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Surface Hydrophobic Modification of T-ZnOw with Silane Coupling Agent

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Abstract. Surface hydrophobic modification of T-ZnOw was experimented with silane coupling agent KH-570(gamma-(methylpropyl acyloxy)trimethoxysilane). It was shown by FT-IR that the whiskers was modified by silane coupling agents molecular compounded with the Zn-OH of whiskers. The effect of grafted modification with KH570 on hydrophobicity of T-ZnOw was characterized with dispersion stability test in an organic solvent and measuring the contact angle between the whiskers on distilled water. The results showed that surface treatment of T-ZnOw with KH570 improves hydrophobicity of whiskers simultaneously, and the modified whiskers have much slower settling rates than the pristine whiskers in the liquid paraffin. The contact angle between the modified whiskers with distilled water is 137.75^o, which is a significant increase.

Introduction

Tetra-needle-shaped zinc oxide whisker (T-ZnOw) is a special whisker with three-dimensional structure, moreover, every needle is a new kind of micro-fiber with a single crystal and the angle between every two needles is $109^o28'$[1,2].The whiskers posses many superior properties such as high strength ,wear resistance and antibacterial effect .Because of its unique structure and properties , it has been considered as an ideal inorganic filler. It will have a wide-spread application in many different activities such as adhesives, rubber, plastic and so forth. Unfortunately, due to the high surface free energy, the whiskers aggregates easily, and this limits its applications in a large extend [3]. Therefore, it is necessary to make a suitable surface modification of whiskers in order to be more evenly dispersed and improve the interfacial adhesion.

Silane coupling agents are recognized as efficient modifier successfully applied in inorganic filler. It is composed of two functional end groups that can react with the matrix and the filler. As a consequence, the silane coupling agent functions as a bridge between matrix and filler and enhances the interfacial adhesion. Meanwhile, it can also reduce the surface free energy of whiskers and improve dispersion under the treatment of Silane coupling agents.

T-ZnOw was successfully treated with KH570 and hydrophobicity of whiskers was studied.

Experimental

Materials. T-ZnOw was supplied by Kunming metallurgical research institute, China. The silane coupling agent, KH570((3-glycidoxypropyl)trimethoxysilane) was purchased from Nanjing Xiangqian Chemical Co. Ltd, and its thinner, anhydrous ethanol was obtained from Tianjin zhiyuan Chemical Reagen Co. Ltd, China.

Surface modification of T-ZnOw

Modification mechanism. The modification mechanism of T-ZnOw with silane coupling agent was given in Fig.1. Scheme A shows the hydrolysis of alkoxy groups of silane coupling agent. In the presence of H^+, alkoxy groups were transformed into silanol groups. Scheme B shows the condensation between silanol groups, and then forming oligomers with a certain degree of polymerization. Scheme C shows the dehydration reaction. This reaction taken place between hydroxyl on the surface of T-ZnOw and hydroxyl of oligomers, eventually forming –Si-O-Si- bond ,and then the final products were gotten.

