

Synthesis and Characterization of Polymerizable Tourmaline Methacrylate

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The surface modification of tourmaline powder with methacrylic anhydride was studied in this work, and the reaction process conditions were optimized according to the experimental parameters of contact angle and turbidity in liquid paraffin. The structure of the modified tourmaline was characterized by means of IR, XRD and SEM. The structural analysis indicated that methacrylic group was attached onto the surface of tourmaline by the reaction of tourmaline with methacrylic anhydride to get a polymerizable tourmaline methacrylate. The experimental results indicated that modified tourmaline presented enhanced hydrophobicity than the unmodified tourmaline.

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I. INTRODUCTION

Early in 1703, Dutch found a new kind of stone in sailing, which could adsorb small and light materials around its surface, such as materials. And people called it “sucked Greystone” at that time [1]. Later in 1768, Swedish scientist Linnei Si found that this ore showed piezoelectric and pyroelectric properties, and it was renamed as “tourmaline” [2]. Tourmaline is a ring-structured silicate mineral and its chemical formula is $(\text{Na,Ca})(\text{Mg,Fe,Mn,Li,Al})_3\text{Al}_6(\text{Si}_6\text{O}_{18})(\text{BO}_3)_3(\text{OH,F})_4$ [3–6]. Tourmaline has a permanent electrode effect, and it can release negative ions and radiate far infrared ray [7].

However, the strong polarity on the surface of tourmaline makes it easy to agglomerate, which leads to poor dispersion stability of tourmaline in polymers. In order to solve this problem and improve their far-infrared radiating and negative ions releasing properties, some works have been focused on the surface modification of tourmaline with organic molecules and several related applications have been accordingly proposed, such as the preparation of functional materials that release far-infrared radiation and negative oxygen ions [8–12]. In this work, we studied the reactivity of tourmaline powders with methacrylic anhydride by checking the turbidities and contact angles of the products, and the results indicated that polymerizable tourmaline methacrylate was obtained by surface modification of tourmaline with methacrylic anhydride. It offered the potential for the preparation of tourmaline-based functional polymers [13].

II. EXPERIMENTAL PROCEDURES

A. Materials and instruments

Experimental Instruments: 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.

Tourmaline powder with diameters of d_{50} 1.75 μm and d_{97} 5.23 μm (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; methacrylic anhydride was obtained from Jinao Chemical Co. Ltd., Anhui, China.

B. Experimental Methods

5 g of super-fine tourmaline powder and 30 mL of DMF were added into a 250 mL three-neck flask, and the flask was heated to predetermined temperature with constant stirring. Then, a certain amount of methacrylic anhydride was added into the above-mentioned solution. The mixture was kept for different periods of time for reaction. After that, the samples were separated by filtration under vacuum, washed three times with anhydrous ethanol, and finally dried and grinded for characterization.

C. Testing and analysis methods

1. The measurement of the contact angle

The powder samples were pressed into a wafer and then the distilled water was dripped onto the surface of the wafer for the contact angle measurements. Every experiments were repeated three times to get the average results [14].

2. The measurement of the contact angle

1 g of the modified tourmaline powder was dissolved in 50 mL paraffin liquid. The mixture was stirred adequately and then kept still for 24h, afterwards the tur-

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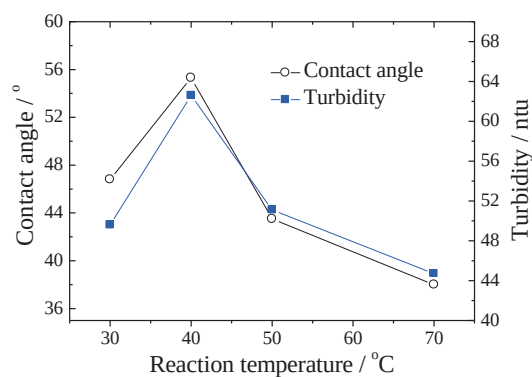


FIG. 1. The influence of the reaction temperatures.

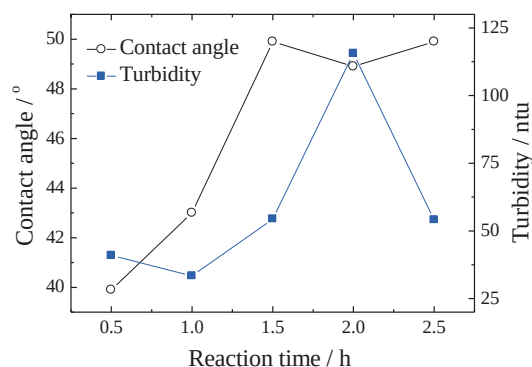


FIG. 2. The influence of the reaction time.

bidity of supernatant liquid was analyzed by the SGZ-2 digital nephelometer.

