Research of Anion Polyester Base Functional Materials

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Abstract—This paper use plum-blossom tourmaline as anion additive, filled to PET recycling material as modifying agents. Successfully prepared a composite material can release anions. The effect of different percent composition on heat distortion temperature and anion releasing performance of polyester recycled materials were studied, plum-blossom tourmaline powder and fracture surface of polyester/ plum-blossom tourmaline were observed by Transmission electron microscopy (TEM) and Scanning electron microscope (SEM). The result showed plumblossom tourmaline powder particulate could easily gather together and formed roughly 0.6 µm particle cluster, tourmaline evenly dispersed in polyester matrix and had good interface combined performance, the addition of tourmaline improved polyester's heat distortion temperature and anion releasing ability. With the increased of plumblossom tourmaline, the release anions contents also increases. When the content reached 8%, anion average releasing quantity achieved 1458 ions/cm³ and it reached WHO's required standard. It can improve people's living environment and conducive to resource recycling, it is an economical and environmentally friendly way to reduce environmental pollution.

Keywords--plum-blossom tourmaline; polyester recycled materials; blending modification; softening point; anion

I. INTRODUCTION

Polyester is the short name of polyethylene terephthalate glycol (PET), propylene glycol, butylene terephthalate, is a kind of excellent performance engineering thermoplastics and developed in the 1950s. Polyester is characterized by high heat distortion temperature and low hygroscopicity; it can maintain excellent electrical properties in humid or high temperature environment, even in hot water. Polyester has good process ability, low friction coefficient and low wear and tear^[1-3].

Plum-blossom tourmaline is an aqueous silicate mineral crystals made of Si, Al, Fe, Na, Ca and Ti elements. It is a kind of tourmaline group minerals, a natural electrical polarity. Surface electric field strength can up to 103V/cm³ and capable of ionization of water molecules; it has strong radiation within $4 \sim 14 \ \mu m$ far infrared, can activate the water molecules, produce reactive oxygen species. It also has electromagnetic shielding, release anions, cleaning up the environment and other functions, those functions are conducive to human health ^[4-6]. By using coarse crushing, airflow superfine pulverizing and wet grinding process, plum-blossom tourmaline processed into functional modifying agents, and applied into engineering plastics, will solve the increasingly serious environmental problems opens a new wav

With the rapid development of industrialization, the demand for polyester is growing rapidly, along with increasing the amount of scrap recycling of polyester. How to re-use and develop polyester recycled materials, namely, filling, blending, enhancing the modification, become an issue of concern. Based on the above objects, this paper study was about polyester scrap blend modifying to response the latest national call of "low carbon", "energy conservation "and " environmental protection ".

II. METHODS

A. Materials and Instruments

Main materials: Polyester recycling materials is provided by a fan factory in Wuxi. Plum-blossom tourmaline was supplied by Yanshan New Materials Design and Research Institute; Silane coupling agent, KH-570, Nanjing DAONING Chemical Co.

Main instruments: Drying oven, 101-1AB, Tianjin Taisite Instrument Co.; High-resolution transmission electron microscope, JEM-2010, Japanese electronics optics company; Mixer, ML-3L, Nantong mechanical mixer company; Vulcanizing machine: XLB-350×350×2, Yingkou new experimental mechanical company; Cold field emission electron microscope (FE-SEM), S-4800, Hitachi; Heat distortion temperature tester, SWB-300A/B ,SHANGHAI S.R.D. scientific instrument CO.,LTD; air anion measuring instrument, DLY-6A232, Zhangzhou, Fujian Lianteng CO.,LTD.

B. Plum-blossom tourmaline Pretreatment

The plum-blossom tourmaline were dried by Drying oven at 105°C and drying 2h to remove the water adsorbed on the surface, then the dried tourmaline added to solution of silane coupling agent with surfactant, ultrasonic treatment 1h after the reaction to end, standing, suction, placed into drying oven at 105°C and drying 2h, allowed to cool down to room temperature until ready to use after grinding.

C. Sample Preparation

Weigh 500g polyester recycling materials, add pretreatment good 0%, 2%, 4%, 6%, 8% (mass fraction) of plum-blossom tourmaline respectively; then mix in the mixer at 220 °C, the material to be removed after mixing evenly, when the material is cooled, vulcanized at 10 MPa, 220°C under the conditions for hot 10 min, remove the mold cooling at room temperature for 15 min. Finally, the cut to 10mm \times 10mm \times 3mm, 15cm \times 10cm \times 3mm samples to make Vicat softening temperature and anion release test.

