Preparation and characterization of tourmaline tetradeceynylsuccinate-vinyl acetate copolymer

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Abstract. This paper, the tetradeceynylsuccinic anhydride was used to modify tourmaline to prepare a polymerizable organic tourmaline tetradeceynylsuccinate, and then copolymerized with vinyl acetate to prepare tourmaline-containing functional copolymer. The structures and morphologies of modified tourmaline and copolymer were characterized by means of IR, SEM and EDX analyses. The experimental results showed that the tourmaline was embedded into copolymer by the process of surface modification and copolymerization and illustrated well dispersion stability in copolymer, and meanwhile the tourmaline-containing functional copolymer had benign far infrared radiation and negative ions releasing properties, and a good mechanical performance.

1. Introduction
The tourmaline was a kind of cricoids silicate mineral belonging to trigonal system [1], the chemical formula was written as $XY_3Z_6(BO_3)_3Si_6O_{18}(OH)_4$, and here $X$ could be $K^+$, $Na^+$ and $Ca^+$; $Y$ could be $Fe^{2+}$, $Mg^{2+}$, $Al^{3+}$, $Li^+$ and $Fe^{3+}$; $Z$ could be $Al^{3+}$, $Fe^{3+}$, and $Cr^{3+}$ [2,3]. The tourmaline was paid a close attention recently for its specific performances, such as piezoelectric and pyroelectric properties, negative ions release and far infrared radiation et al [4-7]. So the tourmaline was widely used in many fields like water treatment, industrial, agriculture and daily life care, etc [8-11].
But tourmaline could be not well dispersed in a polymer matrix for its strong surface polarity [12], and led to the poor performances of tourmaline/polymer composites [13]. So, the surface modification of tourmaline was studied and combined with polymers to get the high-performance tourmaline/polymer composites [14-16]. If the tourmaline powder could directly be introduced into the polymer chain to prepare tourmaline containing functional polymer, it could be of paramount importance for preparing tourmaline containing functional polymer and value-added applications of tourmaline.

In this work, the surface modification of tourmaline was carried with tetradeceynylsuccinic anhydride to get polymerizable organic tourmaline, and then copolymerized with vinyl acetate to synthesize tourmaline containing functional copolymer. The structures and morphologies of modified tourmaline and copolymer were characterized via IR, SEM and EDX analyses, and the synthetic process was studied, its physical and mechanical properties were tested quantificationally.

2. Experimental procedures
2.1. Materials and instruments
Tourmaline powder with diameters of $d_{50}$ 1.75 mm and $d_{97}$ 5.23 mm (purity: 98%) was purchased from Yanxin Mineral Co. Ltd., Hebei, China; N,N-dimethylformamide (DMF, AR grade) was purchased from West Long Chemical Co.; and liquid paraffin was purchased from Tianjin Fuchen Chemical
Reagent Factory; Tetradecenylsuccinic Anhydride from Shanghai Jianglai Industrial Co., Ltd; Acetic acid vinyl ester from Beijing chemical plant.
Fourier transform infrared spectroscopy, Spectrum100, Bose PerkinElmer Instruments (Shanghai) Co., Ltd.; X-ray powder diffraction (XD-2), Beijing Purkinje General Instrument Corporation; Scanning electron microscopy, S-450, Japan's Hitachi Ltd.; Contact angle tester (JC2000C), Shanghai Zhongchen Digital Technology Co., Ltd.; Turbidity (SGZ-2), Shanghai Yue Feng Instrument Co., Ltd; Negative ion tester, AIC-2M, Haina Environmental Technology Development (Shenzhen) Co. Ltd.; Microcomputer control electronic universal testing machine. CMT4304, XieQiang Instrument Manufacturing (Shanghai) Co., Ltd.; Far infrared emissivity measuring instrument, JPC-5X, PARAGON Co., Ltd.

