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Study on the inorganic–organic surface modification of potassium titanate whisker

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ABSTRACT

ZnO coated potassium titanate whisker (PTW) was prepared via a facile chemical method, and coupling agent KH550 was used to modify the surface of ZnO coated PTW. Scanning electron microscope (SEM), X-ray powder diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, ultraviolet spectrophotometer and surface contact angle measurement were used to characterize the effect of surface modification. The results showed that the surface of PTW was uniformly coated by ZnO nanoparticles, and exhibited better ultraviolet absorption when the coating amount of ZnO was 5%. After modified by KH550, the modified ZnO/PTW showed better dispersion in ethanol solvent and the surface of modified ZnO/PTW became more hydrophobic–lipophilic than that of modified uncoated PTW. The method of inorganic–organic surface modification of PTW might be an effective way to greatly improve the compatibility of the whisker and the polymer matrix.

1. Introduction

In recent decades, potassium titanate whisker (PTW, $K_2Ti_6O_{13}$) has been found to be a promising reinforcer among numerous inorganic fillers (glass fiber, carbon fiber, or nanometer materials) for the wear resistant composites, engineering plastics and polymers because of its unique properties such as outstanding mechanical properties, wear resistance, chemical and thermal stabilities, and low hardness [1–4]. The relatively small size and high ratio of length to diameter of PTW are very useful for reinforcing polymer which conventional fillers have not been reported [2,5]. However, owing to the peculiar structure and high surface energy, PTW often exhibits easy aggregation and poor dispersion in polymer matrix, which lead to the decreased performance of target composites [5]. Furthermore, the large surface energy difference between hydrophilic PTW and hydrophobic polymer seems to be the main cause of the poor interfacial interaction.

Thus, the development of high efficient surface modification of PTW for polymer composites is of both fundamental and practical importance [6]. It is well recognized that surface modification can improve the interfacial interaction between the inorganic components and the polymer matrix [7–9]. Recently, researchers mainly used coupling agents to treat the surface of PTW directly [1,6,10] in order to achieve homogeneous distribution of the PTW within the polymer matrix, but the effects of direct coupling on PTW surface was not appreciable due to its tunneling structure and chemical stability [2,11].

In this paper, a facile chemical route was adopted to prepare ZnO coated PTW. Then coupling agent was used for further organic modification and the modified PTW was characterized by means of SEM, EDS, FT-IR, XRD. UV absorption, sedimentation behavior and hydrophobic properties of modified PTW were also studied.

2. Experiment

2.1. Materials

PTW with a diameter of 0.5–1 μm and a length of 10–30 μm was purchased from JinJian Composite Co. Shenyang, China. Zinc sulfate ($ZnSO_4·7H_2O$, AR), Ethanol (C_2H_5OH, AR), Ethylacetate ($C_4H_8O_2$, AR) and coupling agent (KH550, $H_2N(CH_2)_3Si(OC_2H_5)_3$, AR) were received from Nanjing Neng De Chemical Co. Nanjing, China. All reagents were used without further purification.

2.2. Preparation of ZnO coated PTW

0.35 g $ZnSO_4·7H_2O$ was dissolved in distilled water according to the mass ratio of zinc oxide to PTW (weight ratio of ZnO to PTW is 0.05:1). 1 g NaOH was added into the solution to form $Na_2Zn(OH)_4$ solution. Then PTW was added, and the resulting solution were vigorously stirred and heated to 50 °C in a water bath. 5 mL $CH_3COOCH_2CH_3$ was added to the suspension while keeping

