Available online at www.sciencedirect.com
ScienceDirect
JOURNAL OF RARE EARTHS
JOURNAL OF RARE EARTHS, Vol. 32, No. 12, Dec. 2014, P. 1196
www.re-journal.com/en/

Researches on preparation and properties of polypropylene nonwovens containing rare earth luminous materials

YU Yuan (余 媛), WANG Jian (王 建), ZHU Yanan (朱亚楠), GE Mingqiao (葛明桥)*

(Key Laboratory of Eco-Textile of Ministry of Education, College of Textiles and Clothing, Jiangnan University, Wuxi 214122, China)

Received 4 March 2014; revised 24 August 2014

Abstract: Polypropylene composite nonwovens containing rare-earth strontium aluminates $SrAl_2O_4:Eu^{2+},Dy^{3+}$ and functional additives were fabricated by the spun-bonded technique. The optical properties, morphology and mechanical properties of the samples were characterized. Results from scanning electron microscopy photographs (SEM) indicated that the surface of the fiber was destroyed by the addition of rare earth luminescent materials lightly but the thickness of the fiber was uniform. Differential scanning calorimetry results showed that pure polypropylene has the double crystallization peak at 162.3 and 165.1 °C. Studies from X-ray diffraction showed that the nonwoven prepared with the luminescent materials contained the α-monoclinic crystal and β crystalline phase. Furthermore, the afterglow properties were tested, which showed that the afterglow curve of the luminous nonwoven was similar to that of strontium aluminate, and the intensity was more intensive than luminous nonwoven at the beginning. The nonwoven fabricated with the luminescent material did not affect the crystal lattice of the polymer making the materials have potential applications in fluorescent lamps and field emission displays (FEDs).

Keywords: luminescent material; spun-bonded technique; nonwoven; characteristics; rare earths

Nonwoven fabrics are manufactured by a series of disordered fibers and consolidated by simple entanglement, local thermal fusion, chemical binders, etc.[1] They are widely used in many engineering applications such as ballistic protection, thermal insulation, liquid-absorbing textiles, fireproof layers due to the lower processing costs and improved properties[2,3]. Luminous spun-bonded nonwoven is a new type of functional material using the polyester, polypropylene, polyamide as basic material, including rare earth luminescent materials and non-functional additions. Polypropylene are widely applied in various fields. This can be attributed to a series of advantages, good processability, almost zero water adsorption, good chemical resistance as well as wide availability and low cost[4–6]. The luminous spun-bonded nonwoven made of rare-earth strontium aluminates as the rare-earth luminescent material, and fiber-forming polymer as the main raw materials. Rare-earth strontium aluminates are a non-toxic, harmless material with non-radioactive, and absorb visible or ultraviolet light within a few minutes, then can give off light continually for more than 10 h in the environment of darkness and emission wavelength is mainly in the range of 440 to 520 nm.

The luminous spun-bonded nonwoven has a wide range of applications such as house decoration, traffic warning sign, mine, life and recreational. If adding color master batch, the nonwoven will have different color in the bright environment.

As a result of the wide use of polypropylene nonwovens and continuous development of the rare earth luminescent materials[7,8], it is valuable and urgent to manufacture a kind of luminous nonwoven. Then, until now, this research is very a lack. The theoretical basis and test data are not comprehensive, so it is necessary for us to study the new material. In this research, luminous nonwoven was prepared by using rare-earth strontium aluminates and polypropylene as the matrix. The morphology, mechanical properties and optical properties of the luminous spun-bonded nonwoven and the technological parameters were elementarily studied, providing a basis to drive the luminous nonwoven going a step further to develop.

1 Experimental

1.1 Materials

Fiber-forming polypropylene granulate (produced by Shanghai Petrochemical Co., Ltd., type M800E, MFR=8 g 10 min^{-1}) was used to produce nonwoven samples according to the spun-bonded technique. Rare earth luminescent materials were procured by solid-state reaction. $SrCO_3$ (99.5%), Al_2O_3 (GR), Eu_2O_3 (99.99%), Dy_2O_3 (99.9%) and H_3BO_3 (AR) were dispersed by ultra-sonic

Foundation item: Project supported by National High-Tech R&D Program of China (863 Program, 2012AA030313)

* **Corresponding author:** GE Mingqiao (**E-mail:** ge_mingqiao@126.com; **Tel.:** +86-510-85912329)

DOI: 10.1016/S1002-0721(14)60203-9

dispersion for 15 min in a molar ratio of 1:2:0.01:0.02:0.2. Subsequently, the raw materials were ground in a planetary high-energy ball mill and annealed at 1300 °C for 4 h in a weakly reducing atmosphere (10%H_2 and 90%N_2), then the products were smashed and sieved to get the luminescent materials, $SrAl_2O_4$:Eu^{2+},Dy^{3+}.

