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REVIEW ARTICLE

ADVANCES IN AIR FILTERS BASED ON ELECTROSPUN NANOFIBERS

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ABSTRACT

This paper reviews the background and developments of air filters based on electrospun nanofiber materials. Methods of electrospinning in the production of filter materials and their advantages are discussed in detail. Researchers around the globe are working hard to get highly efficient filters at low cost. Famous approaches to build most effective air filters include electrospun nanofiber mats, composite nanofiber mats, and antibacterial nanofiber mats for micro to nano level filtration at a higher rate. Properties like high temperature, alkali, acid, and flame resistance are still constraining the use of nanofiber filters in many industries. Future research should be focused on producing nanofiber mats capable of undergoing extreme conditions.

KEYWORDS

Electrospun, nanofiber, filters, high temperature, electrospinning.

1. INTRODUCTION

In manufacturing, food, medicine, biology, electronics, and other industries' raw material purification, air purification, water purification, and waste discharge are all indispensable industrial production links (Ain and Zaheer, 2019; Rehman et al., 2019). The effective control of airborne pollutants, harmful biological agents, allergens, and aerosol particles are the main issues concerned by people. Generally, the diameter of dust particles floating in the air ranges from tens of nanometers to tens of microns, which are the main ingredients of air pollution. A high efficiency air filter can effectively remove bigger than 0.3μm particles, but not smaller particles. For air purification, the filtration industry has been looking for a material to prepare a filter medium that can effectively filter particles below 0.3μm. Nanofiber materials have attracted people's attention because of their excellent surface to volume ratio and potential to be used in filtration (Huang et al., 2019; Lv et al., 2018; Xu et al., 2016; Poudyal et al., 2018; Kadam et al., 2018).

2. DEVELOPMENT HISTORY OF FIBER FILTER MATERIALS

As early as during the First World War, gas masks using asbestos fiber as filter material appeared. In 1940, the United States prepared glass fiber filter materials and invented patents. From the 1950s to the 1970s, fiber filter materials developed rapidly, and high-efficiency air filters (HEPA) using glass fibers as filter materials appeared and were applied to air purification in rooms (Kosikowska and Biziuk, 2010). In order to further improve the filtration performance, high-efficiency filters made of ultra-fine glass fibers are used, and the filtration efficiency of particles greater than or equal to 0.3μm reaches 99.998%. Subsequently, Japan developed an ultra-high efficiency filter (ULPA); the filtration efficiency of 0.1μm particles can reach as high as 99.9955%. With the emergence and development of new industries, such as electronics, aerospace, precision instruments, which require a high degree of indoor air cleanliness, micron-level fiber filter materials have failed to meet the requirements of filtration accuracy. It is an inevitable trend for the development of filter materials to use nano-sized fibers in the structure of filter materials. There are many methods to prepare nanofiber filter materials, such as drawing, template synthesis, phase separation, self-assembly, and electrospinning (Langmaier and Samec, 2007; Wang and Wang, 2020; Galvan and Barranco, 2016). However, electrospinning is the simplest way to prepare nanofibers (Xue et al., 2019).

3. RESEARCH AND DEVELOPMENT OF ELECTROSPUN NANOFIBER FILTER MATERIAL

In 1902, for the first time in the United States, under the action of electrostatic field forces, fibers were produced using solution jets. In 1934, Formhals proposed electrospinning technology in the United States and applied for a patent. In 1938, Rozenblum and Petryanov-Sokolov prepared electrostatic fibers at the Karpov Aerosol Laboratory in the Soviet Union, and successfully applied them to filter materials (now called nanofiber filters). In 1939, a production plant for filter elements of gas masks was established in Tver. This filter material was prepared by electrospinning cellulose acetate dissolved in a mixed solvent of dichloroethane and ethanol (Lushnikov, 1997). By the end of the 1960s, the Soviet Union already had five factories producing nanofiber filter materials, and the output reached 20 million m^2 per year. With the hard work of the "Donaldson" company, nanofiber filter materials were rapidly emerging in the United States in 1980. In Europe, the commercialization of electrospun fibers began in 1990 (Barhate and Ramakrishna, 2007).

