HYGIENIC PROPERTY AND WATER RESISTANCE OF WATERBORNE POLYACRYLATE/FLOWER-LIKE ZNO COMPOSITE COATINGS

Yan Bao[1,a], Lu Gao[1] and Jianzhong Ma[1,b]

1 *College of Bioresources Chemical and Materials Engineering, Shaanxi University of Science and Technology, Xi'an, 710021, PR, China,*

Corresponding author: baoyan@sust.edu.cn

Another author: majz@sust.edu.cn

Abstract: Polyacrylate as film-forming materials has been widely used in leather finishing, but its compactness significantly obstructs the hygienic property of upper leather. Therefore, considerable efforts have been made to endow polyacrylate with required properties. In this study, we demonstrated a facile and rapid sonochemical process to synthesis the flower-like ZnO nanostructures. The related morphology and structure of product were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Afterwards, flower-like ZnO were introduced into the polyacrylate matrix by physical blending method and the morphology, latex stability, water vapor permeability and water resistance of polyacrylate/flower-like ZnO composites were studied. The results showed that flower-like ZnO assembled by ellipsoid-like nanorods with the length of about 600 nm was successfully fabricated. The average size of flower-like ZnO was 1.2 µm. According to SEM images, flower-like ZnO evenly dispersed were observed in composite matrix. Compared with pure polyacrylate, polyacrylate/flower-like ZnO composites exhibited superior stability. Meanwhile, its water vapor permeability and water resistancewere increased by 52.91% and 53.13%, severally. The reason for this is that ZnO with rough structure can increase voids in polyacrylate film and thus improving hygienic property of polyacrylate film. Additionally, the hydrophilic groups on surface of ZnO can crosslink with polyacrylate chains, which contributed to the enhancement of water resistance. Thus, a promising coating with hygienic property and water resistance for leather finishing agent was approved.

Keywords: Polyacrylate/flower-like ZnO composites, hygienic property, water resistance, leather finishing.

1 Introduction

Significant efforts have been devoted to developing waterborne polyacrylate due to the strict environmental regulations. Waterborne polyacrylate coating, possessing good adhesion, transparent coating and aging resistance, is attractive for leather finishing[1]. However, the hygienic property of leather finished by polyacrylate might be decreased due to its compactness. Besides, the polyacrylate offers weak water resistance under lots of hydrophilic groups[2]. In recent years, the modification of polyacrylate is of great interest and importance. To the best of our knowledge, various methods have been employed to modify polyacrylate, mainly including introducing functional monomers, modifying by polyurethane and introducing inorganic nanomaterials (e,g., SiO_2, ZnO, TiO_2, etc.)[3~8]. Our research group has been engaging in the study on polyacrylate/inorganic nanocomposites[9~13]. Previous research showed that the properties enhancement of polyacrylate film was associated with the morphology of nanomaterials.

In this study, we developed an ultrasonic route to prepare flower-like ZnO, which was acted as a fortifier to the modification of polyacrylate. A serious characterizations of XRD, SEM and TEM were carried out to demonstrate flower-like ZnO and polyacrylate/flower-like ZnO composites. The results indicated that the water vapor permeability, water resistance, mechanical properties and UV resistance of polyacrylate/flower-like ZnO composite film were enhanced by introducing flower-like ZnO.

2 Experimental Section

2.1 Materials

All reactants were of analytical grade and used as received without any further purification. Zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$, 98%, Tianjin FuChen Chemical) and ammonium hydroxide ($NH_3{\cdot}H_2O$, 99%, Hongyan) were used as zinc cation and hydroxide anion precursors, respectively. And Ethylene glycol (EG) was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. Deionized (DI) water and polyacrylate latex were prepared in the laboratory.

