Preparation of modified rare earth lanthanum oxide/polypropylene nonwoven fabric by meltblown method

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Abstract—Lanthanum oxide was organically modified with dopamine and blended with polypropylene, and then lanthanum oxide (La2O3) /polypropylene (PP) nonwovens were prepared by melt blown method. The nonwovens were characterized by FTIR, SEM, TG, mechanical properties and X-ray shielding. The experimental results show that the addition of modified La2O3 makes the fiber arrangement of PP nonwovens more densely arranged and improves the thermal stability of PP nonwovens. The higher the amount of La2O3, the better the X-ray shielding performance of composite nonwovens.

1. Introduction
In recent years, with the development of nuclear science and nuclear industry, all kinds of radiation have an increasing impact on human and environmental production. The development and application of radiation protection materials have attracted more and more attention. At present, the common shielding material for X-ray is still lead products [1]. However, lead is toxic, and due to post use bending and incorrect suspension, the lead skirt is composed of layered thin layers, which has a common cracking problem in practice [2]. Besides, the absorption range of lead-containing composites is above 88 keV and below 40 keV [3,4], but the energy range between 40 keV and 88 keV (especially the conventional energy region used for medical diagnosis) is not well covered. Most of the research on personal shielding materials for X-ray protection has focused on new non-lead and lightweight materials [5]. Kim et al [6] prepared a double-layer tungsten composite yarn containing BaSO4 and polyethylene terephthalate (PET) fiber fabric. The shielding performance of the BaSO4-containing tungsten composite and PET fiber fabric was 0.018 mmPb and 0.03 mmPb, respectively, suggesting that low-dose shielding may help protect aviation crew from scattered radiation. Kim et al [7] prepared a shielding fabric by wrapping polyethylene (PE) yarn around a 30 µm tungsten yarn woven with a pneumatic pressure of tungsten nanopowder applied to the fiber dispersion process. The fabric coated with tungsten nano-powder improved the shielding performance of ordinary tungsten fibers by about 15%, providing relatively effective low-dose radiation shielding at a distance of about 1.2 m from the X-ray imaging equipment.

The absorbed energy of k layer electrons of lanthanide rare earth elements ranges from 38.9 to 63.3 KeV, which effectively makes up for the weak absorption zone of lead and can be completely used as shielding filler for lead substituted materials in the field of radiation protection [8]. Liu et al [9] prepared Gd(AA)3/natural rubber radiation protection materials. Sambhudevana et al [10] filled natural rubber with Gd2O3 modified by methacrylic acid to obtain X-ray protection material, and the modification of
methacrylic acid improved the interface between Gd$_2$O$_3$ and rubber. Gu et al.\cite{11} found that the mass fraction of La$_2$O$_3$ was within 60\%, and its nanoscale inhomogeneous dispersion in the PP matrix; with the increase of La$_2$O$_3$ addition and the corresponding increase of lead equivalent, the rare earth/PP composite protective fiber had better X-ray protection. Lou et al.\cite{12} found that the addition of rare earth oxides between the nonwoven layers can greatly improve the radiation protection properties of the composites. It was also found that used xylene method to remove PP matrix phase from melt-spun rare earth/polypropylene (PP)/thermoplastic polyurethane (TPU) fibers, and prepared rare earth/TPU fibers with X-ray protection properties.\cite{13} P. Vani et al.\cite{14} synthesized rare earth doped barium tellurate glasses and found that the increase of thulium doping in barium tellurate glasses can produce highly efficient high energy radiation shielding materials. At present, there are few studies on rare earth/polymer anti radiation fibers or fabrics.

In this paper, La$_2$O$_3$ was modified by dopamine, and then the modified La$_2$O$_3$/PP composite nonwovens were prepared by melt blown method. The effects of organic modification on the interfacial strength of the composite and the addition of La$_2$O$_3$ on the ray shielding properties of PP nonwovens were investigated.

2. EXPERIMENTAL

2.1. Materials
Polypropylene (PP), spinning grade, density 0.9g/cm$^3$, melt index 25g/min(235°C,2.16kg), Sinopec Group; Lanthanum oxide (nano grade, ≥99.99\%): China Beijing Nonferrous Metals Research Institute; Paraxylene (analytical pure, ≥99.7\%), anhydrous ethanol (analytical pure, ≥99.7\%), acetone (analytical pure, ≥99.5\%), acetic acid (analytical purity, ≥99.5\%); Beijing Tongguang Fine Chemical Company; trimethylolaminomethane (analytical purity, ≥99\%), dopamine hydrochloride (analytical purity, ≥99.9\%): Beijing Chemical Reagent Company.

2.2. Organic modification of La$_2$O$_3$ with dopamine
The proportion of dopamine modification solution was 50\% absolute ethanol, 49\% deionized water and 1\% dopamine hydrochloride according to the mass percentage, and the pH of this solution was adjusted to 8 with appropriate amount of triethylammoniummethane. Then, La$_2$O$_3$ particles equivalent to 25\% of the mass ratio of the above solution were added to it, mixed with ultrasound for 30min, and then air dried at 40°C to remove the solvent to obtain dopamine modified La$_2$O$_3$ particles.

