

Surface Treatment and Application in Acrylic Polyurethane Coating of Nano-Scale ZnO Powders

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In this paper, the nano-scale ZnO powders were prepared by sol-gel method and modified with toluene diisocyanate (TDI). The modified nano-scale ZnO powders can disperse in acrylic polyurethane coating homogeneously. The dispersion stabilization of modified ZnO powders in acrylic polyurethane coating was significantly improved in comparison with the as-prepared ZnO powders, which was due to the introduction of grafted polymers by surface treatment. The ultraviolet absorption ability of nano-scale ZnO powders were tested by UV spectrophotometer, when the modified nano-scale ZnO powders are added into the acrylic polyurethane coating. The addition amount of ZnO powders improve and the ultraviolet absorption ability.

Key Words: Nano-scale ZnO powders, Surface treatment, Ultraviolet absorption.

INTRODUCTION

Zinc oxide has been widely studied over the past two decades since it is a promising material for optical, electrical, catalytic and piezoelectric applications, *e.g.*, solar cells, ultraviolet light-emitting diodes (UV-LED), optical waveguides, varistors, gas sensors, surface acoustic wave (SAW) devices, transparent conducting electrodes and field emission devices. More importantly, ZnO has the direct band gap of about 3.37 eV at room temperature and its large exciton binding energy of about 60 meV, which is significantly larger than the thermal energy at room temperature (26 meV)¹. Thus, ZnO is one of the most promising materials suitable for ultraviolet light resistance. It is reported that nano-scale ZnO powders can be added into the acrylic polyurethane coating to improve its ultraviolet light resistance properties.

But the nano-scale powders are inorganic and are easy to agglomerate due to the drawbacks of traditional method of preparation²⁻⁵. For example of hydrolytic sol-gel method, the reason is that, in the absence of sulfate ions, the precursor consists of fine particles that have been joined together by hydroxyls to form a network structure similar to a gel, so that the precursor is not only difficult to wash, but even after washing and filtration much water is still retained in fine channels of the network. Fig. 1 contains a schematic diagram of this network structure⁶. So the surface treatment of nanoparticles is a necessary work for the well dispersion of nanoparticles in acrylic polyurethane coating.

There are several methods^{7,8} to modify the surface of nanoparticles. The chemical treatment and functionalization

of the nanoparticles surface can be used to enhance the nanoparticles' overall properties for targeted applications⁹⁻¹².

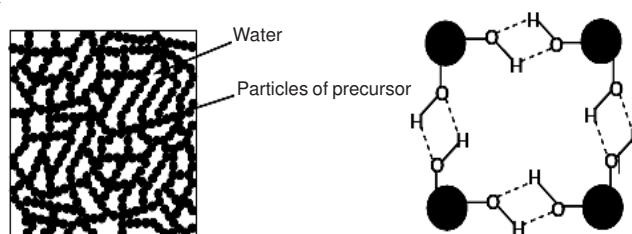


Fig. 1. Schematic diagram of the structure of the precursor in the absence of sulfate ions

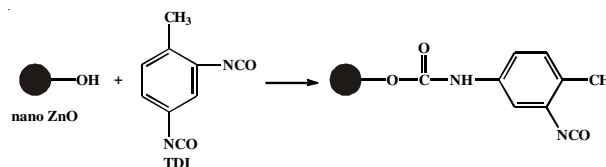


Fig. 2. Modified principle of toluene diisocyanate

In this work, nano-scale ZnO powders were prepared by sol-gel method and modified with toluene diisocyanate (TDI). The modified principle of toluene diisocyanate was shown in Fig. 2. Such processed nano-scale ZnO powders showed good dispersion stability in acrylic polyurethane coating. The ultraviolet absorption ability of nano-scale ZnO powders were tested by UV spectrophotometer, when the modified nano-scale ZnO powders are added into the acrylic polyurethane coating.

