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Structure, properties and application of a novel low-glossed waterborne polyurethane

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ABSTRACT

Waterborne polyurethane (WPU) with low gloss was prepared successfully and used as surface modifier to adjust the gloss of leather. The structure and morphology of the WPU films were characterized by Fourier transform infrared spectrometer (FTIR), Atomic force microscope (AFM) and Scanning electron microscope (SEM). Then the factors affecting the gloss, light transmittance and water absorption of WPU films including varieties and amount of chain extenders, n_{NCO}/n_{OH} molar ratio and 2-[(2-aminoethyl)amino]ethyl sulfonic acid sodium content.etc were studied. Results showed that the WPU film possessed a broad particle size distribution combined with a relatively large particle size. This kind of novel WPU would be widely used in polyvinyl chloride, polyurethane synthetic leather surface.

1. Introduction

The surface properties of leather materials can be easily enhanced by finishing with various coatings to provide different performance characteristics for individual applications, such as suitable gloss, folding resistance, scratch resistance, and chemical resistance. In addition, functional coatings improve the value of leather products. However, most of these traditional solvent-borne leather coatings contain a large volume of volatile organic compounds, which are harmful to the environment and the human health. Recently waterborne polyurethane (WPU) have received increasing attention because they are non-toxic, apyrous and do not pollute the air (friendly to the air) [1–5]. Low degree of gloss is often achieved by adding inorganic matting agent with defined particle size distribution, such as SiO_2 particles, to the formula of coating [6,7]. The disadvantage of this method, however, is that the organic particles are not firmly anchored and can therefore be rubbed out from the coating easily because of their incompatibility with the other organic constitutions of the coating. Consequently, the degree of gloss of the surface can increase over time and the matting effect will be lost gradually [8,9]. Augustin et al. [10–12] reported the preparation of the low-glossed coating, but the composition, including the solvents and powder, was complex and expensive. The WPU emulsion was difficult to be stable, settling, layering, and demulsification happened extremely in Gabriele's reaction system [13]. Therefore, there is still a need for one-component water-dispersible coating agents which are easy to produce and do not require the addition of matting agents. Nowadays, one-component WPU matting resin has attracted more and more attentions in field of the paint industry. The new research strategies are concentrated on how to synthesize the suitable delustrant similar particles that are capable of realizing of WPU matting resin effectively and efficiently without using any matting agent. Particles float in the surface of paint film and increase surface micro roughness in terms of mechanism. Meanwhile the extinction effect is produced by resin itself, the incompatibility between the matting agent and resin can also be eliminated which would improve the rub resistance, folding fastness and rubbing fastness of paint film.

In this paper, we report an easy, novel approach of preparing single component WPU matting resin, which do not require the addition of inorganic matting agents. During the reaction process, 2-[(2-aminoethyl) amino] ethyl sulfonic acid sodium salt (A95) and hydrazine hydrate were used for preparation of waterborne polyurethane, as two crucial chain extension agents, also applied as emulsifier. In the synthesis of sulfonate aqueous polyurethane, Latex particles were completely dispersed into water with a small amount of A95 due to its strong hydrophilicity. The use level and the class of the hydrophilic extender both had influences on their mechanical properties on the surface of the WPU film materials, the WPU preparation by using A95 showed excellent biocompatibility

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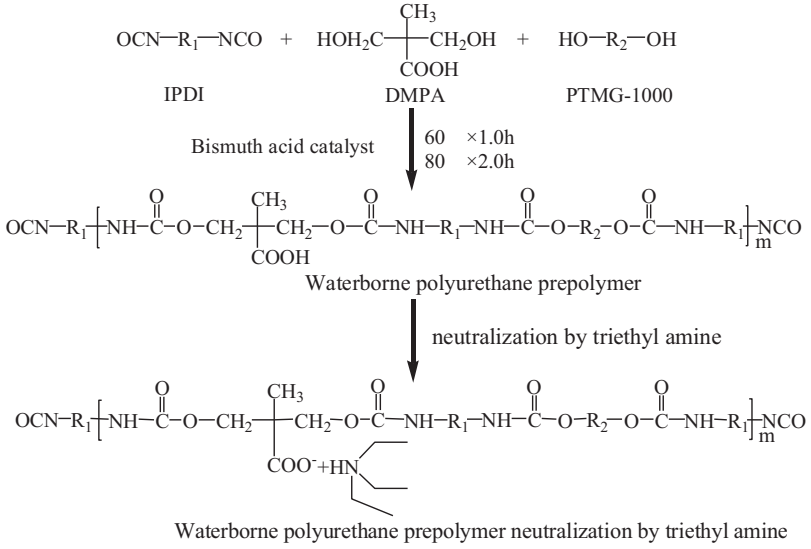


Scheme 1. The synthesis of waterborne polyurethane prepolymer.

