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SHORT COMMUNICATION

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Surface modification of superfine tourmaline powder with titanate coupling agent

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Abstract The effects of surface modification of the superfine tourmaline powder with a titanate coupling agent were discussed by investigating its hydrophobicity and distribution in poly (ethylene terephthalate) (PET). The modified tourmaline powder became hydrophobic, which resulted in better distribution in the PET matrix. The mechanism of the surface modification was analyzed.

Keywords Superfine tourmaline powder · Titanate coupling agent · Poly (ethylene terephthalate) (PET) · Surface modification

Introduction

Tourmaline group crystals had been found to show pyroelectricity and piezoelectricity toward the close of nineteenth century and were investigated by P. Curie, W. C. Roentgen, W. Voigt, and their collaborators until 1910. In the 1990s, Terutaro Nakamura and Tetsujiro Kubo in Japan proposed some novel applications of the tourmaline group crystals [1], which were (1) application to water to be endowed with surface activity, (2) application of the electroplated surface of tourmaline appearing on the face of the pellets, (3) application to the global environmental problem, and (4) synthetic textile fibers by mixing the fine tourmaline powder. So far, tourmaline has been found to improve the quality of water [2–3], to be used in environment decontamination [4–6], and to produce synthetic textile with functions of promoting blood circulation and accelerating metabolism in living bodies [7–9].

We produced tourmaline-containing poly (ethylene terephthalate) (PET) fibers, in view of its special functional properties, and found that the tourmaline powder flocculated obviously in the PET matrix, which made it necessary to modify the superfine tourmaline powder to be used in fibers.

As the tourmaline group is highly diversified in its chemical composition and some of its varieties are treasured gemstones, we chose the abundant dravite to be investigated in our study. We found that the modified superfine tourmaline powder with the titanate coupling agent showed different behaviors in polar and apolar solvents from that of the tourmaline powder without modification and that it distributed much more uniformly in the PET fibers.

Experimental

Materials

The tourmaline crystals were obtained from Shanghai Dazao Gemstone and were ground into powder with an average diameter of 1.35 um with the help of Jiangyin Trade. The titanate coupling agent NDZ130 was obtained from Nanjing Shuguang Chemical Plant. The poly (ethylene terephthalate) was obtained from Jinxing Fiber (Fujian, China). Methylbenzene and acetone were both market products and chemically pure.

Surface modification process

1. Tourmaline powder sample 1: The tourmaline powder with an average diameter of 1.35 um was ground with deionized water in a QMISP04 ball grinder for 2 h and then separated in a centrifuge and dried. The diameters of 90% of the obtained powder were less than 0.37 um.
2. Tourmaline powder samples 2, 3, 4, and 5: Tourmaline powder sample 1 was combined with 1, 3, 5, and 7% (by weight) of the titanate coupling agent NDZ130, respectively, and were dispersed in methylbenzene under refluxing for 5 h at a constant temperature of 88 °C. The suspensions were then separated in a centrifuge and evaporated using a drying oven at 70 °C temperature to obtain the modified superfine tourmaline powder samples 2, 3, 4, and 5.

   In the first procedure, the ability of the tourmaline powder samples to be dispersed in various solvents was checked visually, and the results are listed in Table 1.

   From the macroscopic point of view, the hydrophobicity of the original and the modified powder samples appeared different: the original powder sample 1 without surface modification was stable in the polar solvent (deionized water), whereas the modified tourmaline powder samples flocculated in water and were stable in the apolar solvent (methylbenzene), as confirmed by some other measurements.

Blending and spinning process

PET master batch resins with tourmaline powder were prepared by feeding the PET and modified tourmaline powder into a SHL35 twin-screw extruder at a weight ratio of 80:20. The extruded master batch resins with tourmaline powder were then quenched in cold water and cut into pellet form. The PET fibers with tourmaline powder were prepared by melt spinning and drawing of the master batch resins mixed with pure PET resin in a MST C-400 melt spinning machine (made in Japan). Table 2 summarizes the compositions of the PET/tourmaline fibers in this study.