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China only really began to promote fiber filter materials in the late 1970s, mainly using wet and chemical bonding processing technology, needle punching method, spun-bonding method, and melt blowing method that appeared in the 1980s and 1990s (Wu and Ke, 2009). Although there are almost all the world's fiber manufacturing technologies, the research on electrospun nanofiber filter materials is still in its infancy (Kadam et al., 2018). The nano-scale fiber prepared by electrospinning technology has the characteristics of small fiber diameter, high specific surface area, and large aspect ratio. The nano-fiber mat has high porosity and nano-scale micropores (the pore diameter varies between a few microns) and coherent pores. It has good air permeability, and is easily combined with nano-scale chemical substances or functional substances to prepare nano-fiber mats with unique functions. The following is a preliminary analysis of the latest research developments in electrospinning nano-fiber mat, composite nanofiber mat, and antibacterial nanofiber mat in air filtration.

4. Electrospun Nanofiber Felt

As we all know, in the range of submicron (100nm-1.0μm), the smaller the diameter of fiber felt is, the higher the filtration efficiency. Nevertheless, along with the pressure drop, reducing the air permeability will significantly affect the filter material's filtration performance. However, for electrospun nanofiber felt, because the fiber diameter reaches the nanometer level (below 100nm), the diameter is equivalent to the average free path of air molecules. When the airflow containing particles passes through the electrospun fiber felt, the air can slip on the fiber surface, resulting in a substantial loss of pressure drop before and after the airflow passes through the fiber felt. The substantial reduction is beneficial to the smooth flow of air through the filter material so that the filter performance of the nanofiber felt reaches the ideal performance. Generally, the quality factor is used to evaluate the filtration performance of filter media.

Quality factor is defined as: $Q = -\ln(p)/\Delta P$ (1)

Where p represents permeability and ΔP represents pressure drop. Because -ln (p) is filtration efficiency, so the quality factor is the ratio of filtration efficiency, and pressure drop. Nanofiber filter media has higher filtration efficiency, and lower pressure drop than traditional fiber filter materials, that is, higher quality factor. Therefore, nanofiber filtration materials have better filtration performance.

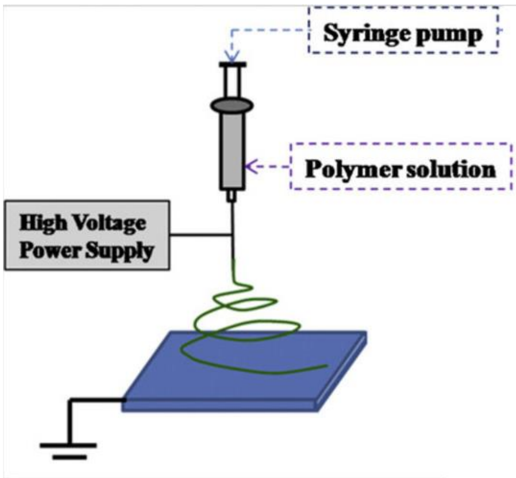

Figure 1: Setup of electrospinning

The influence of spinning solution concentration on the diameter of Nylon6 nanofibers was discussed by Ahn et al. The solution concentration was 15% to 24%, and the diameter of Nylon6 nanofibers could be increased from 80 nm to 200 nm. In addition, the filtration efficiency of Nylon6 nanofiber mat and high-efficiency air particle filter (test particles with a wind speed of 5cm/s and 0.3μm) is compared. The results show that the filtration efficiency of nano-fiber mat can reach 99.993%, which is much higher than that of high-efficiency air particle filter (Ahn et al., 2006). Some researchers compared the filtration performance of traditional glass fiber high-efficiency air filters and electrospun Nylon6,6 nanofiber mats (Park and Park, 2005). For aerosol particles with a particle size of 0.3μm and the wind speed 3m/min. The filtration efficiency of the nanofiber mat is higher than that of the glass fiber filter media, and the surface density of the nanofiber mat is only 16.48g/m^2, whereas the surface density of the glass fiber filter is 81.46g/m^2. The pressure drop of the fiber mat is only 13.27mm mercury column, while the pressure drop of the glass fiber reaches 37.05mm mercury column.

A studied the filtration performance of electrospun fiber mats with different fiber shapes (Yun et al., 2007). Nanofiber mats, beaded fiber mats and particle/nanofiber composite fiber mats were prepared, and tested for their comprehensive filtration performance. It was found that the filtration quality factor of beaded fiber mats and composite fiber mats was higher than that of nanofiber mats (Kalayci et al., 2006). Kalayaci and others also reached the same conclusion. Inserting polymer microspheres into the nanofiber mat can further improve the filtration performance of the entire nanofiber mat. Some researchers explain this phenomenon as the addition of beads and microspheres, which mechanically separates the nanofiber layers, increasing air permeability, thereby improving filtration performance. Some researchers believe that the decrease in volume fraction and the increase in effective surface area of the fibers are the main reasons for improved filtration performance.

