



Synthesis, characterization and fluorescence performance of a novel SAF-based waterborne polyurethane

Taotao Qiang^{a,b,*}, Mimi Han^{a,b}, Xiaoning Li^{a,b}

^a College of Bioresources Chemical and Materials Engineering, Shaanxi University of Science & Technology, Xi'an, Shaanxi 710021, PR China

^b National Demonstration Center for Experimental Light Chemistry Engineering Education (Shaanxi University of Science & Technology), Xi'an, 710021 PR China

ARTICLE INFO

Keywords:

Salicylfluorone
Waterborne polyurethane
Fluorescence property

ABSTRACT

Salicylfluorone-based waterborne polyurethane (SAF-WPU) was synthesized by chemical bonding in the presence of reactive groups, using isophorone diisocyanate (IPDI), 1,4-butanediol (BDO) as the hard segment, polypropylene glycol (PPG) (Mn = 1000) as soft segment, dimethylolpropionic acid (DMPA) as hydrophilic monomer, and salicylfluorone (SAF) as a cross-linking agent. The structure and properties of SAF-WPU were studied by Fourier transform infrared spectra (FT-IR), UV visible spectroscopy (UV-vis), fluorescence spectra, differential scanning calorimetry (DSC), thermogravimetric analysis (TG) and X ray diffraction (XRD) and so on. The results showed that SAF was successfully introduced into the main chain of polyurethane. After the introduction of SAF, the heat resistance and crystallization ability of the film were improved obviously. Further study found that the addition of SAF endowed WPU with fluorescence properties, in a certain range of concentration, the fluorescence intensity increased with fluorophore concentration increased gradually, with a further increase of the fluorophore concentration, the fluorescence intensity decreased, SAF-WPU dispersion has concentration quenching effect. In addition, the fluorescence intensity of SAF-WPU dispersion decreased with increasing temperature of the system. The quenching effect of SAF-WPU was not obvious by using hydroquinone.

1. Introduction

Fluorescent polymer [1–3] is a kind of polymer material which is relative to fluorescent small molecule. It refers to a functional polymer which can emit specific wavelength under the irradiation of a certain energy source [4–6]. Fluorescent polymers not only have the unique properties of fluorescent small molecule materials, but also have very excellent processability. Compared with fluorescent small molecules, it has many advantages, such as chromophore is not easy to fall off, good compatibility with matrix, and it is not easy to be eluted, so there is a growing concern on the study of fluorescent polymers. At present, the preparation methods of fluorescent polymers mainly include active group modification method, initiator method [7], chain transfer agent [8] and functional monomer method [9]. Among them, the active group modification method [10] is the most effective strategy for the synthesis of fluorescent polymers.

In recent years, waterborne polyurethane has been largely utilized in medicine, coatings, adhesives, fabric finishing agents and other industries [11,12], which is attributed to the advantages of its good tailoring and biocompatibility, meanwhile, waterborne polyurethane is in keep with “three premises” (RESOURCE, ENERGY and

POLLUTION-FREE) and “4E principles” (ECONOMY, EFFICIENCY, ECOLOGY and ENERGY). With the progress of society and the improvement of environmental protection requirements, in order to meet people's corresponding needs of products, it is necessary to continuously improve the performance of WPU and enrich the function of WPU products. In order to make up for the above shortcomings, the ideal effects can not achieve only by adjusting the thchnics proportion of waterborne polyurethane. Hence, based on the outstanding structure designability of polyurethane molecules, the comprehensive properties of waterborne polyurethane can be improved by introducing specific functional modifying agents into the action system.