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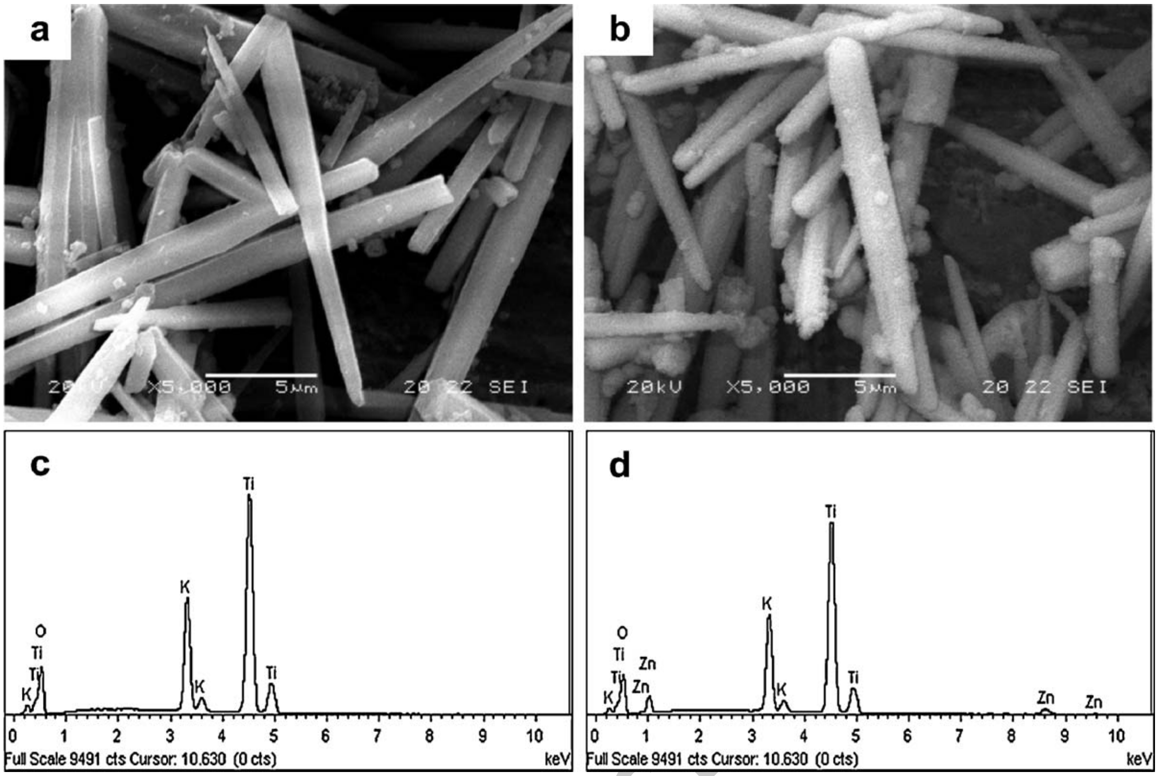


Fig. 1. SEM images of PTW (a) uncoated, (b) ZnO coated and EDS spectras of PTW (c) uncoated, (d) ZnO coated.

vigorously stirred for 2 h. The product was collected by suction filtration and washed with distilled water repeatedly, then dried at 100 °C followed by calcined at 400 °C for 2 h. In this case, ZnO coated PTW (ZnO/PTW) was prepared.

2.3. Preparation of KH550 modified ZnO/PTW

KH550 used at weight fractions from 1% to 5% based on the ZnO/PTW solid loads was dissolved in ethanol aqueous solution (the weight ratio of ethanol to distilled water was fixed at 10:1), and mixed with prepared ZnO/PTW. The mixture was contained mixing for 1 h at 60 °C. The sample was collected by filtration, washed with Ethanol repeatedly to remove excess KH550, and dried in a preheated oven at 80 °C for 24 h, giving the KH550 modified ZnO/PTW. Additionally, the KH550 modified uncoated PTW was also prepared to compare with the KH550 modified ZnO/PTW.

2.4. Characterization

The surface morphologies of ZnO/PTW and uncoated PTW were surveyed by a scanning electron microscope (JSM-5610LV, JEOL, Japan) at an accelerating voltage of 20 kV.

X-ray powder diffraction (XRD) pattern was determined by a Philips X'Pert X-ray spectrometer using Cu Kα radiation with a tube voltage of 40 kV and a tube current of 35 mA.

The Fourier transform infrared (FT-IR) absorption spectra were collected, using a Nexus infrared spectrometer (Thermo Nicollet, USA) which employed a KBr pellet method at room temperature.

The ultraviolet light absorbance of ZnO/PTW composite material at 300, 320, 340, 360, 380, 400 nm were measured by ultraviolet spectrophotometer (TU-1810, Beijing Purkinje General Instrument).

The settling time was recorded and used as an indicator for modified PTW dispersion.