5. Electrospun Composite Nanofiber Mat

Electrospun nanofiber mats have high-efficiency filtration performance, but nanofibers can withstand low strength, are very fragile, easily damaged, and have extremely poor durability. Therefore, nanofiber mats cannot be used as filters alone. In order to apply nanofibers to filtration, it is necessary to compound the nanofibers with the base fabric to increase their mechanical strength. There have been related researches on glass fiber, polyester fiber, cellulose fiber as the filter material of the base fabric for electrospun nanofiber composite. Figure 2 shows a scanning electron micrograph of electrospun nanofibers supported by cellulose fibers from composite (Grafe et al., 2001). The diameter of electrospun nanofibers is about 250nm, while the diameter of cellulose fibers is more than 10μm. The fiber has a practicle mechanical strength, but in practical applications, the filter material will inevitably be subject to external forces such as stretching and friction. Since the strength of the base fabric is greater than that of the nanofiber layer, the nanofiber layer is prone to wear, wrinkling, and falling off. To better protect the nano-fiber layer, a composite structure of nano-fiber interlayer is also present, that is, the nanofiber layer is sandwiched between two base fabrics, nanofiber layer can be protected from surface friction and outside exposure damage, thereby increasing service life.

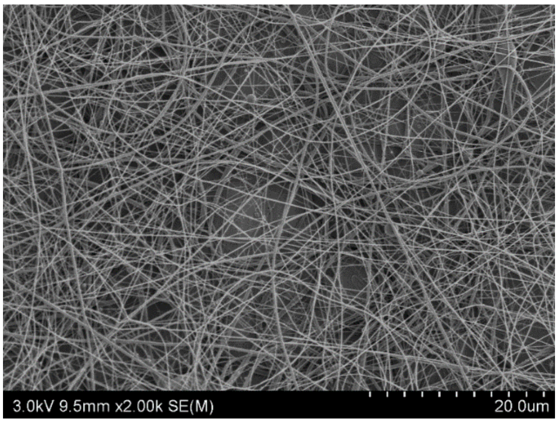

Figure 2: SEM of electrospun nanofiber mat

A group researchers prepared three-layered composite fiber filter media (the middle layer is electrospun nanofibers, and the front and back layers are nonwoven base fabrics) and double-layered fiber composite filter media (Patanaik et al., 2010). The nanofibers are deposited on the nonwoven base fabric, and the durability of the nanofiber layer is tested by circulating compressed air through these two filter media. The pore size of the layer is significantly increased, resulting in a significant change in filtration efficiency and pressure drop. For three-layer fiber composite filter media, there is no significant change in pore size, filtration efficiency, and pressure drop. This shows that the nano-fiber layer's fiber structure in the three-layer composite medium maintained intact, showing durability.

With the appearance of composite nano-fiber mats, the nano-fiber is applied to air filtration, which once again raises the research upsurge of nanofiber filtration materials. Nanofibers are deposited on nonwovens by electrospinning. The diameter of nanofibers (tens to hundreds of nanometers) is 1-2 orders of magnitude smaller than that of nonwovens, and the nano-fibers also have nanometer-size pores. It can be determined that for the filtration of small particles, the nanofiber layer plays a leading role in the composite fiber felt (Rajak et al., 2019). Figure 3 shows the scanning electron micrograph of particle capture after the airflow containing sodium chloride particles pass through the composite filter medium. The diameter of sodium chloride particles is 0.01-0.5 μm.

It can be seen from the figure that more sodium chloride particles are deposited on the nanofiber layer than on the substrate fiber reaching the micron level. The results show that nanofibers can significantly improve the filtration efficiency of submicron particles. A group researchers electrospun Nylon6 nanofibers (fiber diameter is below 500nm) on the traditional air filter, and analyzed the filtration performance of composite filter media under the condition of changing the density of the nano-fiber layer (Li et al., 2006). It is found that increasing the density of nanofiber layer and reducing the diameter of Nylon6 fiber can improve the filtration performance. Some of researchers prepared branched nanofibers by using a novel double bubble electrospinning setup (Ali et al., 2020). PVA and PVP were simultaneously electrospun to fabricate biodegradable branched nanofiber mat which was suggested as highly efficient filter material especially for facemasks.