Table 1 Stability of the tourmaline powder samples in solvents (from visual test)

Tourmaline powder sample	Water	Methylbenzene
1	+	–
2	–	+
3	–	+
4	–	+
5	–	+

Plus symbol (+) indicates that the particles were stable; dash (–) indicates that they flocculated

Methods

Composition analysis of the tourmaline powder

The composition of tourmaline powder sample 1 was determined with a Siemens D5000S energy dispersive X-ray (EDX) system.

Hydrophobicity/hydrophilicity determination

Each tourmaline powder sample was placed in a glass tube. A permeable barrier kept the powder in the tube, but liquid could permeate the tube freely (see Fig. 1). Liquid would permeate into interstices between the powder grains due to capillary effects. Under the same conditions of permeation time, powder weight, and interstice percentage, when the liquid was polar water, with more water permeating into the glass tube, the powder was more hydrophilic; whereas when the liquid was apolar acetone, with more acetone permeating into the glass tube, the powder was more hydrophobic. The different weights of liquid absorbed by different tourmaline powder samples with the same weight in the same time accordingly represented the different hydrophobicities of the different tourmaline powder samples.

A device was designed to accurately measure the weight of the liquid permeating into the powder (see Fig. 2). A glass tube containing the tourmaline powder was suspended vertically under an electronic analytical balance. A

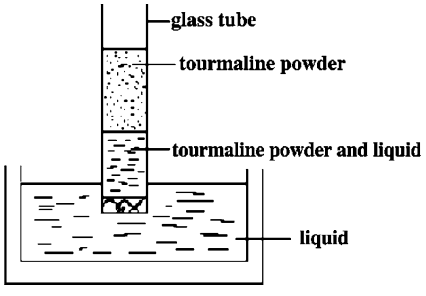
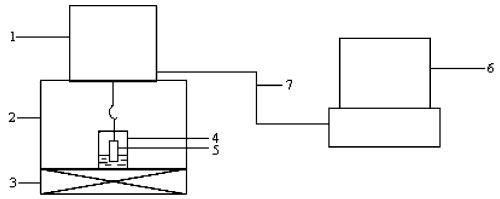


Fig. 1 An outline for measuring hydrophobicity/hydrophilicityof the tourmaline powder samples

Table 2 Compositions of the PET/tourmaline fibers

Fiber specimen	Tourmaline powder	Tourmaline (wt%)	PET (wt%)
PET_1	1	4.0	96.0
PET_4	4	4.0	96.0



1 - electronic analytical balance 2 - support frame 3 - lift table 4 - beaker 5 - glass tube 6 - computer 7 - data wire

Fig. 2 Device for measuring weight of the liquid absorbed by the tourmaline powder

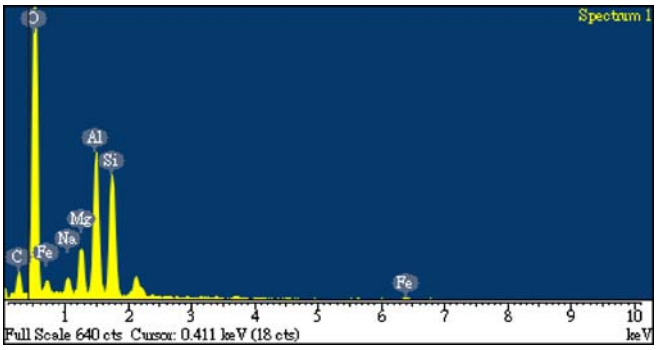


Fig. 3 EDX spectrum of the tourmaline powder sample 1

beaker containing water or acetone was put on a lift table, and the height of the lift table was adjusted so that the bottom of the glass tube only touched the surface of the liquid. A computer was connected to the electronic analytical balance. Using an appropriate computer program, the weight of the liquid absorbed by the tourmaline powder was automatically recorded every 1 s by the computer beginning when the tube first touched the surface of the liquid.

