The Study of Preparation and Properties of Nano-TiO_2 / Waterborne Polyurethane

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Abstract

TiO_2 is an inexpensive and highly versatile material and its performance is much better after becoming nano-TiO_2. Nano-TiO_2 added in waterborne polyurethane emulsion can improve the application performance of waterborne polyurethane. We study the impacts of the dispersant on nano-TiO_2 dispersed in water, determine the optimum dispersion process. By dispersing nano-particle directly to get nano-TiO_2 / WPU composite film. Performances of nano-TiO_2 was discussed through polymorph, infrared spectra, particle size and stability and so on. The results indicated that the nano-TiO_2 particle size is approximately 50nm and the majority of the morphology of the nano-TiO_2 is approximately circular. Performances of nano-TiO_2 / waterborne polyurethane film was discussed through SEM, AFM, contact angle, hygiene, mechanical properties and so on. The analyses of viscosity showed that nano-TiO_2 had the effects on the increase of viscosity and the analyses of grain diameter showed that there were no differences on the stability of polyurethane-emulsion with adding nano-TiO_2 or not, and the composite particle still existed at the nanoscale. Nano-TiO_2 dispersed uniformity in composite film and had no effects on the flatness of it. The contacting angles and hygiene performance tests indicated that composite film had no water-proof properties. The mechanical test manifested that adding nano-TiO_2 had better mechanical properties.

Key words：nano-TiO_2；waterborne polyurethane；dispersant；complex film

1. Introduction

The waterborne polyurethane is the best environmental material in synthetic leather production. It is alternative to solvent-based polyurethane and has the advantages of non-toxicity, environmental protection and easy modification[1]. TiO_2 is an inexpensive and highly versatile material and its performance is much better after becoming nano-TiO_2[2-3]. Nano-TiO_2 added in waterborne polyurethane emulsion can improve the application performance of waterborne polyurethane. New nano-composites have many characters of polyurethane, TiO_2 and nanomaterials in order to improve the mechanical properties of the polyurethane film and antibacterial antifungal properties. However, due to the surface of the

nano-TiO_2 particles tending to agglomeration, secondary particles were formed and it is easy to become a stress concentration point in the composite material. These reasons limit its use[4-6]. In this experiment, we study the impacts of the dispersant on nano-TiO_2 dispersed in water, determine the optimum dispersion process, and then prepare the nano-TiO_2 / waterborne polyurethane composite emulsion, which has better compatibility and can be uniformly dispersed in waterborne polyurethane by ultrasound. It makes nano-TiO_2 / waterborne polyurethane composite membrane have the healthy performance and improve tensile properties in order to provide some theoretical basis for the practical application of the leather materials.

2. Material and Methods

2.1 Materials

Triethanolamine, CR, (Chemical Reagents Sixth Factory, Tianjing); Tripolyphosphate, AR (Chemical Reagents Sixth Factory, Tianjing); Sodium hexametaphosphate, AR (North Fine Chemical Co., Ltd, Tianjing); Sodium carboxymethylcellulose, AR (Kelong Chemical Reagents Factory, Chengdu); Polyethylene glycol (6000) (Binhai Chemical Plant, Tianjing); Sodium dodecyl sulfate, AR (Bodi Chemical Co., Ltd, Tianjing); Sodium silicate, AR (Haiguang Chemical Pharmaceutical Factory, Tianjing); Deionized water (Robust Company); The aqueous polyurethane (solid content of 30%), Thickener 240, Defoamers (Huada Chemical Co., Ltd, Yantai).

2.2 Methods

2.2.1 Preparation of nano-titanium dioxide

Tetrabutyl titanate and acetic acid were slowly added to anhydrous ethanol with magnetic stirring for 30min to form a clear yellow solution A. Water and ethanol were added to a three-necked flask and the concentrated hydrochloric acid was added dropwise to the mixed solution under mechanical stirring, the pH was adjusted to 1, forming a mixed solution B. Solution A was slowly dropped to solution B with stirring continually for about 3h. After 24h aging, the pale yellow sol was obtained. The sol was dried at 80°C and after 8h, the sol was put in a muffle furnace with calcination temperature of 500°C. After grinding the product, nanometer TiO_2 powder can be got.

