Negative Air Ion Release and Far Infrared Emission Properties of Polyethylene terephthalate/Germanium Composite Fiber

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ABSTRACT

PET/germanium composite fibers that with negative air ion release and far infrared emission properties were prepared by adding germanium particles to polyethylene terephthalate (PET) and melt-spinning. The morphology, effect of the germanium content on the negative air ion release, far infrared emission, thermal and mechanical properties of the fibers were investigated. The germanium particles uniformly disperse in the PET fibers when the concentration ranged from 1% to 3 percent. The value of the negative air ions released by the PET/germanium composite fibers increased with increasing content of germanium and reached 1470 ions/cm^{-3} at 3% germanium concentration. The highest far infrared normal emissivity (0.9) was obtained at 3% germanium concentration. The TG and DSC analysis revealed that the two heat histories used had little effect on the PET. The crystallinity of the composite fibers decreased with increasing germanium content. Water fastness testing showed that the PET/germanium composite fibers had excellent and durable negative air ion release and far infrared emission properties. The breaking strength of the fibers decreased with increasing of the germanium content.

INTRODUCTION

With the development of functional textile materials which offer enhancement of health, there is an increasing demand for textiles with even greater benefits to body health. Release of negative air ions, which offer known benefits of air purification, antibacterial deodorization and benefit for healthy, has become an important criteria for determining health benefits of textile product. [1-4]. Additionally, far infrared radiation is regarded as an indispensable characteristic of healthy materials. Use of “healthy fibers” to manufacture functional textiles that possess negative air ion release and far infrared emission properties has become a significant research direction in the field of functional materials.

Tourmaline is widely used in applications such as healthy fibrous products [5-6], far infrared radiation [7-8] and water purification [9-10] because of its negative air ion release and far infrared emission properties. However, as a rare natural silicate mineral, tourmaline is a nonrenewable resource, and the volume in present in the earth is too low to satisfy industry demand, leading to shortages. Tourmaline is a complex natural borosilicate mineral whose general chemical formula is expressed as $XY_3Z_6Si_6O_{18}(BO_3)_3W_4$, where X is Na^+, Ca^{2+}, K^+, or vacancy; Y is Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, Mn^{3+}, Cr^{3+}, Ti^{4+}, or Li^+; Z is Al^{3+}, V^{3+}, Cr^{3+}, or Mg^{2+}; and W is OH^-, F^- or O^{2-}[11]. Therefore, it is difficult to obtain quantities of high purity tourmaline. Consequently, the search for an alternate material with similar desirable properties is on-going.

Germanium is a semi-metallic element, with 4 unbalanced electrons moving irregularly around the nuclei. When exposed to temperatures above 32°C or changes in atmospheric pressure, one of the irregular electrons escapes from its orbit and produces a negative electron, which ionizes the surrounding air, resulting in negative air ions [12]. As a consequence of the thermoelectricity and piezoelectricity characteristics explained above and the fact that the human body temperature is 36.5°C, and the fact that garment pressures generated by human limbs are continually changing, germanium particles can be used to generate negative air ions if they were used as a functional additive and doped into the spinning solution and spun into healthy fibers and textiles. In addition, the far infrared radiation (4-14um) emitted by germanium particles could benefit for body by promoting blood circulation and improving metabolism. It is reasonable to assume that

germanium composite fibers and fibrous products could have a wide range of applications as healthy garment and textile products such as underwear, bed sheets, home-furnishing textiles and interior textiles for vehicles.

In this research, PET/germanium composite fibers were prepared by melt spinning by adding various levels of germanium particles into the PET spinning solution with the aid of a dispersant. The morphology, effects of content of germanium particles in the PET fibers on the negative air ion release, far infrared emission and mechanical properties of the fibers were investigated.

EXPERIMENTAL DETAILS

Materials

The Germanium powder (purity of 99.99%) was supplied by Jin Quankuang Minerals co., Ltd (Shi Jiazhuang, China); The Polyethylene terephthalate (PET) chips were purchased from Wuxi Taiji Industry Co., Ltd. (Wuxi, China); The soft detergents were purchased from Sinopharm Chemical Reagent Co., Ltd China and the functional additive was prepared by our research team.

Preparation of the PET/Germanium Fiber

The PET/germanium composite fibers were prepared by melt spinning. The preparation process was divided into two parts. First, the PET chips were dried in an oven at 110°C for 24 h, and then mixed with germanium powder and special dispersants in a high-speed mixer. The mixtures were then extruded in a twin-screw master batch mixer at 270°C to obtain a master-batch. Second, the required ratios of PET chips and master-batch were blended, dried at 110°C, fed to the melt spinning machine and spun at 270°C into the PET/ germanium composite fibers. In this study, 4 different PET/germanium composite fibers were prepared. The add ratio of each component is listed in *Table I*. A schematic of the melt spinning process is presented in *Figure 1*. All PET/germanium fibers were spun to linear densities of 150Denier/36filaments.