[14] and low surface tension [15]; when using hydrazine hydrate as chain extender, two hard segments structure closed and they were difficult to recur deformation. Thus the prepared WPU emulsion had a regular distribution of molecular, the latex particle was fixed and formed regular microspheres, which can give the WPU film good low gloss, high covering power and excellent emulsion stability. Besides, the WPU films conceal coating surface defects and enhance coating adhesion resistance, scrub resistance, folding resistance and scratch resistance, etc. This kind of novel WPU is potentially used in polyvinyl chloride (PVC), polyurethane (PU) synthetic leather surface.

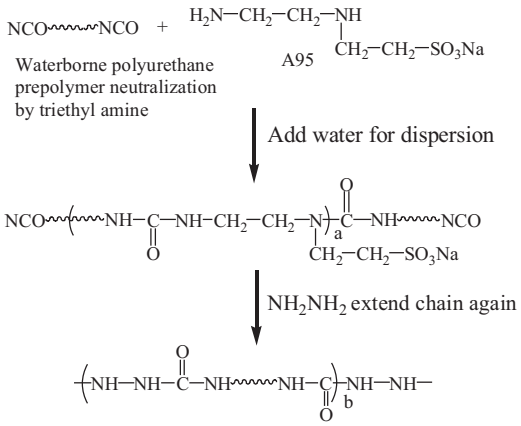
2. Experimental procedure

2.1. Materials

Isophorone isocyanate (IPDI), poly(tetramethylene glycol) (PTMG, 1000 g/mol), 2,2-bis(hydroxymethyl) propionic acid (DMPA), BiCAT 8108 (20% Bi, Bismuth acid catalyst) were supplied by Qingyuan Miller Shi ink company (China). Bismuth acid catalyst (AR grade), 2-[(2-aminoethyl) amino] ethyl sulfonic acid sodium salt (A95, AR grade), triethylamine (TEA), hydrazine hydrate (100%, purity, Hydrazine content 64%) were purchased from Tianjin Bodi Chemicals (China), Tianjin Fuyu Chemicals (China), Dongxing Chemicals (China) and Guangzhou Qintian Chemicals (China), respectively. PTMG was dried and degassed at 80 °C under vacuum for 3 h. DMPA was dried at 50 °C for 48 h under vacuum. A95 was dried with 4 Å molecular sieve before being used.

2.2. Preparation of low gloss waterborne polyurethane

The reaction was carried out in water bath under constant temperature. PTMG, IPDI, and DMPA were mixed and subsequently stirred in the presence of $w_{\text{Bismuth acid catalyst}} = 0.016\%$ ($w_{\text{Bismuth acid catalyst}} = (m_{\text{Bismuth acid catalyst}}/m_{\text{prepolymer}}) \times 100\%$) at 60 °C for 1 h and at 80 °C for 2 h to obtain NCO-terminated prepolymer. After cooling the reaction mixture to 75 °C, TEA was fed into the reactor and mixed thoroughly for 10–15 min to neutralize DMPA in WPU. After the temperature of the reactor was maintained under 35 °C, A95 dissolved in distilled water was added dropwise to the flask under vigorous stirring (1500 r/min) for about 30 min. Then added the hydrazine hydrate solution slowly and continued to react for further 10 min. The reaction was stopped when the infrared absorbance of the NCO groups (around 2260 cm^{-1}) was negligible. The resulting product was low-glossed WPU emulsion with the solid content of about 30%. The reaction process is shown in Schemes 1 and 2.



Scheme 2. The prepolymerization of waterborne polyurethane/urea dispersion.

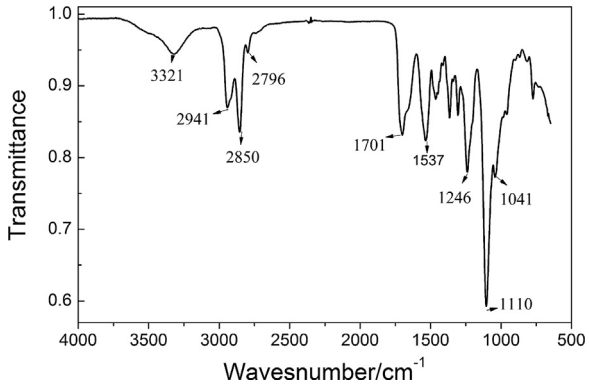


Fig. 1. The ATR-FTIR spectrum of WPU.

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