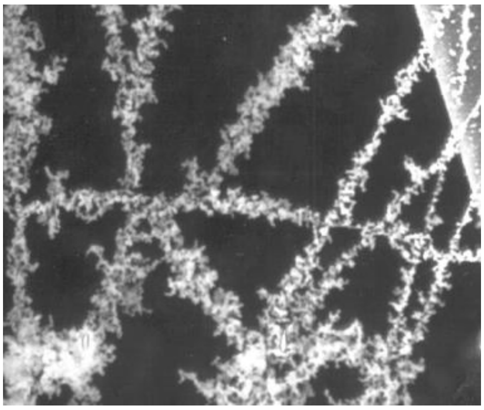

Figure 3: SEM of sodium chloride particles captured by composite filter medium

In the study of composite nanofiber mats, it was found that the smaller the diameter of the nanofibers and the greater the thickness of the fiber layer, the smaller the pore size and the higher the filtration efficiency, but the higher the pressure drop, that is, the more air permeability difference. The quality factor mentioned above to evaluate the performance of filter materials is also applicable to composite filter materials. In order to obtain filter materials with high-quality factors, when preparing composite nanofiber mats, it is necessary to comprehensively consider the nanocomposite on the base fabric. The fiber diameter and fiber layer thickness of the fiber is used to balance the filtration efficiency and pressure drop to achieve excellent filtration quality. There are also many relevant reports at home and abroad about the relationship between filtration efficiency, pressure drop, gas permeability, and its effect on filtration performance.

Some researchers used electrostatic spinning to deposit three types of nanofibers, polyethylene oxide (PEO), polyvinyl alcohol (PVA) and polycaprolactam (PA6), on traditional nonwoven polyester (PET) fiber mats (Dotti et al., 2007). They discussed the air permeability of the composite fiber and found that the permeability of the composite fiber is mainly determined by the nanofiber layer. The thickness of the nanofiber layer can be adjusted by changing the spinning time, that is, the deposition time on the PET fiber mat, so as to achieve the purpose of controlling the permeability of composite fibers. In other study, researcher used the electrostatic spinning method to prepare PEG/PA6 nanocomposite materials based on three traditional filter materials with different filtering effects and analyzed the void structure characteristics of the composite materials and their content with the nanofiber layer in the relationship between the cloth (Babapoor et al., 2017). It was found that with the increase of electrospinning time, the number of nanofibers deposited on the base fabric increased, and the average void area, porosity, and air permeability decreased exponentially. There was a linear relationship between rates.

A group researchers composited nanofiber layers with different thicknesses on the base fabric (Wang et al., 2018). Experiments showed that as the thickness of the nanofiber layer increases, the filtration efficiency increases, and the pressure drop also increases, that is, the permeability decreases. They also used a mathematical model to simulate the filtration process of the composite fiber and found that the filtration performance is not only related to the thickness of the nanofiber layer, but also to the particle size of the filtered gas particles. The particles that can freely pass through the filter medium can reduce the filtering quality factor of the composite fiber material. However, increase in the thickness of nanofiber material can increase the filtering quality factor and improve the filtering performance.

Electrospun PA6, deposited it on nylon/cotton fabric (50:50), and prepared ultrafine PA6 nanofibers mat by changing electrospun parameters, such as solution concentration, electrospun voltage and electrospun time (Vitchuli et al., 2010). It was found that with the increase of electrospinning time, the filtration efficiency of the composite filter material increased obviously, but the pressure drop did not change significantly. It is different from the past that the pressure drop increases with the increase of nanofiber layer thickness, which meets the requirement that people do not sacrifice the pressure drop to improve the filtration efficiency, which also makes the ultrafine Nylon6 nanofiber have a broader application prospect.

Electrospun PEO to test the properties of composite fiber felt on the base cloth of micron fiber (Leung et al., 2010). It was found that the maximum particle size (MPPs) of composite fiber felt decreased with the increase of nanofiber deposition density, the filtration efficiency decreased with the increase of wind speed, and the smaller the particle, the more intense the decrease. The experimental results are consistent with the theoretical results. This is because the increase of wind speed reduces the residence time of particles on nanofibers, thus reduces the chance of collision between Brownian particles and nanofibers, resulting in a decrease of filtration efficiency. They also found that the effect of nanofiber layer thickness on MPPs is less significant than that of nanofiber deposition density. Therefore, it can be concluded that for a certain amount of nanofibers, the fiber density can be reduced by folding to reduce the pressure drop. It can also be considered that a multi-layer nanofiber filter has the same pressure drop as a single-layer nanofiber filter, but the capture capacity of the sub-micron aerosol is much higher.