Infrared spectrum analysis

Infrared spectrum analysis was performed on tourmaline powder samples 1 and 4 with a Nicolet NEXUS670 infrared absorption spectrum analysis instrument (made in USA). The scan scope was 4,000–400 cm^1. Before analysis, tourmaline powder sample 4 was immerged in methylbenzene for 8 h to extract the physically coated titanate coupling agent and dried in an oven at 70 °C temperature.

Scanning electronic microscopy

To observe the distribution of the tourmaline particles in the PET fibers, PET_1 and PET_4 fiber specimens (prepared as discussed in the "previous subsection") were observed using a JSM–5600LV scanning electronic microscope (SEM) (made in Japan).

Results and discussion

Composition analysis of tourmaline powder sample 1

Figure 3 shows the EDX analysis of the composition of tourmaline powder sample 1, which is composed of the elements O, Al, Si, Mg, Fe, and Na. The atomic percentage of Mg in the tourmaline powder is 3.57% and that of Fe is 3.30%, demonstrating that the variety of the tourmaline powder is Fe dravite.

Hydrophobicity/hydrophilicity determination

Results are given in Tables 3 and 4, from which we find that the surface-modified tourmaline powder samples 2, 3, 4, and 5 absorb much less water than sample 1 without modification. However, they absorb much more acetone than sample 1. The data show that the original hydrophilic tourmaline powder sample 1 becomes hydrophobic after surface modification with the titanate coupling agent NDZ130. Among them, tourmaline powder sample 4 is of the best modification effect, absorbing the least water and the most acetone after 30 min of evaluation. Tourmaline powder sample 4 was later mixed with the PET fibers with the benefits mentioned in the "Introduction".

Table 3 Weight of water absorbed by different tourmaline powder samples

Time (min)	Tourmaline powder				
	1	2	3	4	5
10	0.1984 g	0.0012 g	0.0004 g	0.0004 g	0.0004 g
20	0.2118 g	0.0028 g	0.0014 g	0.0012 g	0.0015 g
30	0.2324 g	0.0032 g	0.0020 g	0.0017 g	0.0018 g

Table 4 Weight of acetone absorbed by different tourmaline powder samples

Time (min)	Tourmaline powder				
	1	2	3	4	5
10	0.002 g	0.0042 g	0.0076 g	0.0070 g	0.0064 g
20	0.004 g	0.0095 g	0.0161 g	0.0175z g	0.0155 g
30	0.004 g	0.0122 g	0.0204 g	0.0212 g	0.0189 g