2.2. The preparation of polymerizable organic tourmaline
The super-fine tourmaline powder (10 g) and DMF (40 mL) were added to 250 ml three-neck flask, and heated to predetermined temperature with stirring constantly, then, amount of tetradecenylsuccinic anhydride was added to flask, and reacted 3 hrs at constant temperature. The tourmaline tetradecenylsuccinate (TTDS) were separated by filtration under vacuum, and washed three times with anhydrous ethanol, finally dried and grinded to be used.

2.3. The synthesis of tourmaline tetradecenylsuccinate-vinyl acetate copolymer
Vinyl acetate (50 mL, 0.54 mol) and modified tourmaline powder was poured into a 250 mL three-neck flask and heated to 70 °C. The 8.4mL methanol solution, in which dissolved azobisisobutyronitrile (0.187 g, 1 mmol), were added into the flask with funnel, amount of DMF was added into the flask after 2 hours to adjust the viscosity of copolymer and continued to stir for 8 h at constant temperature to get the tourmaline tetradecenylsuccinate-vinyl acetate copolymer (p(TTDS-VA) copolymer).

2.4. The measurement of the contact angle
The powered samples were pressed into a wafer and then the distilled water was dripped onto the surface of the wafer for the contact angle measurements with contact angle tester (JC2000C). Every experiments were repeated three times to get the average results [17].

3. Results and discussion

3.1. The modified tourmaline

3.1.1 IR spectra
The IR spectra of modified and unmodified tourmaline were showed in Figure 1. The spectrum of unmodified tourmaline (Figure 1a) exhibited its typical absorption bands at 3562 cm⁻¹ (OH groups),
975 cm\(^{-1}\) (Si-O bonds) and 1276 cm\(^{-1}\) (B-O bonds) [18]. In comparison with Figure 1a, the IR spectrum of modified tourmaline (Figure 1b) showed new absorption bands corresponding to methyl at 2935 cm\(^{-1}\), the absorption peak of carbonyl group at 1792 cm\(^{-1}\) and the olefinic bond peak at 1664 cm\(^{-1}\). Besides, the other typical absorption peaks of tourmaline were almost unchanged, except the shift of several wavenumbers [19] for the electronic effect of tetradeucenylsuccinate group. Those results indicated that tetradeucenylysuccinate group was attached onto the surface of tourmaline by modification of tourmaline with tetradeucenylysuccinic anhydride to produce polymerizable organic tourmaline tetradeucenylysuccinate (TTDS).

3.1.2 SEM images
The SEM images of the unmodified and modified tourmaline were showed in Figure 2. There is no agglomerates were observed in the modified tourmaline particles (Figure 2a), and the conglomeration in the unmodified tourmaline particles was apparent (Figure 2b). This was because the organic modification reduced the tourmaline’s surface polarity and surface energy, its agglomeration phenomenon was improved obviously.

![SEM images](image)

Figure 2. SEM images of modified tourmaline (a) and tourmaline (b)

3.1.3 The hydrophobicity test
In order to characterize the hydrophobicity of modified tourmaline quantificationally, the contact angle of tourmaline and modified tourmaline were tested and listed in Table 1. The contact angle of modified tourmaline was up to 119°, which indicates an excellent hydrophobicity compared to that of unmodified tourmaline. This result also indicated that organic group was introduced onto the surface of tourmaline after modification, and reduced the tourmaline’s surface polarity and improved its surface hydrophobic properties.

| Sample           | Contact angle /° |
|------------------|------------------|
| Tourmaline       | 37               |
| Modified Tourmaline | 119             |

Table 1. The contact angle of tourmaline and modified tourmaline

3.1.4 The negative ions releasing
The negative ions releasing amount of air, tourmaline and modified tourmaline were measured and ranked in Table 2. It showed that tourmaline have rather better negative ions releasing performance than air, and the negative ions releasing amount of tourmaline was increased by 3 times after surface organic modification. Those were because the organic modification reduced the surface energy of tourmaline, and improved its dispersion and surface areas, accordance with the result of SEM images.