TABLE I. Compositions of the PET/ germanium fiber.

Samples	Germanium particles content (Wt %)	PET chips (Wt %)
a	0	100
b	1	99
c	2	98
d	3	97

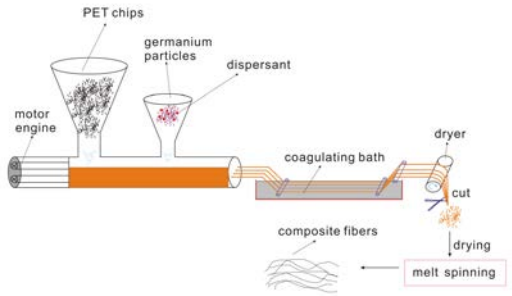

FIGURE 1. The preparation process of the PET/germanium composite fiber.

Morphology Analysis

The surfaces and cross sectional morphologies of the fibers were inspected using a scanning electron microscope (SEM, SU1510, Hitachi, Japan).

Thermal analysis (TGA/DSC)

Thermogravimetric analysis (TGA) of the PET/germanium composite fibers was carried out using a TGA-Q500 thermogravimetric analyzer (TA, U.S.A) which allows the simultaneous detection of mass changes and heat effects during the decomposition of the samples. The samples were ramped from 30°C to 600°C at a heating rate of 10°C /min under nitrogen atmosphere.

Thermal analysis of the PET/germanium composite fibers was carried out using TA-Q200 Differential scanning calorimeter (DSC). The Samples were heated to 400°C at 10°C/min to insure complete melting and then cooled to room temperature. to obtain a crystallization curve for each sample.

Negative Air Ion Test

The negative air ion release properties were measured by an AIC-2 negative air ion tester (ALP, U.S.A). A diagram of the testing device is shown in *Figure 2*. Samples were tested according to the Import and Export Functional Textiles of China (SN/T 2558.2-2011).

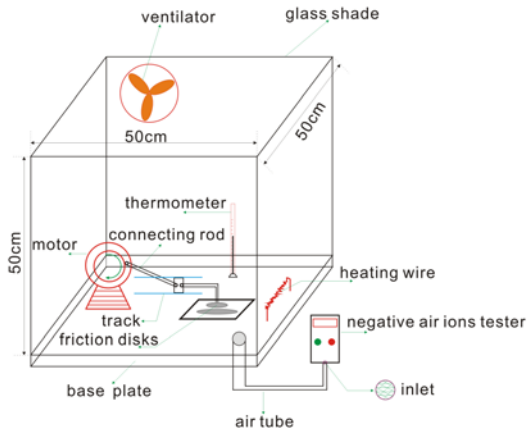

FIGURE 2. The testing device for negative air ions.

The composite fiber specimens used for negative air ions analysis were converted to films with thicknesses of roughly 0.1cm by hot-pressing at 180°C for 5 mins. The hot-pressed film specimens were then cut to dimensions of 10×10×0.1cm for testing. Before the negative air ion test, the fiber film specimens were fitted on the friction disk (*Figure 2*) and kept in the glass shade box for 24 h, during which the temperature and relative humidity were kept at 25°C and 60 percent, respectively. The values of negative air ions (V_{ion}-) released by the composite fiber film specimens were then calculated at temperatures ranging from 25°C to 80°C. The V_{ion}-determined in the first minute were used as the average value of negative air ions released by the PET/germanium composite fiber film specimens.

Far Infrared Emission Test

The far infrared emissivity (broadband between 4um and 14um) of the samples was tested using a TSS-5X far infrared radiant emissivity tester (Beijing Hua Rui technology development co., Ltd, China), according to the testing standard of Healthy Functional Textiles of China (ACS 115-2005).

Water-Fastness Test

In order to study the effect of the water washing on the durability of the negative air ion release and far infrared emission properties of the PET/ germanium composite fibers, wash fastness tests were conducted. The PET/germanium composite fiber film specimens were placed in an automatic sink and washed at 30°C with soft detergent for 50 times, 5 minutes per wash.

Mechanical Testing

The break strength (cN/dT) and break elongation of the PET/ germanium composite fibers were recorded by a YG001B Electronic Single Fiber Strength Tester from Changzhou Jinsong Textile Instrument Co., Ltd, China. The pre-tension on the fiber was 0.75 cN, the test speed was 20 mm/min and the gauge length was 30 m. Twenty individual tests were performed and averages calculated for each composite fiber type. The specific test standard used is the tensile property test of chemical staple fibers of China (GB/T 14337-2008).