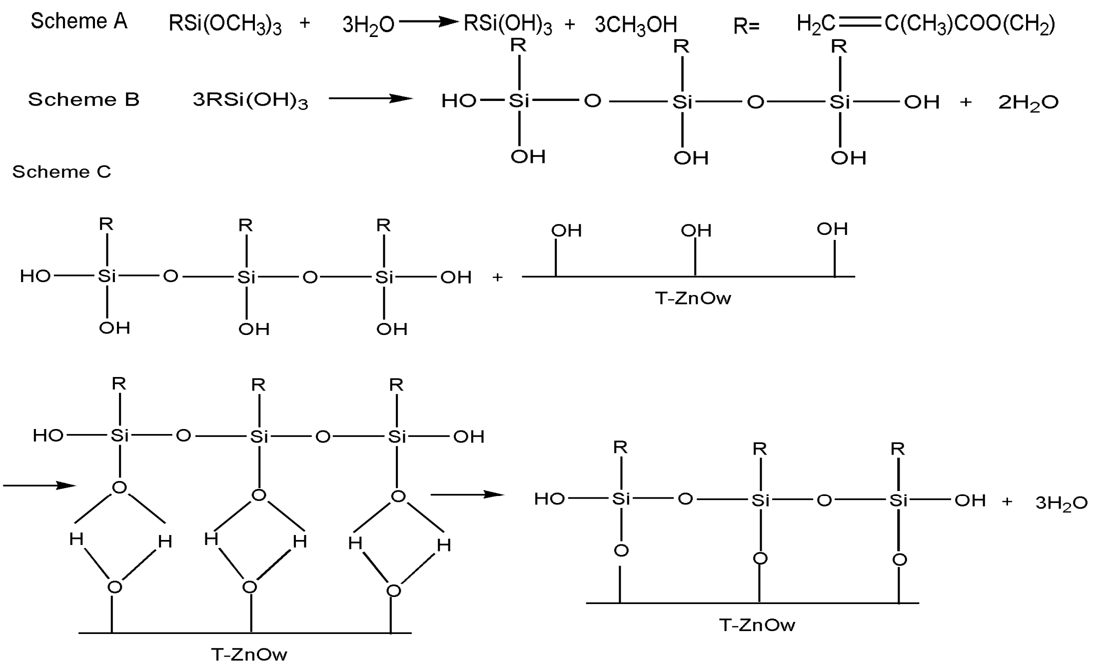

Fig.1 Reaction schemes for the modifiton of KH570 onto T-ZnOw

Experimental method. A certain amount of T-ZnOw were kept in a vacuum box for 12h at 80℃, and then dispersed in 200ml anhydrous ethanol for 20min under stirring. An appropriate amount of KH570 was added drop wise to the mixture. The reaction mixtures were then continually stirred for 4h at 70℃ in a three neck round bottom flask. Modified whiskers were filtered and subsequently washed with distillated water and anhydrous ethanol to remove the unattached KH570. Afterwards, the whiskers were dried completely under vacuum at 120℃ for 12h.

Characterization. FT-IR spectra of samples were recorded by a Nicolet 8700 (US) spectrometer by making their pills with KBr.

The contact angles were obtained by a JC2000A the infusion contact angle /interfacial tension.

Dispersion stability of modified whiskers and pristine whiskers were evaluated in the liquid paraffin.1g different whiskers were added in 15ml liquid paraffin, and then were dispersed by stirring for 3min. The sedimentation volume was recorded every 30min until it remained unchanged.

Results and discussion

FT-IR analysis. Fig.1 shows FT-IR spectra of T-ZnOw that modified and unmodified by KH570. Fig. 1(1) and (2) correspond to the pristine whiskers and modified whiskers, respectively. The broad band at 3450cm^{-1} are attributed to the –OH group on the surface of T-ZnOw, however, the intensity of absorption becomes weak after modifition. It indicates that surface treatment of T-ZnOw with KH570 improves hydrophobicity of whiskers .The bands of 1733cm^{-1} should correspond to C=O of KH570 and the appearance of the bands at 1130 cm-1 and 1000 cm^{-1} are indicative of the formation of Si-O-Zn or Si-O-Si bonds resulting from the reaction of KH570 molecules[4].Meanwhile, the strong characteristic absorption peaks of Si-O-CH_3 of the KH570 at 2817cm-1 and 1190cm-1 became inconspicuous, which was possible due to the hydrolyzation of the KH570 and the hydrolysate interacted with the –OH on the surface of T-ZnOw[5]. All these facts indicate that dehydration reaction occurred between –OH got from KH570 hydrolyzed and –OH absorbed on the surface of whishers.