EXPERIMENTAL

Prepared and treatment of nano-scale ZnO powders:

For clarity, the experimental method was described with seven steps as follows: (1) 2 g of zinc acetate [$\text{Zn}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$] was added into 100 mL of alcohol (95 %) and heated stirring for 2 h (solution A). (2) The addition of certain amount of ammonia with constant into the solution A until the pH value of solution A was set at 6 and then the solution was to form sol. (3) The sol was heated with constant stirring for 1 h at 50 °C to form gel. (4) The gel was put into the muffle furnace at 450 °C for 3 h and then the nano-scale ZnO powders were obtained. (5) The prepared nano-scale ZnO powders were dissolved in 80 mL alcohol (95 %) and heated with stirring for 1 h (solution B). (6) The 0.4 g toluene diisocyanate was added into the solution B and heated with stirring for 2 h at 50 °C (solution C). (7) The solution C was dried in an oven at 100 °C. Finally, the processed nano-scale ZnO powders were prepared.

Characterizations of nano-scale ZnO powders: The crystal form of nano-scale ZnO powders was analyzed by X-ray diffraction analyzer (XRD, D8 ADVANCE, BRUKER). The zeta-potential absolute value of powders was measured by zeta potential analyzer (Zeta PALS; phase analysis light scattering; BIC). Through scanning electron micrograph (SEM, QUANTAFEG 250; FEI) observation, the dispersibility of ZnO nanoparticles was investigated. Finally, the ultraviolet absorption ability of nano-scale ZnO powders were tested by UV spectrophotometer.

RESULTS AND DISCUSSION

X-ray diffraction analysis: Fig. 3 is the X-ray diffraction pattern of the ZnO powders obtained by surface processing. From the pattern, we can see that the powders' crystal structure was wurtzite of ZnO. This shows that ZnO nanoparticles were prepared successfully in this work.

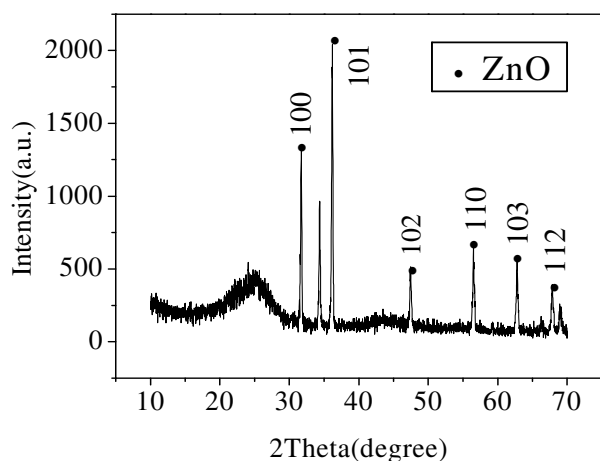


Fig. 3. X-ray diffraction pattern of the nano-scale ZnO powders

Decentralized stability of nano-scale ZnO powders:

The reunions between nanoparticles are characterized by zeta potential absolute value. The value is greater and the reunion is slighter. The absolute value of zeta potential of nanoparticles were measured six times and then averaged to ensure the data accuracy. The absolute value of zeta potential of nano-scale

ZnO powders is shown in Table-1. As shown in Table-1, absolute value of zeta potential of modified ZnO powders is greater than native ZnO powders. These indicate that the static repelency of modified ZnO powders becomes bigger than native ZnO powders. The dispersibility of modified ZnO powders is well than native ZnO powders.

TABLE-1
ABSOLUTE VALUE OF ZETA POTENTIAL OF
NANO-SCALE ZnO POWDERS

Number	1	2	3	4	5	6	Mean
Native ZnO powders	8.8	8.6	9.1	9.0	9.3	9.1	9.0
Modified ZnO powders	11.9	12.2	11.8	12.2	12.0	12.3	12.1