The hydrophobicity of the modified PTWs was determined by contact angle instrumental (DSA30, Kruss, Germany). Each sample was tested 7 times on different areas. The values are averages of 7 measurements, and the relative standard deviation is 2.1%

3. Results and discussion

3.1. Scanning electron microscope

The images of ZnO coated PTW and uncoated PTW were shown in Fig. 1a and b, respectively. It is clearly shown in Fig. 1a that the surface of uncoated PTW is smooth, with an average diameter of 0.5–1 μm and an average length of 10–30 μm. Fig. 1b shows the morphology of ZnO coated PTW. One can observe that a layer of thin film with a small amount of dispersed nanoparticles uniformly coated on the surface of PTW. We assumed that the heterogeneous precipitation process occurred on the surface of PTW when added $CH_3COOCH_2CH_3$ into the suspension. There is a chemical equilibrium in the $Na_2Zn(OH)_4$ solution:

$$Zn(OH)_4{}^{2-} \rightleftharpoons Zn(OH)_2 + 2OH^-$$

When $CH_3COOCH_2CH_3$ was added to the solution, it reacted with OH^-. As the consumption of OH^-, the equilibrium began to move to form $Zn(OH)_2$ precipitate on the surface of PTW:

$$CH_3COOC_2H_5 + OH^- = CH_3COO^- + C_2H_5OH$$

$Zn(OH)_2$/PTW precursor was prepared; the precursor was calcined and a layer of thin film with a small amount of dispersed ZnO nanoparticles uniformly coated on the surface of PTW.

The corresponding two-dimensionally scanned EDS spectrum of PTW, shown in Fig. 1c, indicated that a composition of O 69.85, K 8.41 and Ti 21.74 were present on the surface, which was approximately consistent with the formula of $K_2Ti_6O_{13}$. While the two-dimensionally scanned EDS spectrum of ZnO coated PTW

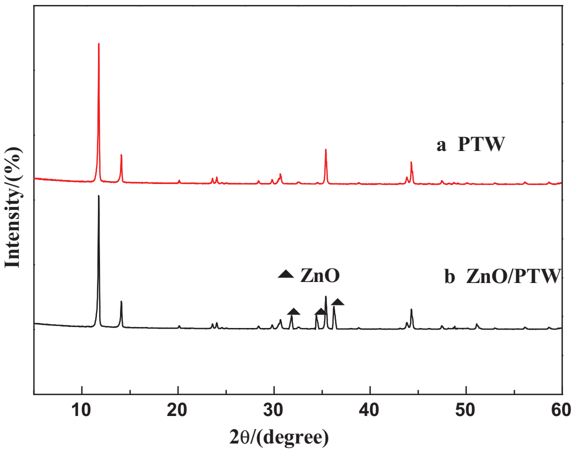


Fig. 2. XRD patterns of (a) uncoated PTW, (b) ZnO coated PTW.

shown in Fig. 1d suggested that Zn was also present in addition to O, K and Ti, and the approximate composition was Zn 2.76, O 70.16, K 7.34 and Ti 19.74. The appearance of the characteristic peak of element Zn also indicated that the PTW was successfully coated with ZnO.

3.2. XRD and FT-IR analysis

Fig. 2 shows the X-ray diffraction (XRD) patterns of uncoated PTW (Fig. 2a) and coated PTW (Fig. 2b). It is obviously observed new peaks in Fig. 2b compared with Fig. 2a. The new peaks are attributed to the diffraction peaks of ZnO corresponded to the crystal faces of (1 0 0), (0 0 2) and (1 0 1).

Fig. 3 shows the FT-IR characters of ZnO/PTW (Fig. 3a) and uncoated PTW (Fig. 3b). The main absorption peaks at the range of 1500 $\mathrm{cm^{-1}}$ to 400 $\mathrm{cm^{-1}}$ appearing in Fig. 3a and b are attributed to the characteristic absorption peaks of PTW. The peak at 470 $\mathrm{cm^{-1}}$ is the characteristic absorption of Zn—O in Fig. 3a and the absorption peaks at 1180 $\mathrm{cm^{-1}}$ and 935 $\mathrm{cm^{-1}}$ become weak and wide in Fig. 3a compared with Fig. 3b. It suggests that there is a certain degree of interaction between coated layer and PTW. The peak at 3450 $\mathrm{cm^{-1}}$ and 1635 $\mathrm{cm^{-1}}$ are assigned to the absorption of water. Combined with the analysis of Figs. 1–3, we can conclude that the surface of PTW is coated by ZnO successfully.