2.3. Preparation of modified La$_2$O$_3$/PP nonwovens
In Hakee twin-screw torque rheometer, dopamine modified La$_2$O$_3$ was mixed with PP for 10 min at a mixing temperature of 210°C and a screw speed of 100 r/min, and then the spinning masterbatch was obtained by granulation. The masterbatch is spun by melt blown method to obtain nonwovens. Melt blown process conditions are as follows: spinning screw temperature 300°C, hot air 200°C, hot air pressure 1.5MPa, nozzle temperature 270°C, extrusion rate of metering pump 2kg/h and receiving distance 30cm. In the final nonwovens, the addition amount of modified Melt blown process conditions are as follows: spinning screw temperature 300°C, hot air 200°C, hot air pressure 1.5MPa, nozzle temperature 270°C, extrusion rate of metering pump 2kg/h and receiving distance 30cm. per 100 phr PP is 0 phr, 5 phr, 10 phr and 15 phr respectively, and the corresponding nonwovens are named 0#, 5#, 10# and 15#.

2.4. Material Characterization
Scanning electron microscopy (SEM) Surface observation of rare earth particles and composite fibers before and after modification was carried out using a Japan Electron JSM-7500F type field emission scanning electron microscope, and the surface gold spraying method was used to prepare the observation samples with a thickness of about 10 nm.
Electron transmission microscopy (TEM) Internal structure of the composite fibers was observed using a Japan Electron JEM-2100F field emission high-resolution transmission electron microscope, and the sections were prepared by the embedding method with a thickness of 50 nm.

Thermal decomposition test (TG) Thermal weight loss test of all samples was performed by Japan Seiko SII-6300 type thermogravimetric analyzer under nitrogen atmosphere, with a temperature rise rate of 20$^\circ$C/min and temperature ranges of 30–600$^\circ$C.

Differential scanning calorimetry (DSC) Differential scanning calorimetry analysis was performed with Seiko SII-6200 differential scanning calorimeter under nitrogen protection and gas flow rate of 50 ml/min. All samples were heated to 220$^\circ$C at room temperature, the scanning rate was 50$^\circ$C/min, and maintained at 220$^\circ$C for 5 min to eliminate the thermal history. The reference material was α-Al$_2$O$_3$. The cooling curve was obtained by cooling from 220$^\circ$C to 30$^\circ$C at a scanning speed of 20$^\circ$C/min; The heating curve was obtained by heating from 30$^\circ$C to 220$^\circ$C at a scanning speed of 10$^\circ$C/min. The melting temperature and enthalpy of the sample were obtained in the second heating curve.

X-ray shielding performance test X-ray shielding performances of these nonwovens were tested with high stability MG324 X-ray machine of Philips, Germany and PTWDCI-8500 precision integral current meter of Austrian Scientific Research Center, radiation protection and nuclear safety medicine institute of Chinese Center for Disease Control and Prevention. The test sample size was 10cm × 10cm × 0.5cm, the voltage was 120kVp, and 2.5mm aluminum filter was adopted. X-ray shielding performance was expressed by lead equivalent.

3. Results and Discussion

3.1. Morphology of dopamine modified La$_2$O$_3$/PP composite nonwovens
SEM photos of different modified La$_2$O$_3$/PP nonwovens are shown in Figure 1. It can be seen from the figure that the fiber diameter distribution of pure PP nonwovens is 2～5 μm, while the fiber diameter distribution of dopamine modified La$_2$O$_3$/PP nonwovens composite nonwovens is 2～10 μm. The addition of modified La$_2$O$_3$ widens the diameter distribution of nonwoven fibers, but the distance between fibers decreases and the number of fibers per unit area increases, indicating that the addition of La$_2$O$_3$ makes the structure of PP nonwovens more compact. Due to the higher viscosity and poor fluidity of La$_2$O$_3$/PP spinning system, the fiber stretching is not enough when it is drawn into fiber by high-speed hot air, resulting in the formation of coarse fibers and uneven diameter distribution in the obtained nonwovens. During the experiment, it can also be observed that the surface of PP melt blown nonwovens containing modified La$_2$O$_3$ is much rougher than that of pure PP melt blown nonwovens.

![Fig.1 SEM images of dopamine modified La$_2$O$_3$/PP nonwovens. (a) 0#; (b) 5#; (c) 10#; (d) 15#](image-url)
Fig. 2 TEM images of dopamine modified La$_2$O$_3$/PP nonwovens. (a) 5#; (b) 10#; (c) 15#

Figure 2 shows the TEM image of dopamine modified La$_2$O$_3$/PP composite nonwovens. It can be seen from the figure that in these nonwovens, the average particle size of modified lanthanum oxide is between 200 ~ 700 nm. With the increase of the content of modified La$_2$O$_3$ in the composite fiber, the particle size distribution of La$_2$O$_3$ becomes larger. The particle size distribution in 15# samples ranges from tens of nanometers to 1 micron, which may be because the increase of filler fraction increases the viscosity of the system and leads to uneven stress during mixing in the screw. However, in general, dopamine modification improves the compatibility between La$_2$O$_3$ and PP matrix, making the overall distribution of particles more uniform. The smaller the particle size of La$_2$O$_3$, the more uniform the distribution, the higher the electron density of absorbing atoms in the composite fiber, the higher the photoelectron absorption efficiency and the better the anti radiation performance. The more uniform the distribution of La$_2$O$_3$, the better the uniformity of shielding performance of the composite fiber.