3.1.5 Far-infrared radiation studies
The far infrared emissivities before and after modified tourmaline were showed in Table 3, which stated clearly that the far infrared radiation rate of modified tourmaline was higher than that of
unmodified tourmaline. This was ascribed that the organic modification improved its dispersion and surface areas, same with the result of negative ions releasing.

Table 2. Negative ions released of tourmaline and modified tourmaline

| Sample            | Negative ion release amount (Number/cm⁻¹) |
|-------------------|------------------------------------------|
| Air               | 180                                      |
| Tourmaline        | 380                                      |
| Modified Tourmaline| 1150                                     |

Table 3. Far-infrared radiation rate of tourmaline and modified tourmaline

| Sample                  | Far infrared radiation rate |
|-------------------------|----------------------------|
| Tourmaline              | 0.86                       |
| Modified Tourmaline     | 0.96                       |

3.2 Tourmaline tetradecenylsuccinate-vinyl acetate copolymer (p(TTDS-VA) copolymer)

3.2.1 IR spectra analysis
The IR spectra of p(TTDS-VA) copolymer were shown in Figure 3. The absorption peaks of OH groups at 3459 cm⁻¹, B–O bonds at 1266cm⁻¹ and Si–O bonds at 944 cm⁻¹ were assigned to the typical bands of tourmaline, and the other absorption peaks of methyl and methylene groups appear at 2932 cm⁻¹ to 2862 cm⁻¹, and carbonyl group occur at 1756 cm⁻¹, C-C bonds at 1438-1125cm⁻¹, and no absorption of double bond was found. Those results were in accordance with the characteristics of p(TTDS-VA) copolymer. This indicated that polymerizable organic tourmaline tetradecenylsuccinate (TTDS) had copolymerized with vinyl acetate to generate the p(TTDS-VA) copolymer.

3.2.2 SEM and EDX analyses
The SEM images and EDX analysis of the p(TTDS-VA) copolymer were showed in Figure 4. The SEM images of polyvinyl acetate and unmodified tourmaline (Figure 4b) that got with the same synthetic procedure of the p(TTDS-VA) copolymer had showed a serious tourmaline agglomeration, and the p(TTDS-VA) copolymer displayed a well distribution of tourmaline (Figure 4a). This was because that tourmaline was introduced into copolymer via the surface organic modification and copolymerization. The EDX analysis of p(TTDS-VA) copolymer was carried and showed in Figure 4c, the copolymer contained Na, Si, K and Ca elements, which are the typical elements of tourmaline and proved that tourmaline was introduced into copolymer.

3.2.3 The measurement of negative ions
The negative ions releasing amounts of p(TTDS-VA) copolymer with different tourmaline dosage were measured and showed in Figure 5. We could found that the amounts of negative ions releasing of p(TTDS-VA) copolymer were almost linear increased with the increasing of modified tourmaline.
content. This further certified that modified tourmaline could be uniformly dispersed in p(TTDS-VA) copolymer [20].

![SEM and EDX of tourmaline tetradecenylsuccinic-vinyl acetate copolymer](image1.png)

**Figure 4.** SEM and EDX of tourmaline tetradecenylsuccinic-vinyl acetate copolymer, (a) tourmaline tetradecenylsuccinic-vinyl acetate copolymer, (b) adding unmodified tourmaline, (c) EDS of tourmaline tetradecenylsuccinic-vinyl acetate copolymer

![Graph of Negative ions releasing of p(TTDS-VA) copolymer](image2.png)

**Figure 5.** Negative ions releasing of p(TTDS-VA) copolymer

**3.2.4 Far infrared radiation studies**

The far infrared radiation of p(TTDS-VA) copolymer at the wavelength of 8-25μm was measured and showed in Figure 6. The data displayed that the far infrared radiation rates of p(TTDS-VA) copolymer with different tourmaline dosages were all high (about 0.95), and have an increased trend with the increasing of additive amounts of modified tourmaline, which was in keeping with the excellent dispersity of modified tourmaline.
3.2.5 The Mechanical property of the p(TTDS-VA) copolymer film