RESULTS AND DISCUSSION

Morphology

Figure 3 shows the SEM image of the germanium powder and the composite fibers. From *Figure 3(a)*, the average size of the germanium powders is approximately 0.1 um and there is slight agglomeration between them. From *Figure 3(b)*, *Figure 3(c)* and *Figure 3(d)*, the surface of the fiber became increasingly rough with an increase of germanium content, especially when the germanium content reached 3% percent. From *Figure 3(d)* many germanium particles are embedded on the surface of the composite fiber.

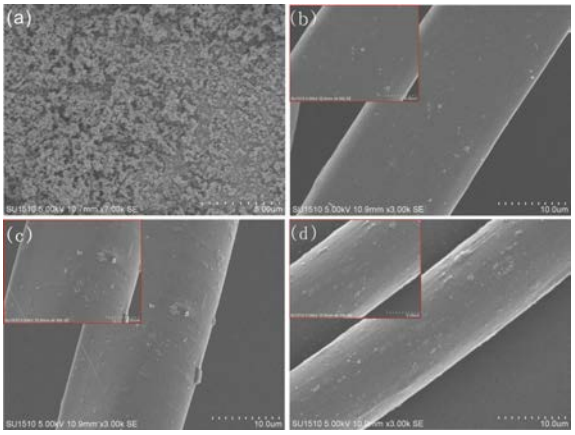

FIGURE 3. SEM images of the germanium particles and PET/germanium composite fibers with various germanium particle contents, (a) germanium particles, (b) 1%, (c) 2%, (d) 3%.

The cross sections of the PET/germanium composite fibers are shown in *Figure 4*. Unlike the smooth surface of the cross section of the pure PET fiber in *Figure 4(a)*, the cross sections of the PET/germanium composite fibers in *Figure 4(b), (c), (d)* are rougher. It is clear that the functional additive caused the germanium particles to disperse well within the interiors of the composite fibers at all concentrations, as there is no evidence of severe agglomeration.

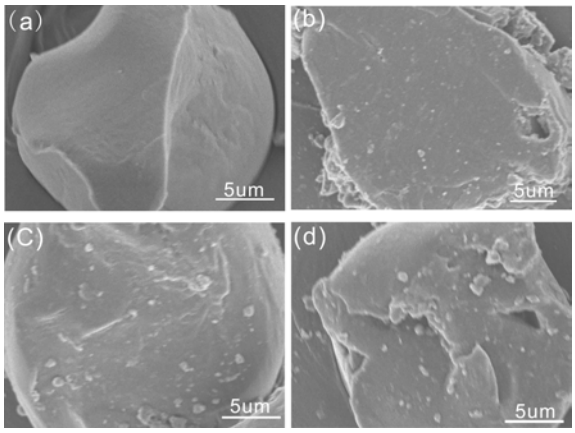

FIGURE 4. SEM images of the cross section of the PET/germanium composite fibers with various germanium particles content, (a) 0%, (b) 1%, (c) 2%, (d) 3%.

Thermal Properties

The thermal stability of the PET/germanium fibers were evaluated by TGA, and the results are shown in *Figure 5*. The weight loss of the composite fibers decreased from 91.25% to 77.46% as the level of germanium particle in the PET fibers increased from 0 to 3 percent. There is only one step in the decomposition for the PET/germanium fibers. Weight loss began at 350°C and was completed by 450°C. As previously mentioned, the preparation temperature of the functional spinning master-batches and the spinning temperature were 270°C. From *Figure 5*, the double thermal exposure at 270°C had little effect on the PET.

DSC curves of the PET/germanium composite fibers and the values of crystallization temperatures (T_c), crystallization enthalpies (ΔH_c) and crystallinity (θ) of the composite fibers are shown in *Figure 6* and *Table II*, respectively. The value of T_c and θ for decreased with increasing content of the germanium particles, whereas ΔH_c increased gradually. This might be due to the retardation of crystallization of the composite fibers. In the melt spinning and process, the mobility of PET molecules was substantially limited by the germanium particles, thus the PET molecules could not form well-defined structures in the composite fibers, leading to the reduced crystallinity of PET in the composite fibers and the decreased values of enthalpies.