2.2.2 The selection of the dispersant

Seven kinds of dispersants were selected as follows: sodium hexametaphosphate (SHMP), sodium dodecyl sulfate (SDS), polyethylene glycol, triethanolamine, sodium carboxymethyl cellulose (CMC), sodium polyphosphate, sodium silicate. 30ml of dispersant solution of the same concentration (mass fraction of 1%) were prepared respectively and then each was added 0.5g nano-TiO_2 powder, with ultrasonic dispersion for 10min in a constant temperature water bath and 540W of ultrasonic power. Finally, the solution was poured into a test tube to measure the pH. The record scattered situation was allowed after standing for 24h. 1ml upper liquid was removed to dilute with deionized water until the constant volume was

50ml, and the absorbance was measured at λmax of the nano-TiO_2. According to the sedimentation phenomena and absorbance, the best dispersant hexametaphosphate was chosen.

2.2.3 Preparation of nano-TiO_2 powder suspension solution

The SHMP's best concentration was determined as 0.3% (water), then 2g nano-TiO_2 was added into 30ml deionized water to contain SHMP. An ultrasonic cell crusher (JY92-2D, China) was used to disperse the nano-TiO_2 with ultrasound at 540W in constant temperature water bath for 10 min.

2.2.4 Preparation of nano-TiO_2 / waterborne polyurethane composite membrane

40g of an aqueous polyurethane emulsion was added to each of the seven beakers, and then different ratios of nano-TiO_2 powder suspension was added respectively, and then an appropriate amount of antifoaming agent and a thickener were added to ultrasonically disperse in a constant temperature water bath for 10min. Finally a uniformly dispersed composite emulsion was obtained. The composite emulsion was poured to the seven glass plates with a thickness of 0.6mm, dried at 50°C for 30min, and then dried at 100°C. Finally, nano-TiO_2 / waterborne polyurethane composite film can be got.

2.2.5 Characterization

A laser particle size analyzer (BT-9300Z, Dandong Baxter Technology) was used to determine the composite emulsion particle size and zeta potential.

A scanning electron microscope (SEM, KYKY1000B, China) was used to observe the distribution of TiO_2 nanoparticles in the composite film surface and cross-sectional. Image analysis software was used to analyze the SEM photographs in order to obtain the data of nano-TiO_2 particle size. An atomic force microscopy (AFM, SPA400-SPI3800N, Japan) was used to observe the surface roughness of the composite membrane.

At room temperature (20°C), the contact angle of nano-TiO_2 / waterborne polyurethane composite film was measured by an optical contact angle measuring instrument (Dataphysics, Germany). The results show the average of the three measurements, the determination of the composite film of vapor permeability, air permeability, tensile strength and rupture elongation by the standards of ASTM E96[7] and QB/T2415-1998.

3. Results and discussion

3.1 The analysis of nano-TiO_2 polymorph

The XRD pattern of nano-TiO_2 powder was recorded by X-ray diffractometer, using Cu Ka radiation at 40 kV and 40 mA with a scan rate of 10°/min. The diffraction angle was ranged from 15° to 80° (shown in Fig.1).

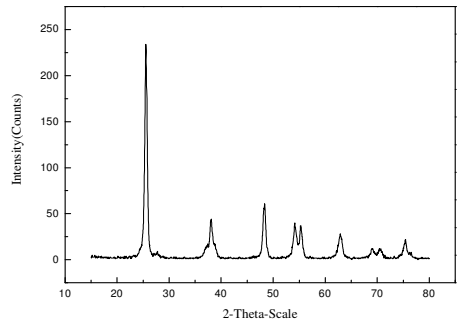

Fig.1 XRD pattern of nanometer TiO_2 powder

Fig.1 shows that nano-TiO_2 diffraction peaks are sharp, compared with the card JPCDS (No. 89-4921)[8]. The strong diffraction peaks appearing at near 25.56°, 38.12°, 48.3° of 2θ, respectively corresponding to (101), (004), (200) crystal planes are nanosized anatase TiO_2 peaks. Meanwhile, there is no other phase of the diffraction peaks in the spectra, which shows that the phase structure is uniform and single of anatase nano-TiO_2. Using XRD data of anatase nano-TiO_2 at the diffraction angles of 2θ, through (Scherre) formula, we can get the result that nano-TiO_2 particle size is approximately 50nm.