The p(TTDS-VA) copolymer with different additive amounts of modified tourmaline were pressed into specimen to test its elastic modulus and tensile strength According to the standard GB 13022-1991, and the results were shown in Figure 7. The Figure 7 exhibited that the elastic modulus and tensile strength of the p(TTDS-VA) copolymer film demonstrate the same trends and reached the maximum when the dosage of modified tourmaline was 3.5%. This was because that tourmaline was introduced into the polymer chains to enhance the force between polymer, and improved its mechanical properties, but excessive tourmaline could lead to the internal defects, so its mechanical properties decreased [21].

4. Conclusion

Tourmaline powder was modified with tetradecenylsuccinic anhydride as organic modifier in this work. The experimental results certified that tetradecenylsuccinate group was attached onto the surface of tourmaline to get polymerizable organic tourmaline tetradecenylsuccinate (TTDS), and then the tourmaline tetradecenylsuccinate-vinyl acetate copolymer was synthesized with the copolymerization of TTDS with vinyl acetate in DMF solution. The results showed that the negative ions releasing quantities of modified tourmaline were increased by 3 times that of unmodified tourmaline, and the far infrared radiation rate of modified tourmaline was increased clearly after modification.

The tourmaline tetradecenylsuccinate-vinyl acetate copolymer displayed an excellent stability, and the negative ions releasing amount and far infrared radiation rate were all increased with the increasing of modified tourmaline content, and the good mechanical properties foreshadowed its potential prospects for development of novel functional materials and functional devices.
5. References
[1] Viti C, Brogi A and Liotta D 2016 J. Struct. Geo. 86 1
[2] Dyar M D, Taylor M E and Lutz T M 1998 Amer. Min. 83 848
[3] Rajajee V, Fletcher J and Rochlen L R 1999 Eur. J. Min. 11 201
[4] Jiang S Y, Radvanec M and Nakamura E 2008 Lithos 106 1
[5] Pal D C, Trumbull R B and Wiedenbeck M 2010 Chem. Geo. 277 245
[6] Tokumura M, Znad H T and Kawase Y 2006 Chem. Eng. Sci. 61 6361
[7] Machi Y 2001 J.Int. Soc. Life Inform. Sci. 19 69
[8] Jie Z, Bing-Hui G E and Peng W 2009 J. Funct. Mat. 40 556
[9] Garda G M, Trumbull R B and Beljavskis P 2009 Chem. Geo. 264 207
[10] Hinsberg V J V and Marschall H R 2007 Chem. Geo. 238 141
[11] Henry D J and Brodkorb M K D 2009 J. South Amer. Ear. Sci. 28 132
[12] Hu Y M, Bian J and Wu Z M 2014 China Non-Metal. Min. Ind. 108 26
[13] Li M, Hu Y M and Li Y 2015 J. Surf. Sci. Nanotech. 13 422
[14] Jen-Taut Y, Han-Hsing H and Wei W 2011 Internat. J. App. Math. Comp. Sci. 21 431
[15] Zheng Y and Wang A 2010 Chem. Eng. J. 162 186
[16] Tijing L D, Amarjargal A and Zhe J 2013 Current App. Phy. 13 205
[17] Garces N Y, Stevens K T and Halliburton L E 2001 J. Crys. Growth 225 435
[18] Jiang B J, Frost R L and Martens W N 2007 Vib. Spectr. 44 42
[19] Zhang K Y, Cheng X H and Hong-Lu Q U 2004 Min. Metal. 13 97
[20] Li C, Thostenson E T and Chou T W 2008 Comp. Sci. Techn. 68 1445
[21] Tjong S C 2006 Mat. Sci. Eng. Rep. 53 73

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