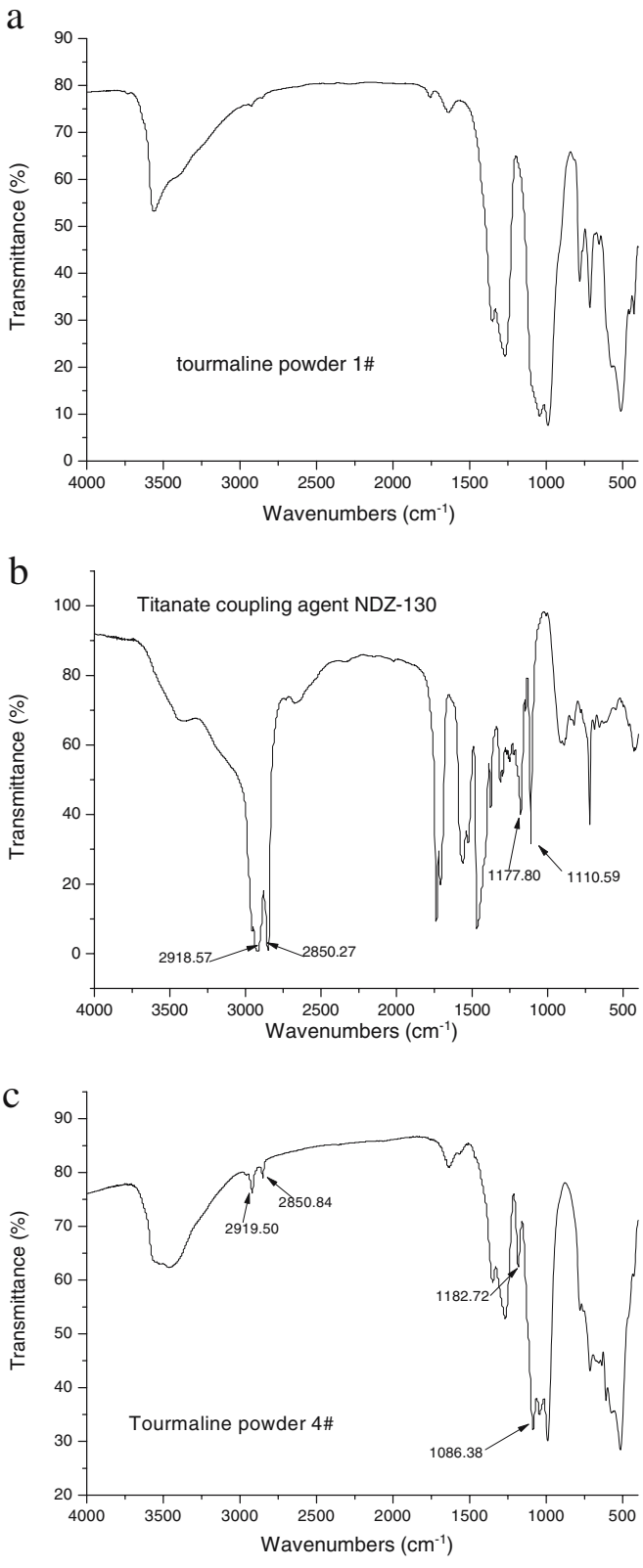


Fig. 4 The infrared absorption bands of the tourmaline powder samples and titanate coupling agent

Infrared spectrum analysis

Figure 4 shows the infrared absorption bands of tourmaline powder 1 without surface modification, titanate coupling agent NDZ130, and tourmaline powder sample 4 modified with 5% (by weight) titanate coupling agent. As shown in Fig. 4c, for tourmaline powder sample 4, strong absorption peaks appear at 2,919.50, 2,850.84, 1,182.72, and 1,086.38 cm^1, but there are no such peaks in Fig. 4a for tourmaline powder sample 1 without surface modification. There are comparatively distinguished characteristic absorption peaks at 2,918.57, 2,850.27, 1,177.80, and 1,110.59 cm^1 in Fig. 4b for the titanate coupling agent NDZ130. As the physically coated titanate coupling agent was extracted from the modified tourmaline powder sample 4 before its infrared spectrum was analyzed, it is reasonably believed that those new peaks of tourmaline powder 4 were caused by the titanate coupling agent NDZ130 chemically bonded with the tourmaline powder.

It was proposed by Monte and Sugerman [10] that titanium-derived coupling agents reacted with substrate surface protons at the inorganic interface resulting in the formation of matrix-compatible/reactive organic -molecular layers on the inorganic surface according to the following chemical mechanism:

$$(Y-R-X-O)_3Ti-OR'+MOH_{\rightarrow}(Y-R-X-O)_3 Ti-OM+R'\mathrm{OH}$$

During the period of pulverizing, hydroxyl groups were chemically bonded on the surface of the superfine tourmaline powder [11]. The [OR'] of the titanate molecules reacted with the hydroxyl groups on the surface of the tourmaline powder and formed a monolayer of the titanate coupling agent on the surface of the powder. Figure 5 shows the mechanism for deposition of a monolayer of the titanate coupling agent on the tourmaline powder. The replacement of the hydroxyl groups on the inorganic tourmaline powder surface with a monomolecular layer of organic functional titanate resulted in the

