Study on the Synthesis and Application of a Bio-Based Polyol Based on Neatsfoot Oil

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Study on the Synthesis and Application of a Bio-Based Polyol Based

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on Neatsfoot Oil

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Abstract:

In order to reduce the dependence on petro-based raw materials in the production of polyurethane, a biobased polyester polyol was synthesized from neatsfoot oil,which is one of bio-derived sources. Neatsfoot oil was first amidated with ethanolamine, ring-opened by epoxy respectively. Then it is polymerized with biobased succinic acid to obtain bio-based polyols. These polyols were subsequently used to synthesize waterborne polyurethane (WPU) with toluene diisocyanate (TDI). During the process, the amine value, hydroxyl value, acid value, molecular weight, emulsion stability, softness of film and application properties were systematically characterized. Structural change of the products were confirmed by infrared spectroscopy (FTIR). Results showed that the hydroxyl value of the fatty amide produced by amidation reaction was 150mgKOH/g and the conversion rate is 92%. After the epoxy ring-opening reaction, the hydroxyl value was increased to approximately 300mg KOH/g. The hydroxyl value and molecular weight of the final polyester polyol was 65mg KOH/g, 2097g/mol respectively. The WPU synthesized from the bio-based polyol and TDI has excellent emulsion stability whose films are flexible and possessed good dry/wet rub resistance. Performances of the WPU is comparable to that of commercial waterborne polyurethane products.

Keywords: Polyurethane; neatsfoot oil; bio-based polyol; application properties

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1. Introduction

Polyurethane has been widely used as coatings, foam plastics, adhesives, etc because it possesses excellent physical and mechanical properties1. The main raw materials for synthesizing polyurethane are polyols and isocyanates, which primarily rely on non-renewable petroleum-based resources. With the depletion of global petroleum resources and the resulting environmental issues, some researchers have begun to explore the use of renewable resources for the preparation of polyurethane.

Vegetable oils have consistently been attracted extensive attention by some researchers due to their advantages such as renewability, biodegradability, non-toxicity, low cost,etc2. Wherein Paola Stradolini successfully converted castor oil and soybean oil into polyols by ester exchange, amidation, and epoxy ring-opening reactions3. Coman,etal firstly synthesized olive oil epoxides by epoxidation reaction for olive oil, then two types of bio-based polyols were obtained by ring-opening reactions with acetic acid and ethanol respectively, which can replace petroleum-based polyols in the preparation of soft polyurethane foams4. Kuranska,etal prepared a series of low-viscosity, highactivity bio-based polyols based on waste cooking oil with ethylene glycol, propylene glycol, diethylene glycol, glycerol, and triethanolamine by ester exchange reactions. Then these polyols were applied in the preparation of polyurethane foams, adhesives,etc5. In addition Desroches,etal synthesized series of highly reactive biobased polyols by the reactions between 2-mercaptoethanol and the unsaturated double bonds in rapeseed oil. These

polyols can be used for the preparation of polyurethane coatings and elastomers6. Currently the technologies of producing bio-based polyols from vegetable oils such as castor oil and soybean oil has become relatively mature and achieved industrial-scale application.

However, these crops typically require significant amounts land, which competes with staple crops like rice and wheat for limited land and water resources, thereby leading to the issue of “competing with humans for food.” Therefore, the search for renewable resources for synthesizing polyurethane remains an ongoing endeavor.The present work focuses on preparing an bio-based polyol for polyurethane with neatsfoot oil synthesized by amidation, epoxy ring-opening reactions and stepgrowth polymerization. The reaction mechanism, the proportion and dosage of the reactants, the relevant indicators sucn as the molecular weight, structure of the bio-based polyol has been studied and the application properties are discussed.

2. Methodology

Act neatsfoot oil as raw materials, the amidation reaction, the oxidative and ring-opening reaction, the polymerization of bio-based long-chain diols have been done in sequence in order to obtain a bio-based polyol for the bio-based polyurethane. The scheme of the reactions were described in Fig 1,Fig 2, Fig3. The amine value and conversion rate during the process of the reaction, the hydrogen value of the fatty amide, the hydroxyl value of the biobased long-chain diol, the molecular weight and its distribution, structure of the bio-based polyol, etc were examined respectively.

Fig 1. The amidation reaction of neatsfoot oil with

ethanolamin

Fig 2. The oxidative and ring-opening reaction of

fatty amides

Fig 3. The polymerization of bio-based long-chain

diols with bio-based succinic acid

The bio-based waterborne polyurethane emulsion was synthesized by the bio-based polyol, toluene diisocyanate (TDI) and other auxiliaries.The solid content, emulsion stability, softness and elastic modulus of film-forming of the bio-based waterborne polyurethane emulsion were examined. In the comparative application experiments, the bio-based waterborne polyurethane emulsion and the similar product synthesized by petroleum-based polyurethane emulsion on the market was separately used in the formulation of finishing of leather. The properties of dry/wet rub resistance and flexing resistance of the coating were tested.

3. Result & Discussion

Based on the amine value, the reactive parameters has been optimized, the optimised parameters is n (Neatsfoot oil): n (Ethanolamin) 1:3, reactive time 8h, reactive

temperature 130oC. The amine value, hydrogen value of the fatty amide prepared by the optimized parameters is 12.7mgKOH/g,150mgKOH/g, respectively. The conversion rate is 92%.

Based on the hydroxyl value of the product, the optimised parameters is hydrogen peroxide 50wt%, reactive time 4 hours, reactive temperature 65oC, formic acid 20wt%. The hydroxyl value of the bio-based long-chain diol prepared by the optimised formulation is 300mgKOH/g.

In view of comprehensive considerations such as time,cost,etc of the stepwise polymerization of bio-based polyol, the best parameters is the reactive temperature is 220oC, the consumption of catalyst is 0.3wt%, the reactive time is 6h.The molecular weight and the distribution index (Mw/Mn) of the bio-based polyols are 2097 and 1.72 respectively. FTIR spectra confirmed the progress of each step of the synthesis reaction by the changes in the absorption peaks of the functional groups.

The bio-based waterborne polyurethane emulsion has good emulsion stability and its film is middle hard. The results of comparative application experiments show that properties of the bio-based waterborne polyurethane emulsion can be on a par with those of the petroleumbased polyurethane emulsion on the market.

4. Conclusion

In order to produce an bio-based polyurethane, a bio-based polyester polyol was prepared based on neatsfoot oil. Neatsfoot oil was first amidated with ethanolamine, ringopened by epoxy respectively. Then it is polymerized with bio-based succinic acid to obtain bio-based polyols. These polyols were subsequently used to synthesize waterborne polyurethane (WPU) with toluene diisocyanate (TDI). During the process, amine value, hydroxyl value, acid value, molecular weight, emulsion stability and elastic modulus of film-forming were systematically characterized. Structure were confirmed by FTIR. Results showed that the hydroxyl value of the fatty amide produced by amidation reaction was 150mgKOH/g and the conversion rate is 92%. After the epoxy ring-opening

reaction, the hydroxyl value was 300mg KOH/g. The hydroxyl value and molecular weight of the bio-based polyester polyol was 65mg KOH/g, 2097g/mol respectively. The WPU synthesized from the bio-based polyol and TDI has excellent emulsion stability whose films are flexible and possessed dry/wet rub resistance, who are comparable to that of commercial waterborne polyurethane products.

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