SEM morphology of nano-scale ZnO powders: In order to represent detailed morphological information of the specimens, the SEM images of native nano-scale ZnO powders and modified nano-scale ZnO powders is obtained, as shown in Fig. 4. The obvious agglomeration can be seen in the images of native nano-scale ZnO powders (Fig. 2a) and the homogeneous dispersion can be seen in the images of modified nano-scale ZnO powders (Fig. 2b). This suggests that chemical bonding or physical bonding occurs between the cyano bonds of toluene diisocyanate and surface hydroxide group of ZnO powders. The macromolecular chains grafted on the surface of ZnO powders bring mutual exclusion and steric hindrance effect, thus the surface free energy has been reduced correspondingly and the agglomeration is controlled. The results above further illustrate that toluene diisocyanate has played an important role in the dispersion of nano-scale ZnO powders.

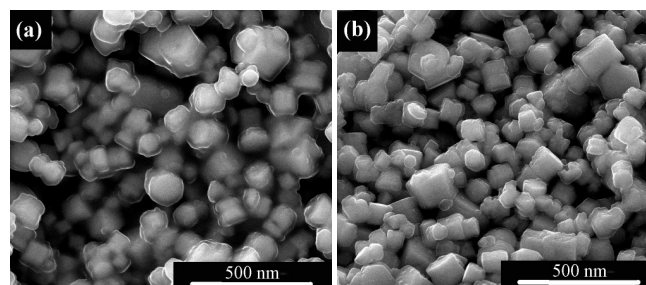


Fig. 4. SEM images of nano-scale ZnO powders; (a) Native nano-scale ZnO powders; (b) Modified nano-scale ZnO powders

Ultraviolet light resistance properties of nano-scale ZnO powders:

The nano-scale ZnO powders were added into the acrylic polyurethane coating under different concentration fraction (mass concentrations were: 0, 0.5 and 1 wt %) to made samples. The ultraviolet absorption ability of different samples was tested by UV spectrophotometer. Fig. 5 is the UV absorption spectrum of different samples. The ultraviolet absorption ability of samples including ZnO powders is increased compared to the samples without including ZnO powders. Meanwhile, the addition amount of ZnO powders increases the ultraviolet absorption ability. So the ultraviolet absorption ability of acrylic polyurethane coating is more which contains nano-scale ZnO powders. It also means that acrylic polyurethane coating, which contains nano-scale ZnO powders has good ultraviolet light resistance properties.

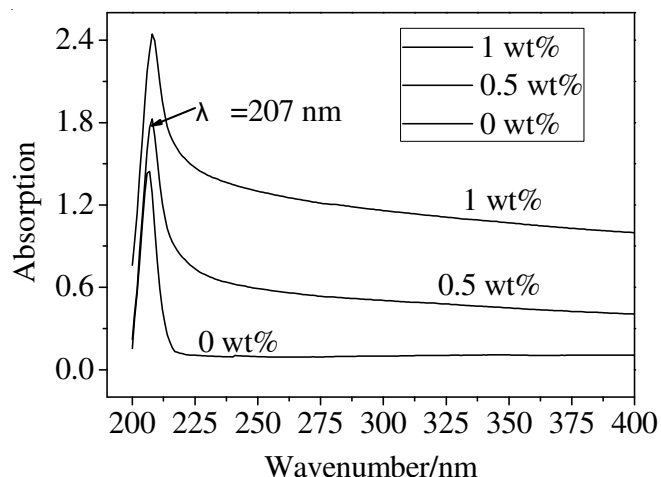


Fig. 5. UV absorption spectrum of different samples

Conclusion

In this paper, nano-scale ZnO powders were prepared with sol-gel method and modified with toluene diisocyanate (TDI). The modified nano-scale ZnO powders presented a more stable colloidal dispersion in acrylic polyurethane coating than that of native ZnO powders. The ultraviolet absorption ability of

nano-scale ZnO powders were tested by UV spectrophotometer, when the modified nano-scale ZnO powders are added into the acrylic polyurethane coating. The addition amount of ZnO powders increase the ultraviolet absorption ability. It also means that acrylic polyurethane coating which contains nano-scale ZnO powders has good ultraviolet light resistance properties.

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