D. Performance Test

The plum-blossom tourmaline samples were made at normal temperature and conventional pressure, using a JEM-2010 transmission high-resolution electron microscope to observe the internal structure; The tourmaline-modified polyester recycling materials section do spraying process, the cross-section microstructure was observed by FE-SEM; Use heat distortion temperature detector test specimens Vicat softening temperature, at the heating rate of 12° C · 6min⁻¹ and the weight load of 877 g, the sample should be dried in an oven at 100°C for 2h before testing; Using DLY-6A232-type air ion measuring instrument test tourmaline modified polyester recycled materials anion release capability, the composites was first placed in the test chamber to balance with atmosphere equilibrated for 12 h, at a temperature of 21 ± 2 °C, the relative humidity of $65\% \pm 2\%$ and a pressure of 130 ± 5 kPa, the test time was 3min.

III. RESULTS AND DISCUSSION

A. SEM, TEM Analysis of Plum-blossom Tourmaline

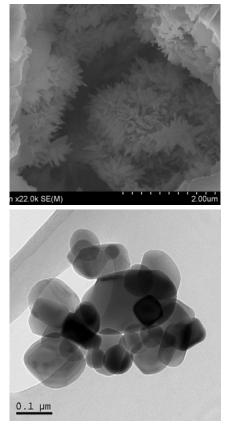


Figure 1. SEM and TEM figure of plum-blossom tourmaline

Fig.1 is a transmission electron microscope figure of plum-blossom tourmaline, the picture shows there are small particles whose size is from tens to hundreds of nanometers in plum-blossom tourmaline, the particles are generally smooth and most of them are cobblestone shape, because the Nano-size effect, these particles agglomerates together to form particle clusters around 0.6 μ m.

B. FE-SEM Analysis of Composite Section

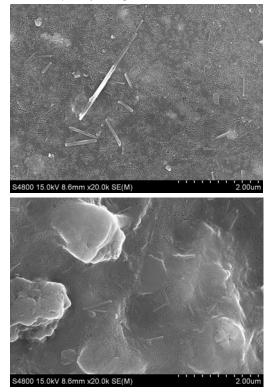


Figure 2. SEM figure of polyester section modified by plum-blossom tourmaline (×20 000 times)

Fig .2 is a scanning electron micrograph of polyester recycled materials modified by plum-blossom tourmaline. The surface treatment and blending processes of plumblossom tourmaline particles directly affect them dispersion in the polyester. Comparing a and b of Fig.2, we can clearly observed that plum-blossom tourmaline particles are uniformly dispersed the polyester matrix and having a particle size of roughly 0.7 μ m, the particles morphology is similar spherical, and we can clearly observe that the contact effect of plum-blossom tourmaline particles treated by surface treatment and matrix interface is good, at the same time we can see some materials likes needle inside dispersed in the matrix, this should be glass fiber added in the matrix during the production process.

C. Vicat Softening Temperature Test

Heat resistance is a basis to measure the maximum temperature of a material. For the same materials, the higher the softening temperature, the better the heat resistance of materials. In order to study the effects of different content of plum-blossom tournaline on polyester heat resistance, this experiment use SWB-300A/B Vicat softening point and load heat distortion temperature tester to study the heat resistance of the samples with different amounts of plum-blossom tournaline.

TABLE I.
VICAT
SOFTENING
TEMPERATURE
OF
DIFFERENT

CONTENT OF PLUM-BLOSSOM TOURMALINE
VICAT
SOFTENING
VICAT
VI

content	0%	2%	4%	6%	8%
VST/°C	212.2	213.5	214.2	215.7	215.0

The effects of different plum-blossom tourmaline content on the heat resistance of the samples are shown in Tab.1, the softening temperature of the sample not added plum-blossom tourmaline is 212.2 °C, with the increase of the content of plum-blossom tourmaline, the Vicat softening point temperature of the sample is gradually rising, in an amount of 6%, it reaches to the relative highest point 215.7 °C. From the entire Vicat softening temperature trends, the effects of adding plum-blossom tourmaline on Vicat softening point of the sample is relatively small, but to varying degrees, have increased the Vicat softening temperature of the sample.