III. RESULTS AND DISCUSSION

The modification effects on the tourmaline power under various conditions were studied by the parameters of turbidity and contact angle.

A. The influence of the temperature

The influences of reaction temperatures on the contact angles and turbidities of the modified tourmaline were shown in Fig. 1. It indicated that the contact angle and the turbidity in the liquid paraffin of the modified tourmaline increased rapidly at first and then fell down with further increase of the temperature. The maximum contact angle and turbidity simultaneously appeared at 40 °C. Therefore, the temperature of 40 °C was selected as the optimal reaction temperature in the following experiments.

B. The influence of the reaction time

The influences of reaction times on the contact angles and turbidities of the modified tourmaline were shown in Fig. 2. The contact angle increased with the increase of reaction time when the reaction time was less than 1.5 h.

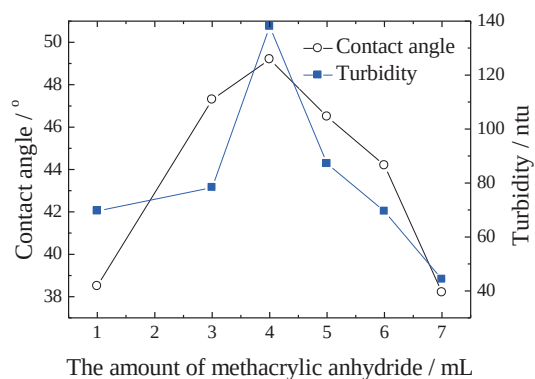


FIG. 3. The influence of the dosage of methacrylic anhydride.

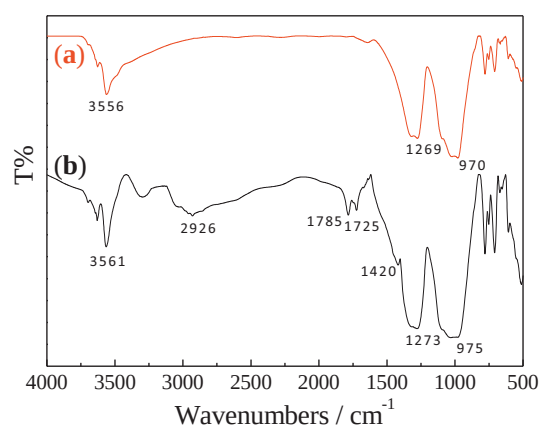


FIG. 4. IR spectra of (a) tourmaline and (b) modified tourmaline.

The turbidity of product in liquid paraffin increased first and then decreased with further increasing the reaction time, reaching the maximal value at 2 h.

C. The influence of the amount of methacrylic anhydride

The influences of the amount of methacrylic anhydride on the contact angle and turbidity of the modified tourmaline were shown in Fig. 3. Both curves of contact angle and the turbidity indicated that the turbidities and contact angles of the modified tourmaline reached their maximum when the dosage of methacrylic anhydride was 4 mL. And the modified tourmaline exhibited good hydrophobic properties.

D. IR spectra

The IR spectra of the unmodified and modified tourmaline were shown in Fig. 4. In Fig. 4(a), the unmodified tourmaline exhibits absorption bands at 3556 cm⁻¹, typical of OH groups, 1269 cm⁻¹ of B-O bonds and 970 cm⁻¹ of Si-O bonds [15]. In comparison with Fig. 4(a), the IR spectrum of modified tourmaline (Fig. 4(b)) showed new absorption bands corresponding to methyl at 2926

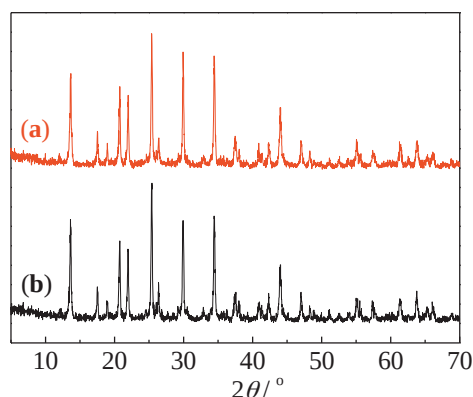


FIG. 5. XRD spectra of (a) tourmaline and (b) modified tourmaline.