2.2 Synthesis of Flower-like ZnO and Polyacrylate/Flower-like ZnO Composites

For synthesis of flower-like ZnO, 5 mmol of zinc acetate was added into a mixture solution of EG and deionized water (EG:DI=1:1) under magnetic stirring to form a transparent solution. Then, NH3·H2O was dropped into the zinc acetate solution with regulating pH to 8 under continuously stirring for 30 min. The precursor slurry was then transferred into ultrasonic grinder with 2 s pulse-on and 1 s pulse-off in one pulse cycle. The precursor slurry was irradiated for 30 min. Ultimately, the precipitation was centrifuged, washed thoroughly with deionized water and absolute ethanol, and then dried at 60 °C for 6 h to obtain a dried ZnO powder.

For synthesis of polyacrylate/flower-like ZnO composites, the synthetic method was mentioned in the previous work[13].

2.3 Characterizations and Measurements

X-ray diffraction (XRD) patterns of flower-like ZnO were recorded by a D/max 2550 V diffractometer with Cu Kα radiation. The morphology and high resolution structure of flower-like ZnO were determined by scanning electron microscope (FE-SEM, Hitachi S-4800, Japan) and transmission electron microscopy (TEM, Tecnai G2 F20S-TWIN, America). Besides, SEM was also used to observe the existence status of flower-like ZnO in polyacrylate matrix.

For properties measurements, the W30/060 water vapor transmission rate test system was employed to measure the water vapor permeability of composite film. Water resistance of composite films was determined according to GB/T2223.1996. And Gotech AI-3000 servo control testing machine was applied to test the tensile strength and elongation at break of composite film. The UV transmittance curves of film were obtained by using Cary-5000 ultraviolet-visible-near infrared spectrophotometer.

3 Result and discussion

3.1 Structure and morphology

The structure and chemical composition of flower-like ZnO were confirmed by XRD patterns (Fig. 1). The obtained diffraction peaks located at 2θ =31.6°, 34.3°, 36.2°, 47.5°, 56.5°, 62.7°, 67.9 ° and 76.8° matched with (100), (002), (101), (102), (110), (103), (112) and (202) plane of ZnO (JCPDS No.36-1451), respectively. Furthermore, there was no extra peak in the XRD patterns, suggesting the prepared flower-like ZnO sample showed high purity. Fig.2a showed SEM image of flower-like ZnO. It can be observed that an integral flower-like ZnO was spliced by ellipsoidal-like ZnO with the length of about 600 nm, together with some isolated 1D spheroid and twin-spheres. The size of flower-like ZnO was around 1.2 µm.

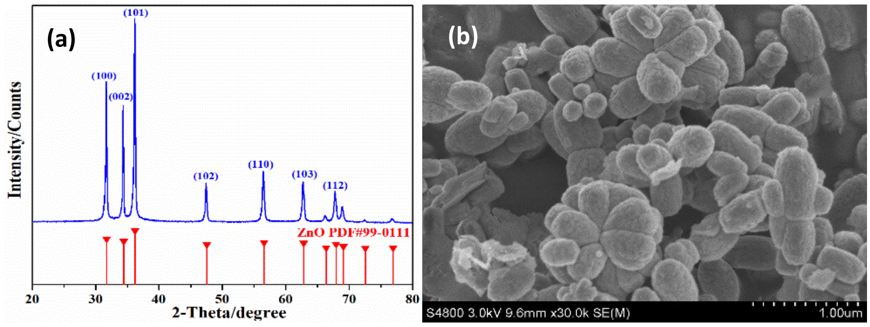

Fig. 1. (a)XRD pattern of flower-like ZnO, (b) SEM image of flower-like ZnO.

The prepared flower-like ZnO nanoparticles were introduced into polyacrylate emulsion to form composite film. Above all, the existence status of flower-like ZnO in polyacrylate matrix was investigated. It can be seen that cross-section of pure polyacrylate film was smooth without obvious cracks and bulges in Fig.2a. Different with pure polyacrylate film, the evenly dispersed flower-like ZnO nanostructures (bumps) were observed in composite matrix (Fig.2b).