Fig. 3 TG and DSC diagrams of polypropylene composite nonwoven fabric with 0#, 5#, 10# and 15# of dopamine modified lanthanum oxide addition, respectively

Figure 3 shows the TG and DSC of polypropylene composite nonwoven fabric with 0#, 5#, 10# and 15# of dopamine-modified lanthanum oxide addition, respectively. The thermal degradation temperature of polypropylene with different modified lanthanum oxide additions under nitrogen atmosphere was determined by thermogravimetric analysis (TG). The initial decomposition temperature of PP in meltblown nonwovens is around 410°C. When the temperature reaches 457°C, the decomposition rate of PP reaches the fastest. The heat loss residue of the nonwoven fabric is 0% at this point, indicating that no carbon compounds are present in the residue. The initial decomposition temperatures of the modified La$_2$O$_3$/PP composite nonwoven fabric were 412°C, 413°C and 412°C, respectively, and the heat loss residuals were 4.3%, 6.0% and 9.6%, indicating that the residuals contained modified La$_2$O$_3$. With the addition of dopamine-modified La$_2$O$_3$, the decomposition rate of the modified La$_2$O$_3$/PP composite nonwoven also decreased, and the residual amount of thermal weight loss also gradually increased, indicating that the addition of dopamine-modified La$_2$O$_3$ improved the thermal stability of the modified La$_2$O$_3$/PP composite nonwoven, which may be caused by the increase in molecular weight due to the formation of chemical bonds between dopamine-modified La$_2$O$_3$ and PP.
From the DSC plot, it can be seen that the addition of lanthanum oxide changed the melting peaks of polypropylene to two, and the melting points changed from 163°C to 157°C and 164°C, and two crystalline forms appeared. It may be because the La$_2$O$_3$ modified by dopamine surface combines with PP molecular chains to form a graft copolymer with increased intermolecular spacing. During the formation of PP crystalline nuclei, La$_2$O$_3$ modified by dopamine restricted the movement of polypropylene molecules, resulting in the formation of two crystalline forms. The crystallinity of the composite nonwoven is lower than that of the pure PP nonwoven, probably because the grafting of dopamine onto the PP substrate hinders the formation of PP crystallites.

3.2. Morphology of dopamine modified La$_2$O$_3$/PP composite nonwovens

[Diagram of modified lanthanum oxide/polypropylene composite nonwoven X-ray shielding performance test chart]

The energy of most X-ray particles produced at medical X-ray tube voltages below 130 kVp is usually less than 88 keV [8]. To study the shielding effect of composite fibers, a tube voltage of 120 kVp was chosen for testing. X-rays have a strong penetrating ability and absorb energy only when they interact with the shielding material. The interaction between x-rays and matter depends mainly on the photoelectric effect. The photoelectric effect is the interaction of the incident photons with the internal electrons, which are fixed in number. Therefore, by increasing the density of composite fibers and increasing the number of electrons per volume, the probability of photoelectric effect of composite fiber materials can be effectively increased. Fig. 4 shows the test graph of X-ray shielding performance of dopamine-modified La$_2$O$_3$/PP composite nonwoven fabric. Fig. 4 Test graph of X-ray shielding performance of modified La$_2$O$_3$/PP composite nonwoven fabric. Combined with the TEM diagram, it can be seen that the protection effect of the fiber is positively correlated with the lanthanum oxide addition fraction, and the higher the La$_2$O$_3$ addition fraction, the corresponding increase in lanthanum oxide distribution density, and the better the X-ray shielding performance of the composite nonwoven fabric.

4. Conclusion

In this paper, lanthanum oxide was organically modified with dopamine and filled into polypropylene matrix, and then meltblown method was used to prepare rare earth/polypropylene composite nonwoven fabric. The addition of dopamine-modified lanthanum oxide makes the nonwoven fiber arrangement more dense and improves the thermal stability of the polypropylene nonwoven. Based on the random influence of fiber formation in the meltblown process, the amount of rare earth added to the nonwoven fabric was limited, and the limit of rare earth mass addition was 15 parts, but the higher the lanthanum oxide addition, the better the X-ray shielding performance of the composite nonwoven fabric. The
interfacial compatibility of La$_2$O$_3$ modified with dopamine and PP matrix was significantly improved, and the X-ray shielding performance became significantly stronger with the addition of La$_2$O$_3$, which provides a reference for the subsequent research and industrial application of La$_2$O$_3$/polypropylene composite fibers.

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