3.2 The infrared spectra analysis of nano-TiO_2

A Fourier transform infrared spectroscopy (EQUINOX55, Bruker) was used to measure the IR spectrum of nano-TiO_2.

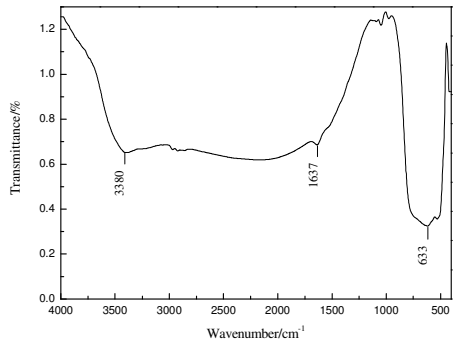

Fig.2 IR spectrum of nano-TiO_2

Fig.2 shows the peaks of the OH stretching band (νOH) of anatase nano-TiO_2 is observed at 3380cm^{-1}, the peaks of H-O-H absorption are at 1638cm^{-1} and the peaks of the Ti-O stretching band (νTi-O) of anatase nano-TiO_2 are observed at 621cm^{-1}.

3.3 The surface morphology and particle size of nano-TiO_2

Gold is sprayed to nano-TiO_2 powder and a scanning electron microscope (SEM) was used to observe the morphology and particle size of the TiO_2 nanoparticles.

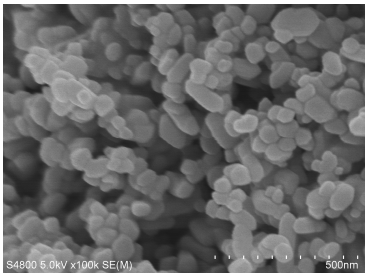

Fig.3 SEM images of nano-TiO_2

Fig.3 shows the majority of the morphology of the nano-TiO_2 is approximately circular and some are oval and rectangular. Nano-TiO_2 particle size is calculated by Scherrer formula and the size is about 50nm.

3.4 The particle size and stability of nano-TiO_2 / waterborne polyurethane composite emulsion

Because the viscosity of waterborne polyurethane is low, it's inconvenient in its application. The thickener is added to appropriately increase the viscosity. In order to investigate the impacts of TiO_2 nanoparticles on the composite emulsion viscosity, the particle size and the stability, the viscosity, particle size and zeta potential of different contents of nano-TiO_2 composite emulsion are determined. The data are shown in table 2. Zeta potential is an important indicator to characterize the stability of the dispersion[9]. Zeta potential values between ± 40 and ± 60, shows good stability.

Nano-TiO_2 mass fraction (%)	0	0.5	1	2	3	4	5
average particle size of composite emulsion (nm)	132	150	156	170	179	160	155
Zeta potential of composite emulsion (mv)	-45.2	-44.7	-43.1	-42.6	-41.2	-40.4	-41.9
viscosity (mPa/s)	1500	1540	1660	1810	1950	1860	1720

Table.1 Comparison of Nano-TiO_2 / waterborne polyurethane composite emulsion particle size, viscosity and zeta potential

Table.1 shows that with the increase in the contents of nano-TiO_2 composite emulsion, the particle size is gradually increased and the viscosity is also increased, which shows that the addition of nano-TiO_2 increases the viscosity of the polyurethane and is conducive to the polyurethane industrial application. Due to the aqueous polyurethane as anionic and titanium dioxide nano-particles with a positive charge on the surface, nano-TiO_2 would neutralize part of charges of the water-based polyurethane after mixed. Then composite emulsion Zeta potential was slightly lower than that of without adding nano-TiO_2. But it is still within the range of emulsion stability, which shows that the addition of nano-TiO_2 does not affect the stability of the water-based polyurethane emulsion.