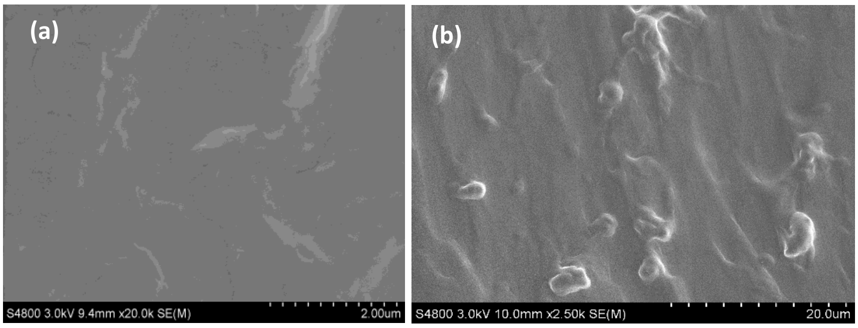

Fig. 2. SEM images of (a) polyacrylate film and (b) polyacrylate/flower-like ZnO composite film.

The investigation of the water vapor permeability, water resistance, mechanical properties and UV transmittance are necessary to evaluate the nature of composite film. Fig. 3 depicted the water vapor permeability and water resistance of composite film. It can be found the water vapor permeability and water resistance of composite film including ZnO were simultaneously enhanced. The reason of this result was that a rough structure of flower-like ZnO can produce abundant interface gaps between flower-like ZnO and polyacrylate matrix, which promoted water vapor across the film. For water resistance, this can be interpreted that the hydroxyl groups and positive charge on the surface of flower-like ZnO could react with the carboxyl groups on polyacrylate chains, which reducing the number of hydrophilic groups of film. Compared with pure polyacrylate film, the water vapor permeability and water resistance of composite film were increased by 52.91% and 53.13%, severally.

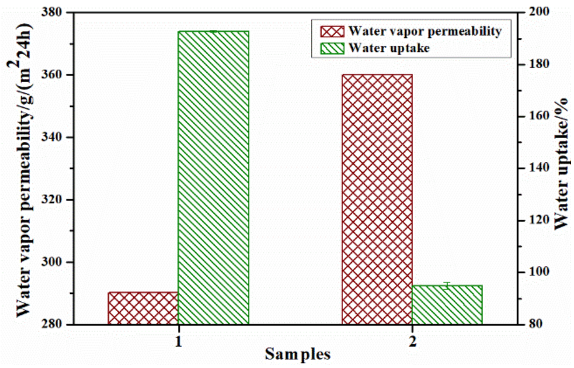

Fig. 3. Water vapor permeability and water resistance of polyacrylate film (Sample 1) and polyacrylate/flower-like ZnO composite film (Sample 2).

As leather finishing agent, the mechanical properties of film plays an important role for leather performance. In this work, the mechanical properties of composite film were inspected by testing its tensile strength and elongation at break. As shown in Fig. 4a, the tensile strength of composite film was better than that of pure film, but the elongation at break was lower, which was consistent with the results of polyacrylate/hollow ZnO nanospheres in our previous work[13]. Due to the enhancement of interface effect between flower-like ZnO and polyacrylate film, the tensile strength of composite film was increased. But as inorganic matter, ZnO nanoparticles with certain rigidity cause the crazes in the film, resulting in the decline of elongation at break. In conclusion, polyacrylate/flower-like ZnO composite film can meet the needs of leather finishing. In addition, the UV transmittance of both samples was determined in Fig. 4b. Polyacrylate/flower-like ZnO composite film had a lower UV transmittance than polyacrylate film, suggesting the composite film possessed a higher UV resistance. This result might be explained by well-known mechanism that ZnO nanoparticles possess absorption and scattering for UV light. When the UV light irradiated on the composite film, the intensity of UV irradiation for the film was reduced through flower-like ZnO absorbing and dispersing UV light in all directions.