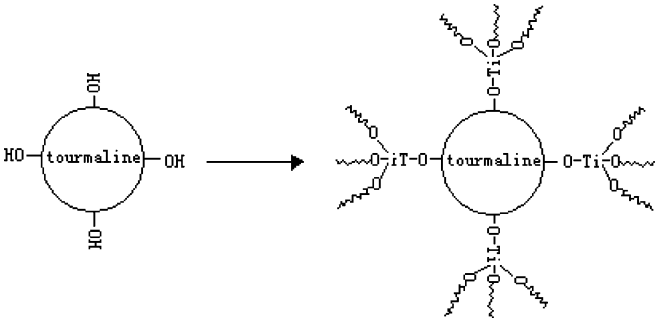
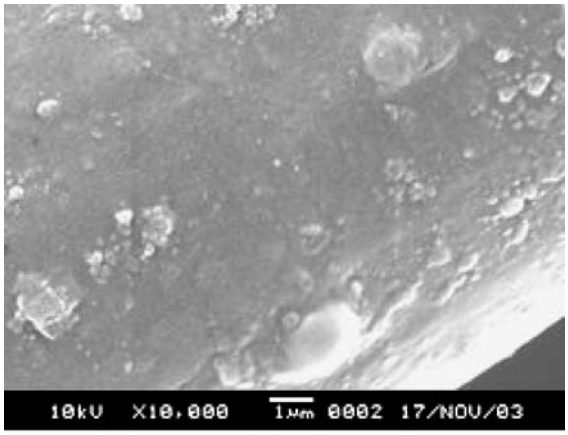
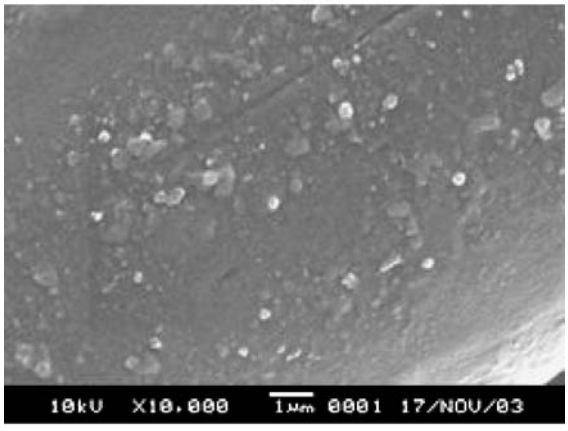


Fig. 5 The modification mechanism for deposition of a monolayer of the titanate coupling agent on the surface of the tourmaline powder



a PET_1



b PET_4

Fig. 6 SEM micrographs of the surface of PET/tourmaline powder samples

modification of the tourmaline powder from hydrophilic to hydrophobic. As shown in Tables 3 and 4, the efficiency of modification was considerably distinct, and among the modified samples, sample 4, which was modified with 5% (by weight) titanate coupling agent, was the best, absorbing the least water and the most acetone.

Compatibility between tourmaline powder and PET

Typical SEM micrographs of the surface of PET/tourmaline fiber specimens are summarized in Fig. 6a,b. It is interesting to note that many dispersed tourmaline powder with diameters ranging from about 0.5 to 3 μm are found to be dispersed in the PET matrix. The average diameter of the original tourmaline powder is about 0.37 μm. Some of the tourmaline powder apparently coagulated during the preparation processes of the PET/tourmaline fiber specimens. As shown in Fig. 6b, the average particle size of the tourmaline powder increased slightly to 0.5 μm in the PET_4 specimen. However, the average particle size increased significantly to about 1 μm of the PET_1 with tourmaline powder sample 1 without surface modification. The results clearly suggest that, modified with the titanate coupling agent, the tourmaline powder could be relatively well dispersed in the PET matrix by melt blending; however, significant aggregation occurred when the tourmaline powder without surface modification was filled in the PET matrix.

As we indicated before, tourmaline powder sample 4 had a monolayer of the titanate coupling agent on its surface. When the coated, superfine tourmaline powder was intermingled with the PET, three long carbon chains at the other end of the titanate coupling agent would form chemical bonds with the PET matrix and provided polymer compatibility and van der Waals entanglement. The titanate coupling agent functioned as molecular bridges at the interface between the inorganic tourmaline powder and the PET matrix.

Conclusion

When the superfine tourmaline powder was modified with the titanate coupling agent NDZ130, a monolayer of the titanate coupling agent was formed on the surface of the tourmaline powder, which made it hydrophobic. Therefore, the tendency of the superfine tourmaline powder to agglomerate in the PET was reduced and better dispersion in the PET matrix was obtained.

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