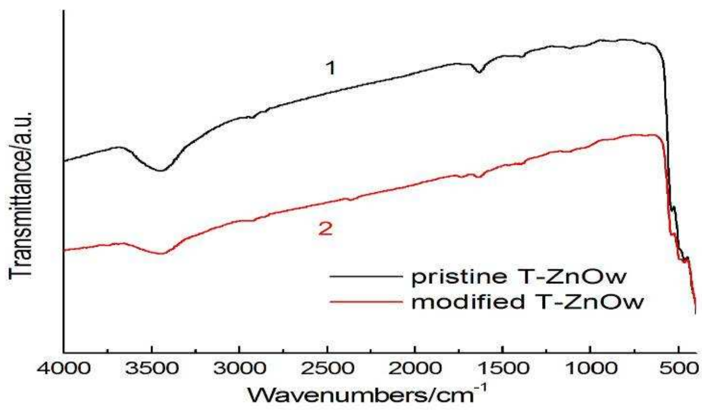

Fig.2 FT-IR spectra of pristine whiskers and modified whiskers

Dispersion stability test in liquid paraffin. As the pristine T-ZnOw contains a large number of hydroxy group on its surface, it is considered as a highly polar substance and, thus, it is less compatible to non-polar solvent such as liquid paraffin. T-ZnOw tends to strongly agglomerate into bundles and shows poor dispersion in liquid paraffin.Consequently,the suspensions separated very quickly into sediments .The particles are easy to form a loose sediments under the role of bridging effect. However , there was a layer of organic film coated whiskers after modification that could yield a better compatibility between the whiskers and liquid paraffin. The whiskers were completely wetted and well dispersed. The modified whiskers had much slower settling rates and they remained in the supernatant for long time[6]. As fig.3 shown , the settling rates of the pristine T-ZnOw was much faster than the modified whiskers before 400 minutes. From 400 minutes to 1600 minutes, the sedimentation volume of pristine T-ZnOw was constant, while the midified whiskers' sedimentation volume reduced continuously .At last , they were respectively stayed at 7.9 ml and 5.9 ml. That was because bridging effect didn't play a role in the process of settlement and the sediments formed by the whiskers were close .

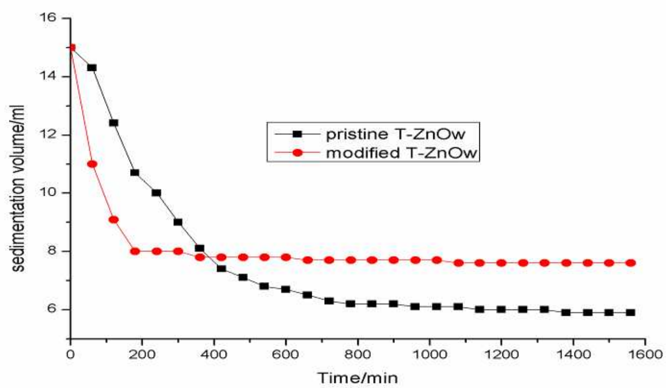

Fig.3. Sedimentation behavior of whiskers before and after modification in liquid paraffin

Contact angle test. Fig.4 shows the contact angle between T-ZnOw and distilled water. Good is obviously seen from Fig. 4(a), for the modified T-ZnOw, the good hydrophobicity showed in Fig.4(b). The visual comparison indicts that KH570 play an important role in changing T-ZnOw from hydrophilicity to hydrophobicity.

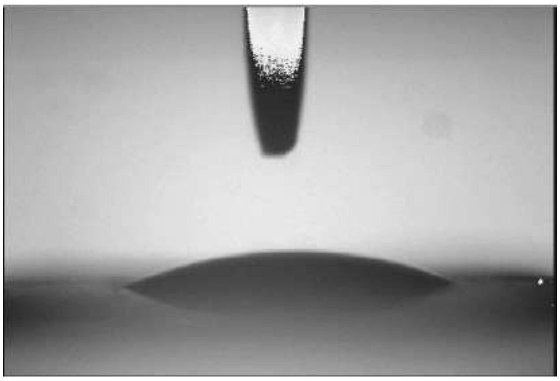

Fig.4(a) contact angle between pristine whiskers on distilled water

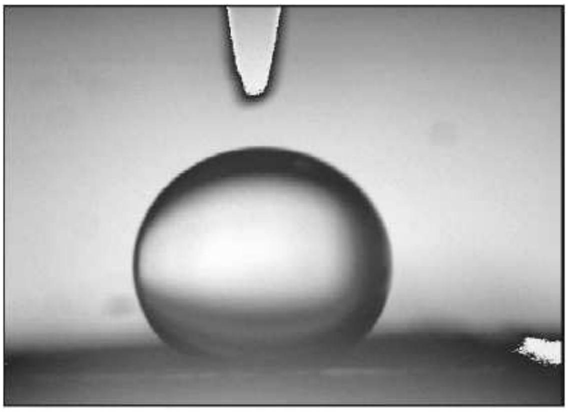

Fig.4(b) contact angle between modified whiskers on distilled water

Conclusions

Surface modification and characterization of T-ZnOw were studied. The results showed that surface treatment of T-ZnOw with KH570 improves the whiskers dispersion and hydrophobicity. It was showed by FT-IR that the hydroxide hydrolysating of KH570 can react with the hydroxide on the surface of T-ZnOw.

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