3.5 The analysis of the surface waterproof performance of nano-TiO_2 / waterborne polyurethane composite membrane

The contact angle is one of the most common methods of evaluating the solid surface waterproof. When the contact angle is greater than 90°, the solid surface has water repellency[10]. In order to investigate the impacts of nano-TiO_2 composite membrane surface properties, the contact angles of the composite membranes were measured. Composite film is composed by different crystal forms containing different amounts of nano-TiO_2.

Tab.2 Contact angle comparison of nano-TiO_2 / waterborne polyurethane composite membrane

Nano-TiO_2 mass fraction (%)	0	0.5	1	2	3	4	5
Average contact angle (°)	65.2	67.2	68.6	72.4	75.1	73.3	70.5

From Tab.2, with the increase in the contents of nano-TiO_2, the contact angles of the composite membrane are gradually increased. When the nano-TiO_2 mass fraction is 3%, the maximum contact angle of the composite film is 75.1°. With the increase in the contents of nano-TiO_2, the contact angle becomes larger, which is mainly because these nano-TiO_2 particles present in the composite film will prevent moisture in a polyurethane film surface wetting so as to indirectly cause the contact angle of the composite film to become larger. When the nano-titanium dioxide contents are 4% and 5%, the contact angles become smaller, which may be caused by nano-TiO_2 agglomeration. No matter how much nano-TiO_2 is added, the contact angle was always less than 90°, without the waterproof performance, which may be related to the selected film forming properties of aqueous polyurethane.

3.6 The hygiene and mechanical properties analysis of nano-TiO_2 / waterborne polyurethane composite film

The water vapor permeability and the permeability are important indicators of performance of the synthetic leather hygiene (wearing comfort). In order to investigate the impacts on the performance of hygiene, the water vapor and air permeability of different contents of nano-TiO_2 composite film are measured. The results are shown in Fig.4 and Fig.5.

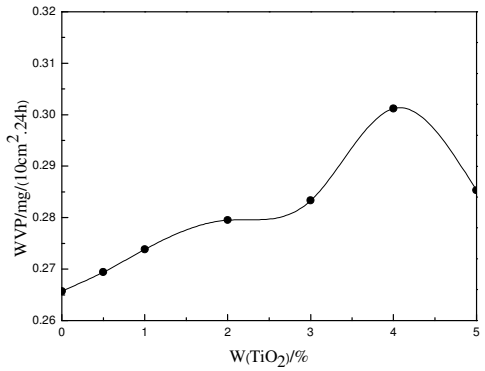

Fig.4 Relations between vapor permeability of nano-TiO_2 / waterborne polyester composite membrane and nano-TiO_2 mass fraction

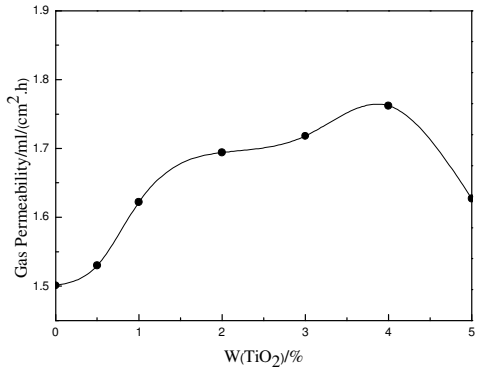

Fig.5 Relations between water vapor permeability of nano-TiO_2 / waterborne polyester composite membrane and nano-TiO_2 mass fraction

Fig.4 and Fig.5 show that the addition of TiO_2 helps to improve the water vapor permeability and air permeability of the composite film. When the nano-TiO_2 content is 4%, the water vapor and vapor permeability of composite film present are the highest. The water vapor permeability and air permeability of the composite film are increased, which is mainly due to the nano-TiO_2 polyurethane film distribution increasing the gap of the film. With the addition of nano-TiO_2, nano-TiO_2 is agglomerated so that water vapor permeability and permeability are declined.