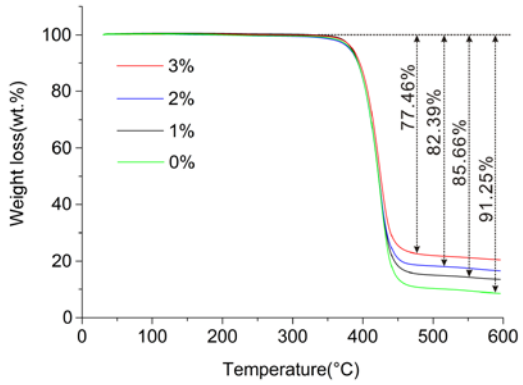

FIGURE 5. TG curves of the PET/germanium composite fibers with various germanium particles content.

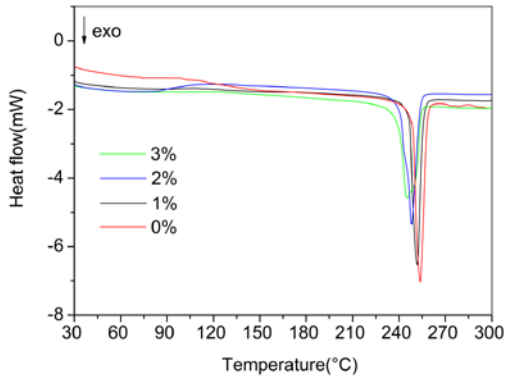

FIGURE 6. DSC curves of the PET/germanium composite fibers with various germanium particles content.

TABLE II. The crystallization temperatures (T_c), crystallization enthalpies (ΔH_c) and crystallinity (θ) of the PET/germanium composite fibers.

Sample	T_c (°C)	ΔH_c (J/g)	θ (%)
0%	254.13	52.83	37.71
1%	252.41	51.03	36.43
2%	248.75	48.92	34.92
3%	244.86	45.97	32.81

Negative Air Ion Release Properties

Figure 7 illustrates the value of negative air ions (V_{ion}-) released by the composite fiber film specimens (black line) and the V_{ion}- released by the same fiber film specimens after being washed 50 times (red line), respectively. As the black line in *Figure 7(a)* shows, the value of negative air ions obtained by testing the pure PET fiber specimen in dynamic mode under constant frictional force and pressure at 25°C was 80 ions/cm^{-3}. As the germanium content increases, the amount of negative air ions released increases rapidly and is proportional to the add level of germanium powder. The value of the negative air ions approached 1930 ions/cm^{-3} at 3% germanium. This suggests that textiles or clothing made from the PET/germanium fibers could have comfort and health benefits.

In order to investigate the effect of temperature on the negative air ion release properties of the germanium composite fiber films, samples containing 2% germanium were tested temperatures of 5°C increments from 25°C to 80°C in static mode. The obtained values of V_{ion}- are represented by the black line in *Figure 7(b)*. It is evident that the release value of negative air ions increases with increasing of temperature. Further, the value began to increase significantly when the temperature surpassed 35°C. This is likely due to the thermoelectric properties of the germanium. It is well known that germanium is a semi-conductive element and one of the irregularly moving can break away from its original orbit when the temperature exceeds 32°C, and produce an electron, resulting in ionization of the surrounding air [12]. Once the temperature reached 70°C, amount of the negative air ions released approached 580 ions/cm^{-3}. Increasing the temperature above 70°C resulted in no further increase in ion release.

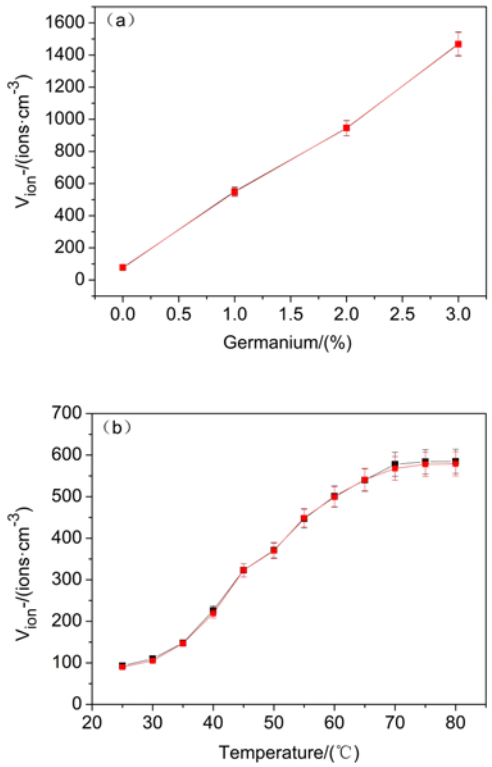

FIGURE 7. The average values of the negative air ions released by the PET/germanium composite fibers tested under different conditions (black line: PET/germanium composite fibers; red line: after being washed 50 times).