At present, the synthesis and application of fluorescent polyurethane have been reported [13,14], mainly focused on the use of fluorescent dyes as chain extender or capping agent to modify polyurethane, while the fluorescence buildup and fluorescence change with external circumstances were even frequently neglected. In this study, the active group modification method [15–17] was used to introduce the crosslinking agent SAF into WPU to make it react with isocyanate groups on polyurethane, thus introducing SAF into the main chain of waterborne polyurethane in the form of chemical bonding, which can limit the migration of chromophore and prepare environment-friendly

* Corresponding author at: College of Bioresources Chemical and Materials Engineering, Shaanxi University of Science & Technology, Xi'an, Shaanxi 710021, PR China.
E-mail address: qiangtt515@163.com (T. Qiang).

fluorescent aqueous polyurethane materials with high fastness, low mobility, good water resistance, solvent resistance, heat resistance and other functions. In addition, it can be compared with the traditional solvent based polyurethane in performance and function [18,19].

2. Experimental

2.1. Main materials

Isophorone diisocyanate (IPDI, Shanghai Chemical Co., Ltd. D B) was purified by distillation under a reduced pressure of 1330 Pa at 120 °C. Polypropylene glycol (PPG) (Mn = 1000 g/mol, Aladdin) was dried by distillation under a pressure of 1330 Pa at 110 °C. 2,2-Dimethylol propionic acid (DMPA, Shanghai Mclean Biochemical Co., Ltd.) was dried in an oven at 120 °C for 48 h. 1, 4-butanediol (BDO), absolute ethanol and acetone were supplied by Tianjin Kermel Chemical Reagent Co., Ltd. Triethylamine (TEA) was purchased from Tianjin Tianli Chemical Reagent Co., Ltd. Salicylfluorone (Aladdin) and di-n-butyltindilaurate (DBTDL, Shanghai Qing Chemical Co., Ltd.).

2.2. Synthesis of SAF-WPU

The fluorescent emulsion of SAF-WPU was prepared according to the procedure shown in Fig. 1. IPDI and PPG were first added into a dry four-necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser. To this contents, 2 wt.% BDO (based on the total solid content of IPDI and PPG) was added, then catalyzed by DBTDL (0.03 wt.% based on the total solid content of IPDI and PPG) was added dropwise to the flask under stirring. After mixing, the mixture was reacted at 50 °C for 20 min, then the prepolymerization of polyurethane was carried out at 70 °C for 1 h. To the above mixture, DMPA (based on the total solid content of IPDI and PPG) was added to carry out the chain extension for 2.5 h at 80 °C. Subsequently, the cross-linking reaction occurred when 0.05 wt.% SAF (based on the total solid content of IPDI and PPG) was added into the system until NCO content reached a theoretical value to produce crosslinked structure prepolymer. The NCO content was monitored via a standard dibutylamine titration method [20]. A suitable amount of acetone was added to the system to reduce its viscosity. When the reaction mixture was slowly cooled down to 40 °C, TEA (neutralization degree was 100%) was added to the system and reacted with the carboxylic group in the side chain of prepolymer for 30 min to form quaternized NCO-terminated prepolymer. Finally, deionized water was added into the system with agitation at high shearing rates to emulsify the solution. A SAF-WPU fluorescent emulsion was obtained after removal of acetone from the emulsion at 50 °C by rotary vacuum evaporation under the reduced pressure.

2.3. Fabrication of films

The fluorescent emulsion was cast in a Teflon plate to form the film for further testing with the volatilization of medium, which was placed at ambient temperature for 48 h, and then in a vacuum system at 60 °C for 2 days.

2.4. Characterization

FTIR spectroscopy was used to monitor the incorporation of SAF in the polyurethane matrix and to verify the final chemical structure of the polymer. Infrared spectra were collected in a Fourier transform infrared spectrophotometer (PerkinElmer Spectrum 100), and the scanning frequency range was 4000–500 cm⁻¹.

The UV–vis spectrum was recorded on the SHIMADZU spectrophotometer UV-1800 using SAF-WPU emulsion with the concentration of 0.4×10^{-6} – 1.5×10^{-6} mol/L at 25 °C, and the spectral scanning range of wavelength was 400–700 nm.