A studied the filtration performance of multi-layer nanofibers and monolayer nanofiber composites (Zhang et al., 2010). The electrospun polyacrylonitrile (PAN) nanofibers were sandwiched between two layers of carbon fibers to form a sandwich structure. The pressure drop and filter quality factors of nanofiber filter media with single-layer nanofiber filter and multi-layer sandwich structure were compared under the same electrospun time. The experimental results show that under the same thickness, the quality factor of multi-layer nanofiber filter media is much higher than that of single-layer filter media because the pressure drop of multi-layer nanofiber filter material does not increase significantly.

6. Electrospun Antibacterial Nanofiber Felt

Air filter materials are often exposed to the open air and are easily attacked by bacteria, fungi ,and other micro-organisms. When micro-organisms attach to the filter material with dust and live and multiply with dust as food, it will not only seriously affect the filtering performance of the filter material, but also reduce its service life. The micro-organisms that often appear on the filter materials are Glucococcus, Serratia, klebsiella, Cladosporium, and aspergillus. In order to make the filter material have antibacterial performance, some people have tried to introduce antibacterial groups on the surface of the filter medium. However, the effect is not ideal, because most micro-organisms enter the filter material with atmospheric particles, along with the growth of particles, greatly reducing the chance of contact between the antibacterial groups and micro-organisms, reducing the antibacterial efficiency. Antibacterial nanofiber material can be prepared by electrospinning polymer solution containing antibacterial groups.

Using the characteristics of small fiber diameter and large specific surface area, the antibacterial performance can be greatly improved. In order to introduce the antibacterial group into Nylon6 fiber, Added three kinds of dimethylhydantoin derivatives with different structures into the spinning solution, electrospun the nanofiber felt with the diameter of 100-500nm, and carried out the antibacterial test (Tan and Obendorf, 2007). It was found that all the Gram-negative and positive bacteria were killed 40 minutes later. The antibacterial effect of fiber felt was better when the content of hydantoin derivatives increased. A group researchers added $AgNO_3$ to cellulose (c), polyacrylonitrile (PAN) and polyvinyl chloride (PVC) polymer solutions, and prepared three kinds of antibacterial fibers by electrostatic spinning, in which dimethylformamide in the spinning solution was used as both the solvent of polymer and the reductant of silver ions (Lala et al., 2007).

Thus, silver nanoparticles distributed on the surface of the electrospun fiber. Through the antibacterial test, it is found that the electrospun fiber felt containing silver nanoparticles has a good antibacterial effect. Some researchers added benzyltriethyl ammonium chloride to polycarbonate solution (PC) (Sun et al., 2017). The polycarbonate (PC) nanofiber felt with antibacterial function was successfully prepared in the medium of chloroform as a solvent, and the antibacterial test of gram-negative, positive, and klebsiella bacteria was carried out. It was found that the antibacterial efficiency could reach 99.9%, and the filter performance test was carried out and found that antibacterial fiber filter material has higher filtration efficiency.

Conclusion

With the development of modern science and technology, the level of industrialization continues to improve, people's awareness of environmental protection is gradually strengthened, the world's demand for filter materials is increasing year by year, and higher requirements are put forward for the air purification industry. In the field of air filtration, electrospun nanofibers have gradually replaced the traditional textile and non-woven filter materials. Dimensional filter materials also helped in rapid development.

(1) The rapid development of electrospun nanofiber filter materials injects fresh blood into the nonwoven air filter materials and has achieved remarkable results in practical applications. With its unique excellent performance, it has been widely used in many countries. The proportion of nanofiber filter material will further increase in the future.

(2) The emergence of various composite nanofiber air filter materials greatly increases the types and efficiency of air filter materials, but there are still many problems to be solved. When the nanofiber felt is compounded with the substrate, such as the adhesion between the substrate and the nanofiber felt, the balance between the composite nanofiber filter efficiency and pressure drop, etc. Therefore, the structure and properties of electrospun composite nanofiber filter materials still need further research and exploration.

(3) The development of antibacterial nanofiber filter materials is due to the higher requirements of sterile filter materials. With the application of filter materials in different places and conditions, the performance requirements of filter materials are becoming higher and higher. General air filter materials do not have the properties of high-temperature resistance, acid and alkali resistance, flame resistance, which greatly limits the application field of filter materials. Electrospinning technology is still in its infancy in the preparation of functional nanofiber filter materials, but it is believed that the preparation and application of electrospinning functional nanofibers will have great potential in the future.

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