It is notable that when tested at 25°C using the dynamic friction impact mode, the V_{ion}- of film specimen pressed from fibers containing 2% germanium reached 944 ions/cm^{-3} whereas the V_{ion}- of the same specimen tested using the static mode was only 585 ions/cm^{-3} when tested at 80°C. This says that the piezoelectric properties of the germanium have a stronger influence on the release of negative ions than the thermoelectric properties when added to PET.

From *Figure 7(a)* and *Figure 7 (b)*, the negative ion release properties of the PET/germanium blends decreased only slightly after 50 washings. possessed an excellent and durable negative air ions releasing property, which mean that water washing had little effect on the negative air ions releasing property of PET/germanium composite fibers.

Far Infrared Emission Properties

Figure 8 illustrates the far infrared normal emissivity of the PET/germanium composite fibers before being washed (black line) and after being washed 50 times (red line). The data indicates that the far infrared emission emissivity of the PET/germanium composite fiber significantly increased over that of the PET fiber. The normal emissivities of all the PET/germanium composite fibers are greater than 0.8, which satisfies the minimum requirement for far infrared emission textiles. The data indicates that this requirement is satisfied even at 1% germanium add; however, there is little change in emissivity at higher add levels.

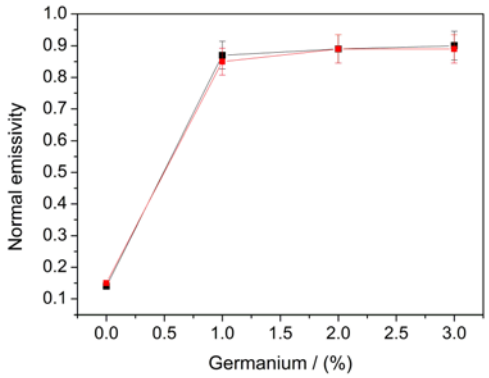

FIGURE 8. Curves of the far infrared emissivity of PET/germanium composite fibers as a function of germanium particles content; (black line: PET/germanium composite fibers; red line: after being washed 50 times).

The red line in *Figure 8* shows the far infrared normal emissivity obtained after the PET/germanium composite fibers were washed 50 times. The fact that there is little change in emissivity after 50 washings indicates a high degree of durability. Thus, the PET/germanium composite fibers or fibrous products would be suitable for many applications including health friendly underwear, bed sheets, home furnishing textiles and vehicle interiors.

Mechanical Properties

Mechanical properties of the PET/germanium composite fibers are plotted in *Figure 9.* As can be seen from the data, the germanium particles had negative effects breaking strength and elongation at break; both properties decreased with increasing concentration of germanium particles in the composite fibers. Compared to the breaking strength of the pure PET fiber, the value decreased about 50% when the germanium particles reached 3% concentration, and the elongation at break was reduced by 7.6 percent. There are two reasons for the decrease in breaking strength. First, the thermal data showed that crystallization was hindered by the germanium particles, leading to lower breaking strength. Second, the photographs showed agglomeration of the germanium particles within the fibers, leading to a lot of small pores and flaws in the interior of the fibers. Therefore, the fibers broke more easily when stretched. Additionally, the germanium particles tend to make the fibers more brittle, leading to the decreased elongation at break.

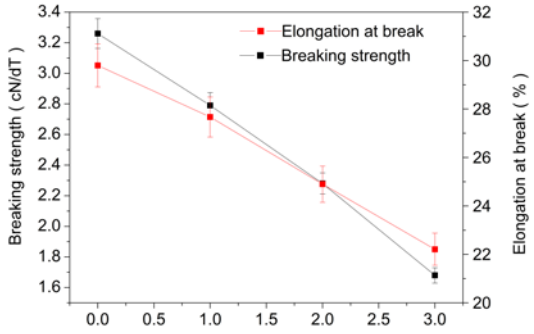

FIGURE 9 The breaking strength and elongation at break of the PET/germanium composite fibers.

CONCLUSION

In this paper, PET/germanium composite fibers were successfully prepared by melt spinning through the use of a special dispersant. The value of the negative air ions released by the PET/germanium composite fiber increased with increasing content of germanium particles and testing temperature. The maximum value obtained 1470 ions/cm^{-3} at 3% germanium content. The PET/germanium composite fibers also showed good far infrared emission properties, reaching levels as high as 0.9. The negative air ion release and emissivity of the fibers were nearly

unchanged after 50 washes, indicating a high degree of durability. The germanium particles contained in the fiber had negative effects on breaking strength and elongation at break. Breaking strength of the composite fiber decreased about 50% when the germanium concentration reached 3 percent.

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