High-performance Electret and Antibacterial Polypropylene Meltblown Nonwoven Materials Doped with Boehmite and ZnO Nanoparticles for Air Filtration

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Abstract: The current pandemic caused by COVID-19 has intensively triggered the development of high-performance air filters. Polypropylene (PP) is widely used as the raw material of meltblown nonwoven materials and is the core layer in air filters, such as masks. In this study, an electret PP meltblown nonwoven with antibacterial activity was developed, and nano boehmite (AlOOH) and nano-ZnO were employed as electret and antibacterial agents, respectively. AlOOH (0.5-2.0 wt%) and ZnO (1.0 wt%) were doped into the PP matrix using a twin-screw extruder, and the resulting masterbatches were applied as raw materials to produce nonwoven materials via a meltblown process. The as-prepared nonwoven samples were characterized by means of SEM, IR and DSC/TG. After corona charging, the filtration efficiency was determined by a filtration tester, charge decay was measured by an infrared electrostatic tester, and the antibacterial properties were evaluated (evaluation method: AATCC 100-2012). A dosage of AlOOH greater than 1.0 wt% endowed the nonwoven material with high filtration efficiency, and 1.0 wt% ZnO brought about antibacterial activity. Corona charging was an effective means to charge the nonwoven electret, and the charges were quicker to decay in air than in a sealed bag. The as-prepared meltblown nonwoven filter is a remarkably promising filter for air filtration.

Keywords: Polypropylene, Meltblown nonwoven, Electret materials, Filtration, Antibacterial materials

Introduction

Polypropylene (PP), a kind of polyolefin, is one of the three most widely used polymers. Benefiting from a suitable processing temperature, high tensile strength, good chemical corrosion resistance, and low moisture absorption, one of the most important applications of PP is as a raw material for fiber and nonwoven fabric, and PP has received unprecedented attention during the current COVID-19 pandemic [1-5]. There are two main types of PP nonwovens, spunbonded and meltblown, which have been applied in hygiene (diaper, sanitary napkins), surgical materials, filters, masks, hair caps, blowing loops, etc. During the current pandemic of respiratory diseases, such as the novel coronavirus, increasing attention has been given to the improvement of filtration performance and other functions of spunbonded and meltblown nonwoven fabrics generally used as protective equipment, such as in masks [6-8].

There are two main ways to improve the filtration performance of nonwoven fabrics without obviously increasing the air resistance. One method is to make fibers finer in diameter. The size of a thin melt blown fiber is approximately 1-3 μm, and practically, decreasing diameter will be at the expense of yield [9-12]. Electrospinning is a simple and convenient process to fabricate superfine fibers. However, due to the use of organic solvents and lower yields, the industrialization cost of this method is still very high [13,14]. The other method to improve the filtration performance of nonwovens is electret technology. After being treated under an electrostatic field, fibers or cloth containing electrets exhibit long-term electric polarization and effectively enhance the ability of the fabrics to absorb bacteria, particle matter (PM), virus contaminants, or aerosols [15,16].

Micro/nano tourmaline is widely used as an electret enhancing compound in PP nonwoven industrially [17,18], and some other oxides have also been researched, such as TiO2 [19], BaTiO3 [20], Al2O3 [21], and SiO2 [22]. Li et al. reported that a dual polymer (PS/PVDF, polystyrene/polyvinylidene fluoride) system showed good electret properties, and their nonwoven material had high efficiency and low resistance [23]. A similar report was made by Cai et al. (PS/PAN, polystyrene/polyacrylonitrile) [24]. Boehmite, the γ-AlOOH of bauxite, has a layered structure similar to graphene. Boehmite has a large porosity, large specific surface area, good dispersion, good compatibility and good heat resistance. Nano boehmite has been researched in electrospun fibers to enhance the electret effect of fibers [25-27]. Low preparation efficiency and low strength resulted in these electrospun webs (nonwoven) remaining in the lab. The electret polarization process can affect the electret effect and further the filtration performance of nonwoven fabric [28,29]. However, the charge of an electret nonwoven fabric...
will gradually decay until it disappears, leading to filtration failure. The conditions and methods of the electret process for charge retention and decay have also been studied [30,31].