The thermal migration properties of fluorescent groups in SAF-WPU were tested by AATCC standard [21]. As shown in the Fig. 2, a layer of SAF-WPU emulsion was evenly coated on a glass plate with a size of 120 mm × 70 mm, after drying, the film with a thickness of about 0.2 mm formed, then the forming film was divided into the equal area A and B. Subsequently, the area A was covered with the size of 30 mm surface container, and the area B did not make any special treatment. Finally, the glass plate was placed in the oven at 60 °C for 24 h. The films with the same weight in the area A and the area B were taken respectively, then were dissolved and prepared to a solution of the same concentration. And the absorbance of the solution in the UV and visible light regions were tested. The heat transfer rate M_p was calculated according to the following Formula (1):

$$M_p = \frac{C_B - C_A}{C_A} \times 100\% \quad (1)$$

where M_p is heat transfer rate, C_A is the fluorophores concentration of area A, and C_B is the fluorophores concentration of area B.

The fluorescence spectrum was recorded on a RF-5301 PC (SHIMADZU company) luminescence spectrometer to examine the fluorescence intensity of SAF-WPU emulsion. In this paper, the correlation between SAF-WPU concentration, temperature, quencher agent and fluorescence intensity of SAF-WPU emulsion was studied.

Thermal stability analysis: Thermogravimetric analyses (TGA) of WPU and SAF-WPU were performed in a TGA Q5000 (thermogravimetric analyzer) (TA instrument). The samples were placed in an alumina crucible and heated at 10 °C/min from 40 °C to 600 °C under a N₂ atmosphere, where the flow rate of N₂ was 30 mL/min.

X-ray Diffraction (XRD, D/max2200PC, Japan) studies were performed to analyze the crystallinity of the polyurethane membrane films by using CuK_α X-radiation at 40 kV and 30 mA with a scan rate of 4°/min. The diffraction angle ranged from 5° to 60°.

Transmission electron microscope (TEM, Naivete G2 F20 S-TWIN, FEI company) was employed for the morphology of latex particles.

Atomic force microscopy (AFM, STP3800N/SPA400, NSK) was employed for microscopic investigation of film surface roughness. Under the condition of 25 °C, a few specimens of films were placed on the sample table. The surface morphology of the film was observed in the range of 2 μm × 2 μm by changing different multiples under tapping mode and the scanning rate was 1 Hz.

Scanning electron microscope (SEM) was employed for film morphology observation. The samples were fractured in liquid nitrogen, and then they were coated with gold and tested by a LEO 1530VP (LEO Company) scanning electron microscope.

3. Results and discussion

3.1. Structure analysis of SAF-WPU by FTIR

FT-IR spectra of PPU, SAF-WPU and SAF are shown in Fig. 3. As shown in the Fig. 3, the FTIR spectra of SAF showed a broad peak formed by hydroxyl association at 3371 cm⁻¹, an internal bending vibration absorption peak of benzene ring at 1300 cm⁻¹ and a absorption peak of C–H on benzene ring at 587 cm⁻¹. Both the FTIR spectrum of PPU and SAF-WPU exhibited the characteristic absorption peaks of polyurethane at 3324 cm⁻¹ [ν(NH)], 2867 cm⁻¹, 2936 cm⁻¹ [ν(CH₂)], 1710 cm⁻¹ [ν(C=O)], 1107 cm⁻¹ [ν(C–O–C)]. The typical peak of –NCO in the polyurethane prepolymer (PPU) at 2259 cm⁻¹ disappeared in the SAF-WPU, demonstrating the generation of urethane bond in SAF-WPU. Therefore, we believe that SAF component has been embedded successfully into the polyurethane chain.

3.2. UV–vis absorption analysis

UV–vis absorption spectra of SAF-WPU emulsion is shown in Fig. 4b. The spectrum of SAF-WPU showed two absorption peaks with

Download English Version:

<https://daneshyari.com/en/article/7105566>

Download Persian Version:

<https://daneshyari.com/article/7105566>

[Daneshyari.com](https://daneshyari.com)