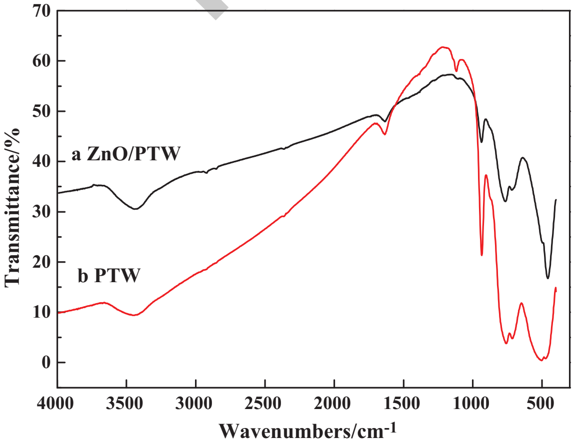


Fig. 3. FT-IR characters of (a) ZnO coated PTW, (b) uncoated PTW.

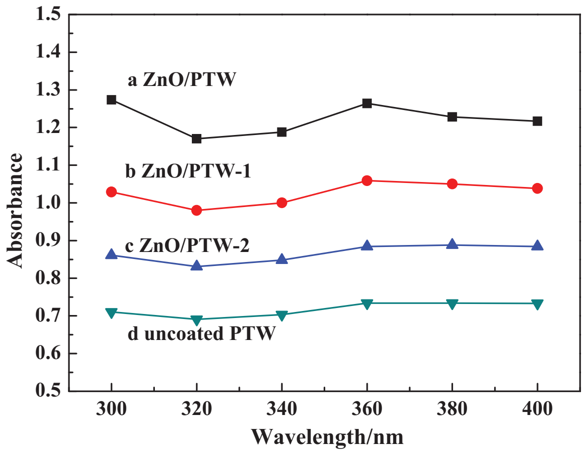


Fig. 4. Influence of coating amount of ZnO on ultraviolet light absorbance of samples.

3.3. The effects of different coating amount of ZnO on UV absorption

By adjusting the weight of $ZnSO_4 \cdot 7H_2O$ and PTW, ZnO/PTW-1 (weight ratio of ZnO to PTW is 0.10:1) and ZnO/PTW-2 (weight ratio of ZnO to PTW is 0.15:1) were obtained. Suspensions were prepared by mixing distilled water with 0.04 wt.% ZnO/PTW, ZnO/PTW-1 and ZnO/PTW-2, respectively, and agitating ultrasonically for 15 min. Then the UV absorbance of these suspensions was determined.

ZnO nanoparticles have the ability to absorb the long-wavelength ultraviolet (UVA, wavelength 320–400 nm) and middle-wavelength ultraviolet (UVB, wavelength 280–320 nm) [11]. Fig. 4 shows the UV absorbance of suspensions. All suspensions have UV absorption at the corresponding wavelength. The absorbance of the suspension of ZnO/PTW is higher than other suspensions. We also find that the UV absorbance decrease with the increasing of coating amount. The results indicated that when increasing the coating amount, superfluous ZnO nanoparticles agglomerate on the surface of PTW and the size of ZnO nanoparticles increases. Agglomeration and increasement of size cause the reduction of the surface areas of coated PTW and have a negative effect on UV absorption.

3.4. Settling times studies of KH550 modified ZnO/PTW and PTW

Suspensions were prepared by mixing 0.5 wt.% KH550 modified ZnO/PTW, PTW with ethanol, respectively. Then put the

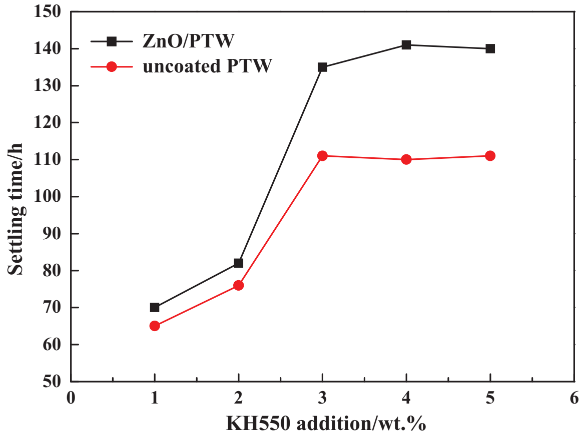


Fig. 5. The settling times of KH550 modified ZnO/PTW, PTW in ethanol solvent.

suspensions stood undisturbed at room temperature and recorded the settling times.