Most electret-treated nonwoven fabrics and their products, such as masks, are generally viable for two years, but the charges will be reduced rapidly over the course of dozens of days after unpacking. Therefore, improving the fiber polarization function and endowing nonwoven fabrics with antibacterial and antiviral functions are the main approaches to increase the performance of nonwoven products. Nano ZnO is often used as a kind of photoactive semiconductor material as it has good antibacterial activity [32,33]. Our research group has also studied its antibacterial application in PP nonwoven fabrics [34]. Moreover, the nanoparticles of ZnO and boehmite are ordinary inorganic oxides, which have been verified to have no obvious toxicity, especially at low doses, and have been applied in health care materials [35,36]. In this research, both nano boehmite (AlOOH) and nano ZnO were synergistically used to add electret and antibacterial activity to PP melt-blown nonwovens. The as-produced melt-blown nonwovens were characterized by means of DSC/TG, tensile testing and SEM and FT-IR to determine the structure; the materials were further evaluated for filtration efficiency, electret effect, and antibacterial activity.

Experimental

Materials
Polypropylene (melt flow rate, MFR: 1500 g/10 min) was obtained from Shandong SWT New Material Technology Co., Ltd. (Yantai, China). Nanometer boehmite (AlOOH, average particle size: 20 nm) was purchased from Xuancheng Jingrui New Material Co., Ltd. (Xuancheng, China). Antibacterial masterbatches (20 wt% of nano-ZnO) were made from PP and nano-ZnO in our lab.

Preparation of PP Electret Masterbatch with Antibacterial Activity
To obtain the PP electret masterbatch used as meltblown raw material, the blending of PP and nano-AlOOH particles was carried out in a 16 mm Benchtop Twin-Screw Extrusion Pelletizing Line (Labtech Engineering Co., Ltd., Samutprakarn, Thailand) with two feeders. First, pristine PP and AlOOH particles were added from the main and side feeders and were blended at a 8:2 ratio to prepare a 20 wt% electret masterbatch. The temperature of each heating zone of the twin-screw extruder was set based on Table 1.

Second, the electret masterbatch containing 20 wt% AlOOH was diluted by pristine PP in the same twin-screw extruder under the same process conditions (Table 1) to give PP electret masterbatches with AlOOH contents of 0.5 wt%, 1.0 wt%, and 2.0 wt%. The antibacterial activity of PP nonwovens with 1.0 wt% nano-ZnO has been previously demonstrated [34], and the same dosage (1.0 wt%) of nano-ZnO was introduced here by adding a homemade antibacterial masterbatch (Table 2). Finally, the as-prepared electret and antibacterial masterbatch samples contained 1.0 wt% ZnO and approximately 0.5 wt%, 1.0 wt% and 2.0 wt% AlOOH, which were referred to as AlOOH-0.5, AlOOH-1.0, and AlOOH-2.0, respectively.

Preparation of Meltblown Nonwoven
Meltblown nonwoven fabric was prepared on meltblown equipment (SH-RBJ, Shanghai Sunhoo automation equipment Co., Ltd., Shanghai, China). Each heating area of the melt jet machine was set based on the parameters given in Table 3.

Corona Charging
Self-designed and commissioned corona equipment was applied to charge the melt blown nonwoven fabrics for electrets. The electret conditions were as follows: high

| Table 1. Temperatures of twin-screw extruder heating zones |
|----------------------------------------------------------|
| Heating zone | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Temperature (°C) | 160 | 160 | 165 | 170 | 175 | 175 | 165 | 165 | 160 | 155 |

| Table 2. Recipe for the electret PP masterbatch with antibacterial activity |
|--------------------------------------------------------------------------|
| Sample | PP masterbatche |
| 20 % ZnO | 0.5 % AlOOH | 1.0 % AlOOH | 2.0 % AlOOH |
| 1 | 5 | 95 | 0 | 0 |
| 2 | 5 | 0 | 95 | 0 |
| 3 | 5 | 0 | 0 | 95 |

| Figure 1. Illustration of the meltblown process. |

AIOOH was diluted by pristine PP in the same twin-screw extruder under the same process conditions (Table 1) to give PP electret masterbatches with AIOOH contents of 0.5 wt%, 1.0 wt%, and 2.0 wt%. The antibacterial activity of PP nonwovens with 1.0 wt% nano-ZnO has been previously demonstrated [34], and the same dosage (1.0 wt%) of nano-ZnO was introduced here by adding a homemade antibacterial masterbatch (Table 2). Finally, the as-prepared electret and antibacterial masterbatch samples contained 1.0 wt% ZnO and approximately 0.5 wt%, 1.0 wt% and 2.0 wt% AIOOH, which were referred to as AIOOH-0.5, AIOOH-1.0, and AIOOH-2.0, respectively.