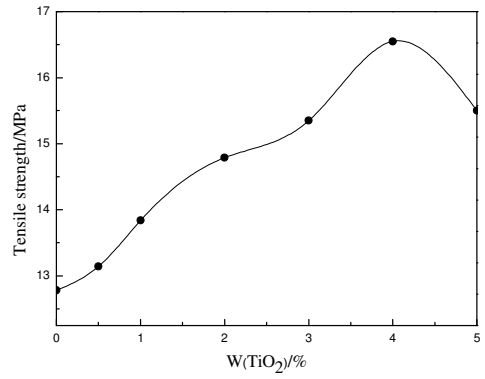

Fig.6 Relationship between tensile strength and nano-TiO_2 mass fraction

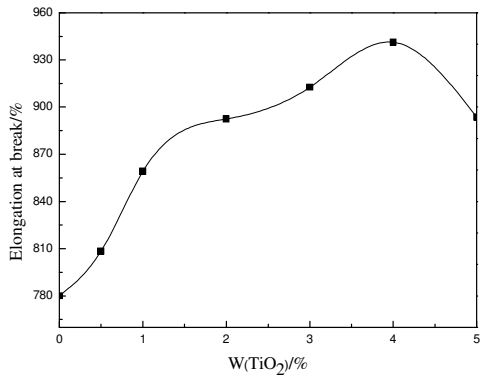

Fig.7 Relationship between composite membrane elongation and nano-TiO_2 mass fraction

Fig.6 and Fig.7 show that the addition of nano-TiO_2 can improve the tensile strength and elongation of composite membrane. When the nano-TiO_2 content is 4%, the elongation at break is 941.2%, the tensile strength is increased by 29.49% compared with blank film while the elongation at break is increased 20.6% compared with blank film. The mechanical properties of composite film are the best, which is mainly because nano-TiO_2 is a kind of inorganic material and has high hardness and strength[11]. When added in the waterborne polyurethane, nano-TiO_2 will strengthen the tensile and elongation at break of polyurethane. But with the further increasing of nano-TiO_2 contents, the tensile strength and elongation at break will also fall because the higher nano-TiO_2 contents in the polyurethane, the more seriously it gathers and particle reunion phenomenon will make up. As reunion particles easily cause the matrix to be damaged resulting in the force concentration. With the external force, reunion particles produced slip with each other, making the system performance degrade.

3.7 Distribution of nano-TiO_2 composite film

The distribution of nano-TiO_2 in the composite membrane is observed by a scan electron microscope. The results are shown in Fig.8.

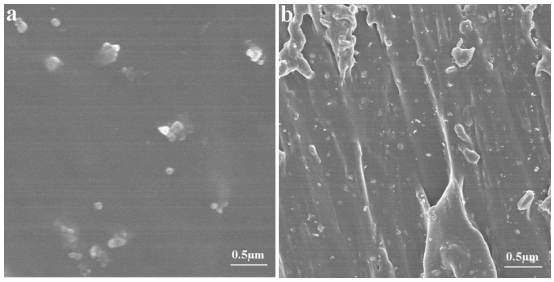

Fig.8 SEM images of the mass fraction of 4% nano-TiO_2 / waterborne polyurethane (PU) composite membrane on the surface of (a) cross section; (b) SEM

Fig.8 shows that when the nano-TiO_2 content is 4%, nano-TiO_2 generally exists in the form of monodisperse in the composite membrane and spreads evenly. When particle size is about 50 ~ 100nm, they are mostly in a state of complete isolation with each other while a small amount is partly in reunion, but it does not affect the performance of the membrane. This can be confirmed by the health performance and mechanical performance test.

3.8 Effects of nano-TiO_2 on the planeness and evenness of the composite membrane

The surface microscopic structure of the composite membrane is observed under an atomic force microscope (AFM) and the results are shown in Fig.9.