The dispersions of these suspensions were assessed by measuring their settling behaviors. The settling times of the KH550 modified ZnO/PTW and PTW are given in Fig. 5. The KH550 modified ZnO/PTW yielded much higher settling times than those KH550 modified PTW. This indicates that KH550 onto ZnO/PTW can provide a better surface coverage on the surface and effectively prevent the whisker from agglomeration. When the amount of KH550 was 4 wt.%, modified ZnO/PTW reached maximum settlement time. And while the amount of KH550 was 3 wt.%, modified PTW reached maximum settlement time. The possible reason is that more active sites increased on the surface of ZnO/PTW and higher amounts of KH550 absorbed on the surface of ZnO/PTW after coated with ZnO.

3.5. Surface contact angle measurements and surface free energy calculations

The contact angle (θ) of inorganic particles is a useful indicator of wettability, giving important information on the compatibility of inorganic particles with polymer matrix [12]. A variety of methods are available for measuring the surface contact angle of powders [13–16]. To quantify the lipophilic–hydrophilic property of the whiskers and to evaluate the effect of KH550 modified ZnO/PTW and PTW, the static contact angles were measured by two-liquid method [17] in this paper.

Fig. 6 shows the static contact angles of water on the 4 wt.% KH550 modified surfaces of ZnO/PTW, 3 wt.% KH550 modified uncoated PTW and ZnO/PTW. The contact angles of the two modified samples are higher than 90°, indicating that the surfaces of the two modified samples are hydrophobic while the surface of ZnO/PTW is still hydrophilic ($\theta = 54.6°$). We also observed that the contact angle of water on the KH550 modified surface of ZnO/PTW ($\theta = 103.3°$) was higher than that of KH550 modified surface of uncoated PTW ($\theta = 90.3°$). The surface free energies and components of modified/unmodified PTW were calculated using values of γ and θ listed in Table 1 according to the followed equations [18,19]:

Table 1
Surface free energies (γ/mJ m^{-2}) and components of ethylene glycol, water [20] and their contact angles (θ) on the modified ZnO/PTW, PTW at 20 °C.

Liquids	γ_L	γ_L^d	γ_L^p	θ_1	θ_2
Water	72.8	21.8	51.0	103.3°	90.3°
Ethylene glycol	48.0	29.0	19.0	75.0°	60.0°

γ_L represents surface free energies of liquids; γ_L^d and γ_L^p refer to dispersive and polar components, θ_1 and θ_2 refer to contact angles of modified ZnO/PTW and PTW.

$$\gamma_S = \gamma_S^d + \gamma_S^p \tag{1}$$

$$\frac{\gamma_L(1+\cos\theta)}{2} = (\gamma_L^d \gamma_S^d)^{1/2} + (\gamma_L^p \gamma_S^p)^{1/2} \tag{2}$$

where γ_L is the surface free energy of liquid; θ is the contact angle; γ_L^d and γ_L^p are the dispersive and polar components of the surface free energy of liquid; γ_s is the surface free energy of solid; γ_S^d and γ_S^p are the dispersive and polar components of surface free energies of solids. The calculated results also listed in Table 2.

From Table 2, it is obvious that the surface of unmodified PTW is hydrophilic. Its interface interaction with polymer matrix might be very weak. After modification by KH550, the surface free energies of modified samples greatly reduced compared with untreated PTW and the value of the polar component of modified ZnO/PTW was lower than that of modified uncoated PTW, which demonstrated that the surface of KH550 modified ZnO/PTW had more hydrophobic and lipophilic [22], an increase of the dispersion in polymer