| Table 3. Temperatures of the meltblown machine heating zones |
|-------------------------------------------------------------|
| Heating zone | 1 | 2 | 3 | 4 | Filter | Spinneret |
| Temperature (°C) | 160 | 200 | 225 | 225 | 225 | 225 |
The melting point of PP was 165 °C (Figure 5b), and it was not obviously affected when AlOOH was added. The introduction of AlOOH indicated that TDT decreased with increasing dose of ZnO, as inorganic oxides, ZnO and boehmite (AlOOH) exhibited less absorption in their IR spectra. A small amount of hydroxyl oxides appeared near 3300 cm$^{-1}$ and those at 1455 cm$^{-1}$ and 1367 cm$^{-1}$ were assigned to bending vibrations of C-H bonds, which also appeared in the spectra of nonwoven PP/ZnO/AlOOH. As inorganic oxides, ZnO and boehmite (AlOOH) exhibited less absorption in their IR spectra. A small amount of hydroxyl oxides appeared near 3300 cm$^{-1}$ and were not found in nonwoven samples because of their low content.

**Thermal Properties of Meltblown Nonwovens**

The influence of AIOOH and ZnO on the thermal properties of the obtained nonwoven materials was evaluated by DSC under a N$_2$ atmosphere. Previous work demonstrated that a 1.0 wt% dose of ZnO slightly increased the thermal decomposition temperature (TDT). The introduction of AIOOH indicated that TDT decreased with increasing dose (Figure 5a), which was attributed to water generated due to decomposition of AIOOH.

$$2\text{AIOOH} \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O}$$  \hspace{1cm} (1)  

The melting point of PP was 165 °C (Figure 5b), and it was not obviously affected when AIOOH was added. The AIOOH did not decompose at 225 °C, as this is the temperature of the spinneret and the highest temperature in the process of forming the PP fiber, which indicates that the
nonwoven processing conditions were not strongly affected when introducing AlOOH at less than 2.0 wt%.

**Pore Sizes and Filtration Performance**

The pore size distribution and porosity of the obtained meltblown nonwoven materials were tested and are shown in Figure 6. Compared with pure PP nonwoven samples with a 15.3-16.0 µm pore size distribution, the other samples with AIOOH and ZnO had larger pore sizes, and the porosity increased with the addition of boehmite (Figure 6b). The average pore sizes of PP, PP-AIOOH-0.5, PP-AIOOH-1.0 and PP-AIOOH-2.0 were 15.5 µm, 15.7 µm, 15.8 µm and 15.9 µm, respectively; this increasing trend was attributed to the coarsening of the fiber diameter with increasing boehmite content.

A comprehensive indicator of filter performance is the quality factor (QF), which is defined as follows (2):

\[
QF = -\ln(1 - \eta) / \Delta \rho
\]

(2)

where \( \eta \) is the filtration efficiency of the nonwoven solution.

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**Figure 3.** Meltblown nonwoven samples made from different masterbatch; (a) pure PP and PP containing 1.0 wt% ZnO, (b) 0.5 wt%, (c) 1.0 %, and (d) 2.0 wt% boehmite.