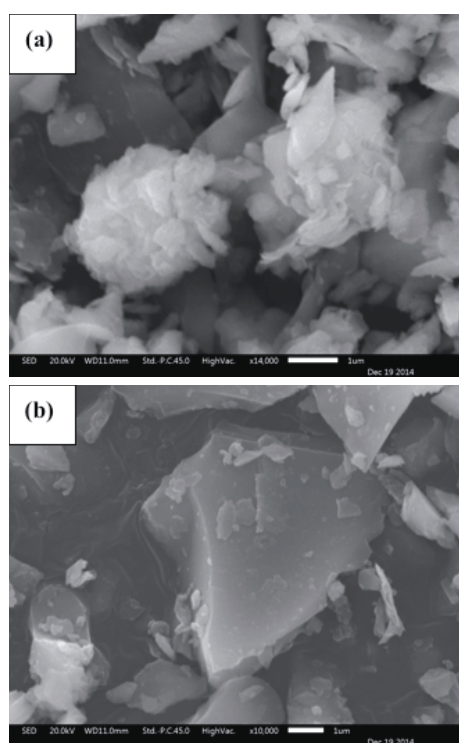


FIG. 6. SEM images of (a) tourmaline and (b) modified tourmaline.

cm^{-1} and another absorption bands methylene at 1420 cm^{-1} , and two absorption peaks of carbonyl group at 1785 and 1725 cm^{-1} . Besides, the other absorption peaks (e.g., corresponding to the OH, B–O and Si–O bonds) all

red-shifted to longer wavenumbers [16], indicating that methacrylic groups were attached onto the surface of tourmaline by reaction of methacrylic anhydride with the surface hydroxyl groups to produce the tourmaline methacrylate.

E. XRD patterns

The XRD patterns of unmodified and modified tourmaline were shown in Fig. 5. The characteristic peaks of unmodified and modified tourmaline were almost identical, and no new peaks appeared or vanished. This result indicated that the modifications of tourmaline with methacrylic anhydride did not alter the crystal structure of tourmaline and only the surface properties of tourmaline were changed.

F. SEM images

Figure 6 showed the SEM images of the unmodified and modified tourmaline. The conglomeration in the unmodified tourmaline particles was apparent (Fig. 6(a)), and no agglomerates were observed in the modified tourmaline particles (Fig. 6(b)). This observation was attributed to the strong surface polarities of the tourmaline particles before modification, which facilitated the conglomeration of the particles. After organic modification, both the surface polarity and surface energy of the tourmaline decreased, and thus the dispersivity of tourmaline particles was improved.

IV. CONCLUSION

In this paper, the reactivity of tourmaline with methacrylic anhydride was studied to obtain organically modified tourmaline. Their structures have been characterized by IR, XRD and SEM. The experimental results showed that the modified tourmaline displayed enhanced hydrophobicity and improved dispersity. The structural analysis indicated that methacrylic group was attached onto the surface of tourmaline via the reaction between tourmaline surface groups and methacrylic anhydride, resulting in polymerizable tourmaline methacrylate. This study offered the practicability for the preparation of tourmaline-containing functional polymers.

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- [1] L. D. Tijing, M. T. G. Ruelo, A. Amarjargal, *et al.*, Chem. Eng. J. **197**, 41 (2012).
- [2] D. L. Guerra, S. P. Oliveira, E. M. Silva, *et al.*, Int. J. Miner. Process. **102**, 25 (2012).
- [3] L. P. Ogorodova, L. V. Melchakova, I. A. Kiseleva, *et al.*, Thermochim. Acta **539**, 1 (2012).

- [4] F. Pirajno, R. Seltmann, Y. Yang, GSF **2**, 157 (2011).
- [5] J. P. Meng, J. S. Liang, G. C. Liang, *et al.*, Nonferrous Met. Soc. China **547**, 16 (2006).
- [6] T. Setkova, Y. Shapovalov, and V. Balitsky, J. Cryst. Growth **318**, 904 (2011).

- [7] C. Li, E. T. Thostenson, T. W. Chou, *Compos. Sci. Technol.* **68**, 1445 (2008).
- [8] Y. Wang, J. T. Yeh, T. Yue, *et al.*, *Colloid. Polym. Sci.* **284**, 1465 (2006).
- [9] M. Méndez-González and J. V. Cauich-Rodriguez, *Bio ceramics* **724**, 262 (2004).
- [10] Y. Hu and X. Yang, *Appl. Surf. Sci.* **258**, 7540 (2012).
- [11] L. A. Groat, G. Giuliani, D. D. Marshall, *et al.*, *Ore Geol. Rev.* **34**, 87 (2008).
- [12] J. S. Liang, L. J. Wang, G. K. Xu, *et al.*, *J. Rare Earth* **24**, 281 (2006).
- [13] H. Ding, S. C. Lu, Y. X. Deng, and G. X. Du, *T. Nonferr. Metal. Soc.* **17**, 1100 (2007).
- [14] N. Y. Garces, K. T. Stevens, L. E. Halliburton, *et al.*, *J. Cryst. Growth* **225**, 435 (2001).
- [15] Y. Fuchs, M. Lagache, J. Linares, *CR Geosci.* **334**, 245 (2002).
- [16] B. J. Reddy, R. L. Frost, W. N. Martens, *et al.*, *Vib. Spectrosc.* **44**, 42 (2007).