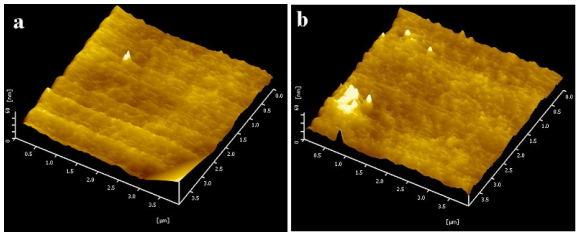

Fig.9 3D morphology of nano-TiO_2 / waterborne polyurethane composite film

Fig.9 (a) and (b) are atomic force microscope pictures of composite film: (a) blank composite film (b) nanometer TiO_2 content of 4% of composite film. The figures show that the relative roughness (Ra) and root mean square roughness (Rms) values are 3.661 and 5.446 when nano-TiO_2 is not mixed in waterborne polyurethane while Ra and Rms values of adding nano-TiO_2 composite membrane are 3.826 and 5.468, which shows that the compatibility of nano-TiO_2 in waterborne polyurethane is very good, inorganic nano-TiO_2 has no larger gathering, and nano-TiO_2 does not affect the roughness of the composite membrane on the surface.

4. Conclusion

(1) When the nano-TiO_2 mass fraction was mixed to 4%, the nano-TiO_2 / waterborne polyurethane (PU) composite film tensile is increased to 29.49% compared with the blank film and the elongation at break is increased to 20.6%, which is higher than the blank film. The mechanical properties of the composite film are the best.

(2) The water vapor permeability of composite film is 9.6% and 13.4% respectively higher than that of the blank film. The permeability is respectively 16.7% and 17.4% higher than that of the blank film. From the comparison, the properties of composite film of adding anatase type nano-TiO_2 are better.

(3) Nano-TiO_2 is distributed evenly in the composite membrane and the particle size is about 50-100nm, which has no impact on the roughness of composite membrane of the surface.

5. Acknowledgements

This work was supported by the Graduate Innovation Fund of Shaanxi University of Science and Technology, the Scientific and Technological Planning Programs of Science and Technology Department of Zhejiang Province (2011C31004), the Open Funded Subsidize of Wenzhou University (100061200118).

6. References

[1] B.K.Kim, J.C.Lee, 1996, Waterborne polyurethanes and their properties, Journal of Polymer Science: Part A, Polymer Chemistry, 34(6),1095-1104p.

[2] D P Macwan, P N Dave, S.Chaturvedi, 2011, A review on nano-TiO_2 sol-gel type syntheses and its applications, J Mater. Sci. Technol, 46(2), 3669-3686p .

[3] Lu Hong-rong, Zhang Min, Su Yan-meng, 2009, Modification of nano TiO_2 and its application, Dyeing & Finishing, 35(4), 92-12p.

[4] J. Jordan, K. I. Jacob, R.Tannenbaum, et al, 2005, Experimental trends in polymer nanocomposites-a review, Mater. Sci. Eng. A, 393(1), 1-11p.

[5] Chen YH, Lin A, Gan FX, 2006, Improvement of polyacrylate coating by filling modified nano

TiO_2, Applied Surface Science, 252(24), 8635-8640p.

[6] Guo Wen-lu, Wang Wen-ming, Guo Xiao-jun, et al, 2009, Research on the stability of nano TiO_2 in the system of water dispersion, Applied Chemical Industry, 38(2), 267-269p.

[7] Zhang Jianchun，Huang Jizhi, 2003, Waterproof and breathable Principles of fabric and production technology of laminated fabric, Beijing：China Textile & Apparel Press, 218-220p.

[8] C. Lazau, P. S firloaga, P. Vlazan, 2008, Synthesis and Characterization of Functional TiO_2 Nanomaterials, Chem. Bull, 53(67), 1-2p.

[9] K Niwa, R Kuramoto, S Anandan, et al, 2012, Zeta Potential and Hydrogen Production of Mesoporous Titanium Oxide, Procedia Engineering, 36, 62-67p.

[10] Wang Zhenqi, Wu Xiaoming, Yang Yiping, 2002, Physical Chemistry, Beijing：Chemical Industry Press, 253-258p.

[11] Lin Huaxiang, Wang Xuxu, Fu Xianzhi, 2007, Properties and Distribution of the Surface Hydroxyl Groups of TiO_2, Progress in Chemistry, 19(5), 665-670p.