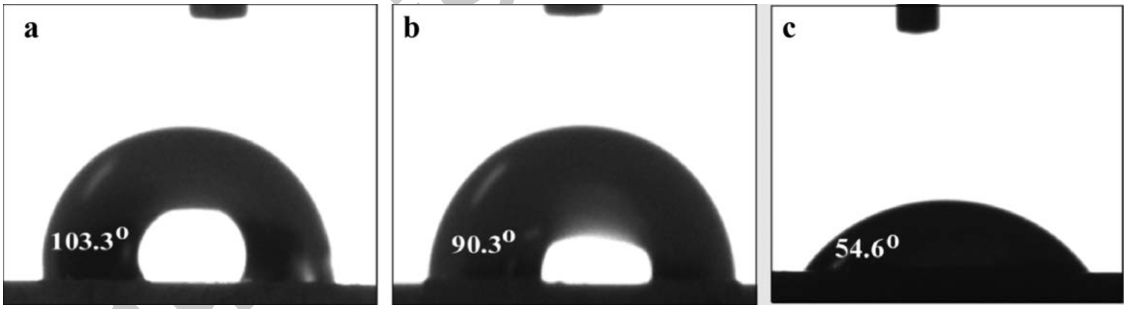
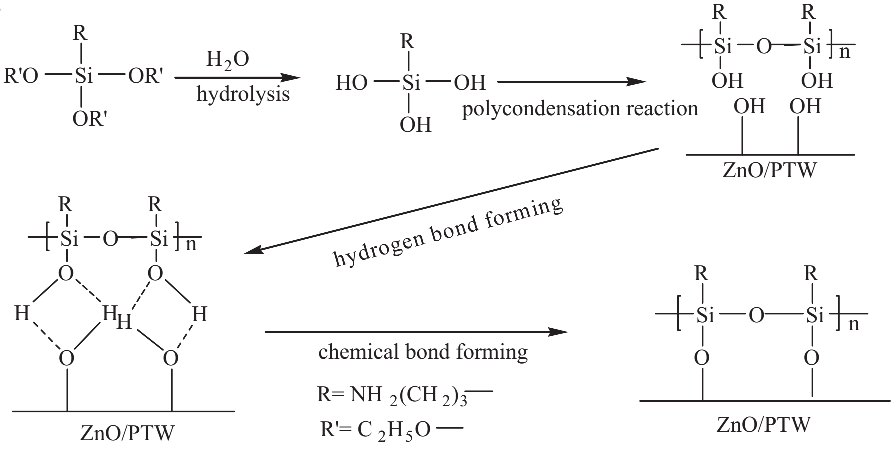


Fig. 6. Contact angles of water on (a) 5 wt.% KH550 modified ZnO/PTW, (b) 3 wt.% KH550 modified PTW, (c) ZnO/PTW.



Scheme 1. The mechanism of KH550 reacts with ZnO/PTW.

Table 2
Surface free energies and components of modified ZnO/PTW, PTW and untreated PTW.

Samples	γ_s/mJ m^{-2}	γ_S^d/mJ m^{-2}	γ_S^p/mJ m^{-2}
Untreated PTW [21]	69.2	20.1	49.1
Modified ZnO/PTW	26.8	26.4	0.4
Modified uncoated PTW	32.3	30.2	2.1

γ_s represents surface free energies of solids; γ_S^d and γ_S^p refer to dispersive and polar components of surface free energies of solids.

matrix and an enhancing of the degree of interface adhesion. We inferred that when the surface of PTW coated with ZnO nanoparticles, it could provide more active sites and it was easier to absorb and react with the coupling agent compared with uncoated PTW.

The effect of ZnO on the surface modification of PTW is to increase the chemical reactivity. ZnO nanoparticles coated on the surface of PTW can increase the surface area that could absorb more amount of KH550 on the surface than uncoated PTW. Meanwhile, KH550 reacts with —OH that provided by ZnO [23] on the surface of PTW. The process of the reaction [24] is shown in Scheme 1. So, ZnO coated on the surface of PTW could increase the chemical reactivity and improve the hydrophobic property of PTW after treated by KH550.

4. Conclusions

ZnO coated PTW has been prepared by a facile chemical method. SEM images, EDS spectra, FT-IR spectra and XRD analysis revealed the successful coating of ZnO on PTW surface, and when the coating amount of ZnO was 5 wt.%, the performance of ultraviolet absorption of ZnO/PTW composite material was better.

After modified by KH550, modified ZnO/PTW showed better dispersion in ethanol solvent; the surface free energy of modified ZnO/PTW had greatly reduced; the value of the polar component of modified ZnO/PTW was lower than that of modified uncoated PTW. Thus modified ZnO/PTW exhibited higher hydrophobic and lipophilic. The possible reason was that the ZnO nanoparticles coating on PTW surface provided more active sites that could interact with KH550 easily than uncoated PTW. The surface of KH550 modified ZnO/PTW was higher hydrophobic and lipophilic, which might be a strong implication for a great improvement in the compatibility of the modified whisker and the polymer matrix.

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