**Figure 4.** FT-IR spectra of raw materials and the obtained nonwoven materials.
and Δp is the pressure drop [37].

A schematic diagram of the electret filter is shown in Figure 7a. The dust, which generally contains bacteria, viruses, and some toxins, was intercepted and absorbed due to the presence of more electrostatic charges after corona charging (Figure 7b). The filtration efficiency of the PP meltblown nonwovens with or without boehmite was not obviously changed before electrization, and after corona charging, it was improved significantly (Figure 7c). When the content of boehmite was 1.0 wt%, the filtration efficiency was the highest and reached 96.3%. In addition, the pressure drop of the meltblown nonwoven materials did not change after corona charging (Figure 7d). The QF of the nonwoven sample with 1.0 wt% boehmite was obviously improved after charging, as shown in Figure 7e, and the electret nonwoven sample presented better comprehensive filtration performance. With increasing boehmite content, the pressure drop decreased, which was caused by the increase in the pore size. For filter applications, especially when used as masks, the pressure drop and breathability are important factors that affected the performance and comfortability. As indicated in Figure 7f, although there were approximate gram weights, a higher boehmite content in the as-prepared meltblown nonwoven particles resulted in better breathability due to the larger pore size.

**Evolution of Filtration Performance after Corona Charging**

It is well known that the electrostatic charge will decay continuously due to moisture in the environment. The charge decay of the as-prepared nonwoven materials was monitored continually in air and in a sealed PP bag at approximately 20 °C and 60 % RH for 7 days (Figure 8). The boehmite endowed the nonwoven solution with a higher surface potential, and a higher AIOOH content brought about more charge when the corona was charged. The effect of storage methods on charge decay was evaluated, as shown in Figure 8b, and sealing and storing the nonwoven particles were
effective in reducing charge decay. At the same time, their filtration performance was evaluated and compared, as shown in Figure 8c-d. In accordance with the charge decay results, the filtration efficiency of the nonwoven material remained if it was stored in a sealed bag.

**Antibacterial Performance**

The antibacterial activity of the as-produced nonwoven material with 1.0 wt% boehmite and 1.0 wt% ZnO was evaluated according to the AATCC 100-2012 evaluation method. The calculation formula for the bacterial reduction percentage (R) is as follows (3):

\[ R = \frac{(D - A)}{D} \times 100, \quad D = \frac{B + C}{2} \quad (3) \]

where R is the percentage of bacterial reduction, A is the number of bacteria after contact and regular culture, B is the
The evaluation results are shown in Table 4, and 3 kinds of bacteria were reduced by more than 90%, which shows that these bacteria were successfully retarded. In addition to having a high filtration performance, the as-prepared nonwovens had good antibacterial performance due to the nano ZnO particles that could produce some radicals, as shown in Figure 9 [34]. In fact, some particles inside these kinds of organic/inorganic hybrid systems can migrate to the (fiber) surface, which maintains and even enhances the corresponding performance [38].

### Table 4. Antibacterial activity results

| Test organism | Escherichia coli ATCC 8739 | Klebsiella pneumoniae ATCC 4352 | Staphylococcus aureus ATCC 6538 |
|---------------|-----------------------------|---------------------------------|---------------------------------|
| Concentration of bacteria (CFU/ml) | 1.6×10^5 | 1.7×10^5 | 1.6×10^5 |
| Sample at 0 h contact time (CFU/sample) (B) | 1.1×10^6 | 1.1×10^6 | 1.1×10^6 |
| Control sample at 0 h contact time (CFU/sample) (C) | 1.5×10^6 | 1.6×10^5 | 1.5×10^5 |
| Sample at 24 h contact time (CFU/sample) (A) | 1.2×10^5 | 9.0×10^3 | 7.0×10^3 |
| Control sample at 24 h contact time (CFU/sample) | 6.7×10^6 | 9.0×10^6 | 1.1×10^6 |
| Reduction (%) (R) | 90.8 | 93.3 | 94.6 |

Figure 8. Charge decay of the electret nonwovens stored (a) in air and (b) in a sealed PP bag. After storage for 7 days, the filtration performance was tested, as shown in (c) and (d).
In summary, we developed a meltblown nonwoven material with high filtration performance and antibacterial activity by doping nano boehmite and nano ZnO particles. After corona charging, the boehmite was an effective electret center in the PP matrix, affording charged surface layers that increased the filtration efficiency and ZnO acted as an antibacterial agent. The dosage of boehmite was optimized, and increasing the content resulted in coarser fibers and affected the spinnability. When 1.0 wt% boehmite was added, the as-prepared nonwoven material had good filtration performance, and 1.0 wt% ZnO endowed the nonwoven material with good antibacterial activity. This kind of masterbatch and its meltblown is a very promising filter material for us in, as an example, mask applications.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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