D. Test of Anions Release Concentration

Anion is a gas ion with negative charge in the air, colorless and tasteless. Scientific experiments show that the number of anions in the air has a great impact on human health. World Health Organization provides fresh air anions content do not less than 1000 ions/cm³. In general, people need about 13 billion anion every day, and our living room, office and entertainment venues often to not meet this requirement, especially in the doors and windows closed in the cold season^[6-9].

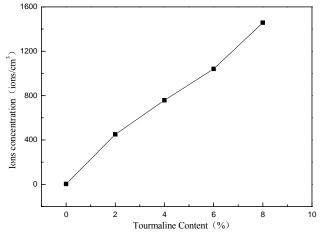


Figure 3. The average anions release concentration of different content of tourmaline modified polyester

In this paper, tourmaline modified polyester recycling materials to test the ability to release anions; the result is shown in Figure 3, tourmaline content was 0%, 2%, 4%, 6%, 8% of the test respectively. The average concentration of anions was 3 ions/cm³, 451 ions/cm³ 758 ions/cm³; 1040ions/cm³; 1458 ions/cm³ respectively. With the tourmaline content gradual increase, the average anions releases of samples have increase, the average release content reached 1458 ions/cm³, reached the level of city park^[10-12], it has played a positive role in protecting the environment.

IV. CONCLUSIONS

(1) The plum-blossom tourmaline is composed of tens to hundreds of nanometers particles, the particles are generally round, shapes, most of them like cobblestone, easy to join together to form particles clusters around 0.6µm.

(2) SEM figure shows tourmaline were successfully dispersed in polyester matrix, have good contact with the

polyester. The particle size is about $0.7\mu m$; do not affect the appearance of the production.

(3) With the tourmaline content gradual increase, the Vicat softening of the sample is also a small increase. When the content was 6%, the temperature reached a relative maximum. Overall, the adding of tourmaline have no significant impact in machining to molded specimen, but have increasing in softening point temperature.

(4) With the tourmaline content gradual increase, the average anions releases of samples have substantial increase. When the content was 8%, the average anions releases level reach 1458/cm³, can meet the needs of daily life.

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REFERENCES

- Xiaomei Yang. Research of PBT recycling material filling, blending and modification [J]. Plastic development, 1995, 21(4): 400-401. (references)
- [2] Sandro D M, Jonas A S, Alex R N, et al. Additional steps in mechanical recycling of PET[J]. Journal of Cleaner Production,2010, (18):92-100.
- [3] Dingshan Yao. The environmental and health materials-Tourmaline [M]. China Textile University Press, 2001.

- [4] azuaki T, Takemi O, Akinori M, et al. Negatively-charged air conditions and responses of the human psycho-neuro-endocrinoimmune network[J]. Environment International, 2008, (34): 765-772.
- [5] Qingshan Li, Jun Liu. Beidaihe standards of air anions concentration determination and evaluation of anions [J]. Chinese journal of environmental management cadre institute, 2008, 18(4):1-3.
- [6] L.Liu,J.Guo,J.Li. The Efect of Wire Heating and Conguration on Ozone Emission in a Negative Ion Generator[J].Electrostatics,2000,(48):81-91.
- [7] Watanabe,H.Noro,Y.Ohtsuka. Physical Effects of Negative Air Ion in a Wet Sauna[J]. International Journal of Biometeorology,1997,(40):107-112.
- [8] Wei Hong , QingShan Li , GuoQuan Guan, etc. Pavement performance and application of anion rubber-modified asphalt [J]. Chinese Science Bulletin, 2012, Vol.57 (18), 2323-2328.
- [9] Wang F, Li Q S, Li F B. Application of a Nano-Material Releasing Anion on Rice Paper[J]. Advanced Materials Research, 2013, 785: 467-470.
- [10] Zhang Yinke, Wang En, Lin Jiasha, etc. Progress of Aero-anion Concentration in Urban Green Space [J]. Shandong foresty science and technology, 2009, (3): 139-141.
- [11] Akisetty C, Xiao F P, Gandhi T, et al. Estimating correlations between rheological and engineering properties of rubberized asphalt concrete mixtures containing warm mix asphalt additive. Constr Build Mater, 2011, 25: 950–956
- [12] Yeh J T, Hsiung H H, Wei W, et al. Negative air ion releasing properties of tourmaline/bamboo charcoal compounds containing ethylene propylene diene terpolymer/polypropylene composites. J Appl Polym Sci, 2009, 113: 1097–1110