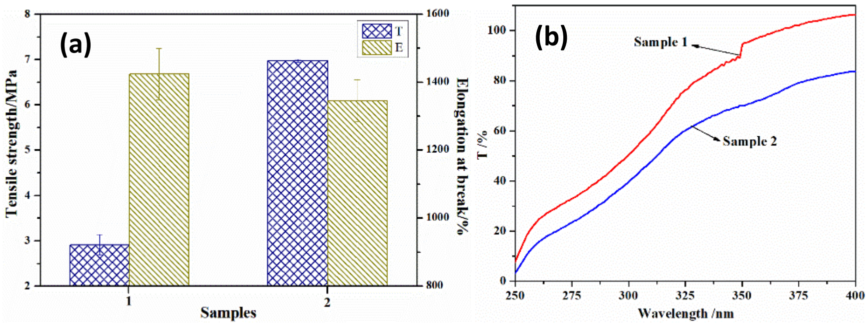

Fig. 4. (a) Mechanical properties of polyacrylate film (Sample 1) and polyacrylate/flower-like ZnO composite film (Sample 2), and (b) UV transmittance of the corresponding film.

4 Conclusions

In summary, we have developed an ultrasonic method for fabricating flower-like ZnO nanostructures with an average diameter of ~1.2 µm. The as-synthesized ZnO products were introduced into polyacrylate matrix whose water vapor permeability, water resistance, mechanical properties and UV resistance were improved. Compared with the pure polyacrylate film, the water vapor permeability, water resistance and tensile strength of composite film were increased by 52.91%, 53.13% and 58.85%, respectively.

References

1. *Zhang K, Shang S, Sun P, et al. Hydrogenated rosin ester latexes/waterborne polyacrylate blends for pressure-sensitive adhesives, J. Appl. Polym. Sci., 133(6), 2016.*
2. *Bao Y, Feng C, Wang C, et al. Hygienic, antibacterial, UV-Shielding performance of polyacrylate/ZnO composite coatings on a leather matrix, Colloids Surf., A, 518, 232-240, 2017.*
3. *Zhu B, Liu J, Chen Y, et al. Superhydrophobic coating with multiscale structure based on crosslinked silanized polyacrylate and nanoparticles, Surf. Coat. Technol., 331, 40-47, 2017.*
4. *Lü T, Qi D, Zhang D, et al. Fabrication of self-cross-linking fluorinated polyacrylate latex particles with core-shell structure and film properties, React. Funct. Polym., 104, 9-14, 2016.*
5. *Huang K, Liu Y, Wu D. Synthesis and characterization of polyacrylate modified by polysiloxane latexes and films, Prog. Org. Coat., 77(11), 1774-1779, 2014.*

6. *Wang X, Shen Y, Lai X. Micromorphology and mechanism of polyurethane/polyacrylate membranes modified with epoxide group, Prog. Org. Coat., 77(1), 268-276, 2014.*
7. *Mikleči J, Blagojević S L, Petrič M, et al. Influence of TiO_2, and ZnO nanoparticles on properties of waterborne polyacrylate coating exposed to outdoor conditions, Prog. Org. Coat., 89, 67-74, 2015, .*
8. *Sheng X, Xie D, Wang C, et al. Synthesis and characterization of core/shell titanium dioxide nanoparticle/polyacrylate nanocomposite colloidal microspheres, Colloid Polym. Sci., 294(2), 463-469, 2015.*
9. *Bao Y, Shi C, Yang Y, et al. Effect of hollow silica spheres on water vapor permeability of polyacrylate film, RSC Adv., 5(15), 11485-11493, 2015.*
10. *Liu J, Ma J, Bao Y, et al. Polyacrylate/surface-modified ZnO nanocomposite as film-forming agent for leather finishing, Int. J. Polym. Mater. Polym. Biomater., 63(16), 809-814, 2014.*
11. *Liu J, Ma J, Bao Y, et al. Nanoparticle morphology and film-forming behavior of polyacrylate/ZnO nanocomposite, Compos. Sci. Technol., 98(16), 64-71, 2014.*
12. *Kang Q, Bao Y, Li M, et al. Effect of wall thickness of hollow TiO_2 spheres on properties of polyacrylate film: Thermal insulation, UV-shielding and mechanical property, Prog. Org. Coat., 112, 153-161, 2017.*
13. *Bao Y, Feng C, Wang C, et al. One-step hydrothermal synthesis of hollow ZnO microspheres with enhanced performance for polyacrylate, Prog. Org. Coat., 112, 270-277, 2017.*