The structure of luminous spun-bonded nonwoven was modified by the addition of 10 wt.% of rare earth luminescent materials. These functional materials are characterized by appropriately high thermal resistance, so they could be applied in spun-bonded process of polypropylene treatment.

1.2 Sample preparation

Luminous polypropylene spun-bonded nonwoven was obtained using the spun-bonded technique, which is an integrated nonwoven technology consisting in linking fiber-forming process with a web-forming process. The strings of molten polymer come out from the extruder head through the multi-hole nozzle where they are blown up by a stream of compressed air and set as fine fibers on a collecting drum (Fig. 1). It is possible to produce monofilaments of different thicknesses through adjusting the process parameters.

1.3 Characterization

The luminous spun-bonded nonwoven surface was determined using a SEM scanning electron microscope (HITACHI SU-1510, Japan). The excitation and emission spectra of luminous nonwoven were obtained at room temperature using a fluorescence spectrophotometer (HITACHI 650-60, Japan) with an emission wavelength of 520 nm and the excitation wavelength was 365 nm. The mechanics' properties of luminous nonwoven were examined and compared with untreated PP nonwoven using a YG026D type multifunctional electronic fabric strength tester at 20 ºC and 65% RH. The afterglow characteristics of the samples were assessed using a PR-305 long afterglow phosphors tester. And the samples were exposed at an illumination intensity of 1000 lx for 15 min, and then the afterglow intensity was measured 10 s later. The phase composition of the luminous spun-bonded nonwoven and the luminescent materials were measured by X-ray diffraction (D8 Advance X-ray diffractormeter, Bruker AXS, Germany) by Cu Kα radiation at a voltage of 40 kV, and current of 30 mA. The range of diffraction angle 2θ is from 3° to 90° and the scan speed is 4 (°)/min at room temperature. DSC measurements were performed using DSC Q200 instruments (Waters, USA) under a flow of nitrogen at a rate of 50 mL/min to avoid oxidation. The samples of about 5 mg were weighed into the crucible and cover was hermetically sealed using the pierced lid. The samples undergone first heating up from 25 to 300 °C at 10 ºC/min, and each sample was heated to the melt at 200 ºC for 3 min to remove any prior thermal history. Subsequently, they were cooled down to 25 ºC with a scan rate of 10 ºC/min.

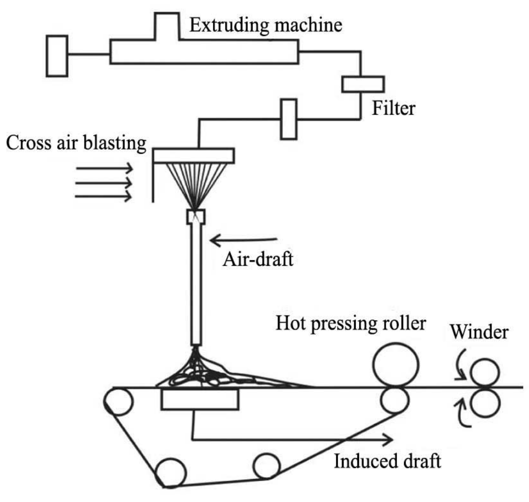

Fig. 1 Luminous polypropylene nonwoven according to the spun-bonded

2 Results and discussion

2.1 SEM analysis

The surface morphologies of $SrAl_2O_4$:Eu^{2+},Dy^{3+} and luminous nonwoven have been observed by SEM. Luminous nonwovens were prepared using a two-step method—at the beginning granulate of polypropylene and rare earth luminescent materials was obtained, and then it was processed by the spun-bonded technique.

The figure shows that the fiber thickness is relatively uniform, and the fiber surface is comparatively smooth, which indicates the addition of rare earth luminescent materials has a little effect on the longitudinal structure of luminous spun-bonded fiber; in other words, luminescent materials inside the fiber were dispersed more evenly. We consider that luminescent materials can be basically dispersed in polypropylene resin at the state of primary particles. Adding luminescent materials in PP will not affect the PP plasticizing and processing performance[9]. But on the surface of the fibers, they were less evenly distributed, and this could affect their luminosity. Obviously, agglomeration of luminescent materials does not affect the formation of nonwoven, and its degree of uniformity is the main factor influencing the brightness of fiber.

2.2 Afterglow intensity profile

The afterglow intensity of luminous nonwoven with different contents of $SrAl_2O_4$:Eu^{2+}, Dy^{3+} and $SrAl_2O_4$:Eu^{2+},Dy^{3+} is shown in Fig. 3. The afterglow properties of luminous nonwoven are dependent on the luminous materials in the nonwoven. We can see that although the contents of $SrAl_2O_4$:Eu^{2+},Dy^{3+} in the nonwoven were