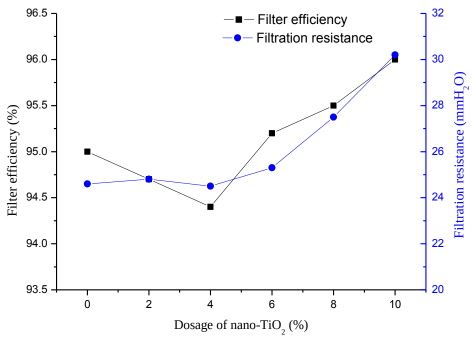
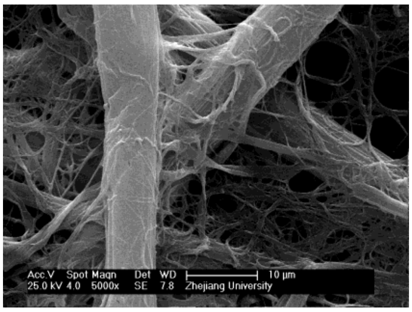


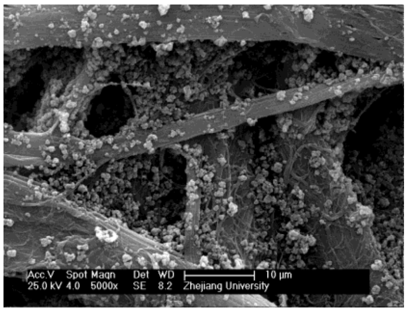
Fig. 6. Effect of nano-TiO_2 dosage on the filter performance of filter material

The filter efficiency and filtration resistance of filter materials loading nano-TiO_2 are shown in Fig.6. It can be seen that with the increase of nano-TiO_2 dosage, the filter efficiency and filtration resistance have the similar change trend, they all decrease slowly at first, and then start to rise when nano-TiO_2 dosage exceeds 4%. A small amount of nano-TiO_2 interferes with the bonding between fibers and increases the porosity of filter material, which results in the decrease of filter efficiency and filtration resistance. When the dosage of nano-TiO_2 dosage exceeds 4%, a large amount of nano-TiO_2 particles depositing on the filter material act as a filter media to increase the filtration resistance and filter efficiency. However, the rise of filter efficiency slow down and the rise of filtration resistance speed up after the nano-TiO_2 dosage exceeds 6%.

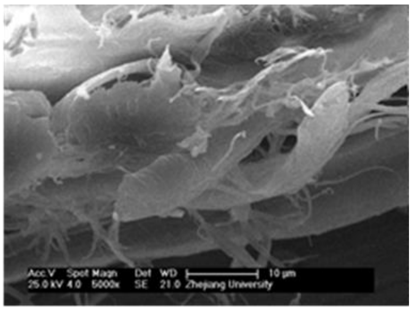
According to the above analysis, filter material loading 6% nano-TiO_2 is an optimum level, at this point, the filter material has relatively high antibacterial activity, burst index and filter efficiency.

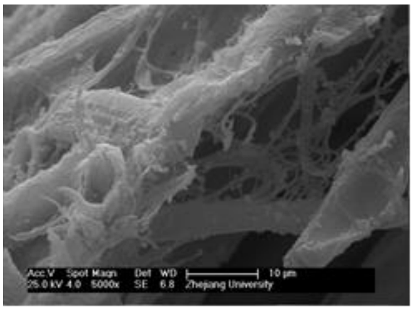
The surface and transverse section morphology of filter materials without nano-TiO_2 and loading 6% nano-TiO_2 are observed by SEM and shown in Fig.7. It can be seen from Fig.7(a) that there are apparent microfibrils raising on the surface of fibers and a porous network structure is formed. Fig.7(b) shows that a large amount of nano-TiO_2 particles are intercepted on the surface of fibers, particularly on the surface of microfibrils. Compared Fig.7(b) with Fig7(d), it can be found that most of the nano-TiO_2 particles are distributed on the surface of the filter material, and less nano-TiO_2 particles are deep inside the filter material, and this distribution is favorable for photocatalysis. Dilute starch solution is used as the dispersion medium of nanao-TiO_2 particles in this experiment, and it acts as a binder to improve the bonding force between fibers and nano-TiO_2 particles and avoids shedding and migration of nano-TiO_2 particles.





(a) Surface with no nano-TiO_2 *(b) Surface loading 6% nano-TiO_2*





(c) Transverse section with no nano-TiO_2 (d) Transverse section loading 6% nano-TiO_2

Fig.7. SEM images of surface and transverse section of filter materials

4. Conclusions

Air filter material made from pure silk fiber has small pore size and high filter performance, but it has low burst index. Adding some cotton fiber improves the burst index, however, it reduces filter efficiency of the filter materials. The experiment results indicate that replacing silk fibers with 10% cotton fibers can obviously improve the burst index of the filter material without reducing filter efficiency too much.

Loading nano-TiO_2 on air filter material endows filter material with antibacterial activity, however, it results in a reduction in burst index. Nano-TiO_2 particles are mainly distributed on the surface of the filter material rather than inside it. The filter efficiency and filtration resistance of air filter material decrease firstly and then increase with the increase of nano-TiO_2 dosage. Considering the burst index, filter efficiency and antibacterial property, filter material loading 6% nano-TiO_2 is an optimum level.

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