Glycerol based polyurethane

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Abstract

This present work is aimed to prepare glycerol based polyurethanes (GPUs). Polyurethanes are formed by the reaction of polyols and diisocyanate. Glycerol is reacted with a non polar group, such as castor oil, palm oil, in order to modify properties of polyurethane before use as a polyols. Transesterification of oil using glycerol is one of the interested methods to convert glycerol to chemicals for making GPUs because it is a convenient method, obtaining biodegradable PU. The cellular structures and morphology of unmodified glycerol polyurethane (UGPU) was compared with GPUs. Scanning electron microscopy (SEM) was used to examine cellular structure in particular cell size. It was found that types of oil affected the morphology of GPUs. An irregular cellular structures are observed in UGPU. In contrast, GPUs from palm oil polyols and castor oil polyols has less bubbles. GPUs, with controllable structures, trend to use in slow released application such as fertilizer release. The advantage of GPU is the ability to control releasing rate by varying type of polyol, so not necessary to coat for several time.

Keywords: glycerol, polyurethane, slow release
1. Introduction

Polyurethanes are important polymers as their mechanical, thermal, and chemical properties can be controlled by the reaction of various polyols and polyisocyanates. Their many uses range from flexible foam in upholstered furniture, to rigid foam as insulation in walls, roofs and appliances to thermoplastic polyurethane used in medical devices and footwear, to coatings, adhesives, sealants and elastomers used on floors and automotive interior.

Developing bio-renewable feedstocks for PU becomes highly desirable for both economic and environmental reasons. In PU manufacturing, vegetable oils can be potential replacements for polyols [1].

Glycerol is a by-product from biodiesel industry that is generated in a large quantity. Despite of the wide applications of pure glycerol, especially for medium and small biodiesel producers, it is too costly to refine the crude glycerol to a high purity for supply in food, pharmaceutical, cosmetics, and many other industries. [2] Polyurethanes are formed by the reaction of an isocyanate with an alcohol in the presence of catalyst, such as triethanolamine, stannous octoate. Glycerol can be used as chemicals to make polyurethane. Three OH groups in glycerol molecule can react with NCO group in Diisocyanate molecule to form polyurethane. For coating applications, it necessary to modify glycerol by introducing a non polar portions, such as vegetable oils, in order to reduce hydrophilicity of glycerol.

2. Method

2.1 Materials

Glycerol (99.5%), castor oil, palm oil, PbO, stannous octoate, methylene diphenyl diisocyanate (Mitsui specialty chemicals co.,ltd.), urea fertilizer (46-0-0)

2.2 Preparing glycerol modified polyols

A round bottom flask equipped with thermometer, stirrer and reflux condenser were charged with one equivalent each of oil and glycerol along with catalyst litharge (0.05%). Reaction was carried out at 240–250°C for 2 h. [3] Each oil was refluxed with glycerol in the presence of PbO to obtain two types of polyols; castor oil polyols (Cp) and palm oil polyols (Pp).

2.3 Polyurethane preparation

The polyols (unmodified glycerol, Cp, Pp) were mixed with methylene diphenyl diisocyanate (MDI) by varying MG : MDI the ratio of 1:1 and 1:2 respectively. Then 1% stannous octoate was added to the mixture. PU solution was cured at 120°C for 15 minutes in the oven. A semi-rigid pale yellow foam with approximately 2 mm. thicked film was observed. The cellular structures of PU were observed by stereoscope with 25x magnification power.

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\begin{align*}
\text{CH}_2 - \text{O} - \text{C} - \text{R} & \quad \text{CH}_2 - \text{OH} \\
\text{CH} & \quad \text{CH}_2 - \text{OH} \\
\text{CH}_2 - \text{O} - \text{C} - \text{R} & \quad \text{CH}_2 - \text{OH} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 & \quad \text{O} - \text{C} - \text{R} \\
\text{CH} & \quad \text{O} - \text{C} - \text{R} \\
\text{CH}_2 - \text{OH} & \quad \text{CH}_2 - \text{OH} \\
\end{align*}
\]

Scheme 1. Transesterification of oil using glycerol
2.4 Study of polyurethane application on urea fertilizer

Urea fertilizer paricles were dipped in the PU solution and cured at 120° for 15 minutes. The morphology of coated particle was observed by scanning electron microscope (SEM).

3. Results and discussion

Fig. 1. SEM show the morphology of UGPU (35X magnification)

Fig. 2. SEM show the morphology of urea fertilizer coated with UGPU (200X magnification)

The results presented in Fig. 1 showed that the cellular structures of UGPU were irregular shape with large holes. It was found that urea part dispersed in the layer of UGPU due to urea dissolved in glycerol partly (Fig. 2).

Fig. 3. SEM of urea fertilizer coated with GPU

SEM micrograph shown in Fig. 3 are represented the boundary of GPU layer that clearly separated from urea fertilizer particle due to the increasing in hydrophobicity of glycerol.

Fig. 4. The images of GPUs obtained from reaction of castor oil polyols (Cp) and MDI: (a) Cp:MDI=1:1; (b) Cp:MDI=1:2

Fig. 5. The images of GPUs obtained from reaction of palm oil polyols (Pp) and MDI: (a) Pp:MDI=1:1; (b) Pp:MDI=1:2

The images presented in Fig. 4 and 5 show the appearances of GPUs obtained from different types of polyols. GPUs from Castor oil polyols (Cp) give less regularity shaped cellular structures than those from palm oil polyols. Castor oil polyols give opened-cellular structures at low Cp:MDI ratio (Fig.4 (a)) and
give more closed-cellular structures when increase Cp:MDI ratio (Fig.4). Palm oil polyols (Pp) give high regularity of closed-cellular structures.

4. Conclusions

The glycerol based polyurethane was easily prepared by the reaction of glycerol and diisocynate such as MDI in the presence of catalyst. To improve the properties of polyurethane, modification of glycerol are needed. Transesterification by using palm oil and castor oil are easy method to introduce non polar portions into the glycerol molecule that affected the properties of PU.

The experimental results indicated that the substituent non-polar part in molecule used in this study trends to improve regularity of cellular structures, specifically hydrophobicity. Types and regularity of cellular structures are controlled by types of polyols and ratio of reactant. Castor oil polyols give more complex structure due to the OH groups in alkyl chain in the castor oil molecule are capable to reacte with NCO groups in diisocyanate molecule resulting in higher degree of crosslinking.

5. Acknowledgment

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References