IOP Conf. Series: Materials Science and Engineering **107** (2016) 012048 doi:10.1088/1757-899X/107/1/012048

Synthesis and characterization of free-isocyanate polyurethane as renewable coating materials

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Abstract. Green synthesis of diethyl ethane-1,2-diyldicarbamate (M1) as starting dimer of free-isocyanate polyurethane from an excess of diethyl carbonate and ethylene diamine catalyzed by TBD (1,5,7-triazabicyclo-[4,4,0]dec-5-ene) at 80 °C for 4 hours has been carried out. The product has high yield and purity up to 92% and 99,18%, respectively. The product was obtained in the form of rod-shaped white crystals and characterized with ^{1}H-NMR, ^{13}C-NMR and FTIR spectroscopy. Polyurethane (P1) has successfully synthesized via polycondensation methods by reacting of M1 with *cis*-2-butene-1,4-diol. This reaction also catalyzed by TBD organo catalyst. P1 chemical structure has been confirmed using ^{1}H-NMR and FTIR techniques.

1. Introduction

The use of materials which obtained from petroleum resources have to be replaced, due to the availability of petroleum will be depleting [1]. One alternative that should be taken to replace or reduce the use of petroleumas raw material is to re-use natural materials that is renewable and sustainable. In addition, the advantages in using of starting material from natural resources are cheaper, easily available and environmentally friendly [2]. Therefore, some researchers have been using materials from nature to replace material derived from petroleum resources, such as in the synthesis of polyurethane.

Polyurethane is one of the polymeric material which is very important in many applications, such as adhesives, coatings technology, foam, and etc [3-5]. The advantages of this polymer is to have a good anti-corrosion properties that can be used as coating materials in the the transportation industry, petroleum, and household appliances made of metal [4]. The use of polyurethane as a coating material because of its resistance to dissolution, abrasion and give effect in the brightness of the paint [6]. Conventionally synthesis of polyurethane today still use the initial material such as phosgene or isocyanate compound [7-9]. Besides having a toxic properties, both of these compounds are also not environmentally friendly as well as derived from petroleum. Isocyanate compounds have also been reported to cause irritation and long-term asthma [10]. In addition, the isocyanate compounds are also very sensitive to water, so that in its use requires special media and more energy in the synthesis of polyurethanes via the isocyanate [11]. The research also reported that the toluene diisocyanate can release carcinogenic aromatic amines group. Therefore, it is necessary to do the synthesis of non-

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isocyanate or non-phosgene polyurethane that are environmentally friendly by using green chemistry-based material.

The use of carbonate compounds as raw material in the synthesis of polyurethane to be very interesting, where the compound is classified as green chemistry compound. These compounds can be synthesized from carbon dioxide (CO_2) [12], a derivative of urea [13,14], methanol [15], and others. Some researchers have used the carbonate compound as a replacement for isocyanates or phosgene in the synthesis of polyurethane [16,17]. In addition, other carbonate compounds such as cyclic limonene dicarbonate [18], cyclic carbonate [19], carbonate modified epoxy resin [20] and others, have also been reported as a raw material in the synthesis of polyurethane. Before the polymerization reaction forming a non-isocyanate polyurethane, carbonate compounds such as dimethyl carbonate is usually converted into carbamate compounds [16,21]. Carbamate compounds is an intermediate product and can form polyurethanes when reacted with diol compounds, directly [1]. Firdaus [16] has successfully synthesize carbamates compounds from dimethyl carbonate with the aid of a TBD (1,5,7-triazabicyclo-[4,4,0]dec-5-ene)catalyst. In addition, other studies have also successfully to synthesize carbamates compounds from dimethyl carbonate using acid functional ionic liquid catalyst [21]. Diethyl carbonate compounds have also been reported as a starting material in the synthesis of carbamate compounds in a high yield, which is catalyzed by TBD catalyst [22]. However, the use of di-carbamate compounds from diethyl carbonate as the starting material in the synthesis of polyurethane has not been done.

Therefore, in this study will be carried out of synthesis free-isocyanate polyurethane from diethyl carbonate compounds as raw material and catalyzed by the TBD catalyst.

2. Experimental

2.1. Materials

All reagents were purchased without further purification. The starting materials, diethyl carbonate (DC) and ethylene diamine (ED) were obtained from Merck, as well as for tetrahidrofuran (THF), ethanol, and n-hexane. *Cis*-2-butene-1,4-diols and 1,5,7-triazabicyclo-[4,4,0]dec-5-ene (TBD) were purchased from Sigma Aldrich.

*2.2. Syntesis of Diethyl Ethane-1,2-diyldicarbamate(**M1**)*

All of the starting materials such as diethyl carbonate and ethylenediamine were characterized with FTIR (fourier transform infra red) and TLC (thin layer chromatography) before used. An excess of diethyl carbonate (50 mmol) were reacted with 5 mmol of ethylene diamine. This reaction were catalyzed with TBD (10% mmol eq. to DC) organocatalys. The solution were slowly stirred at controled temperature, 80 ^{O}C. This reaction were monitored with TLC, to stop the reaction until ethylene diamine spot disappeared. The obtained product were characterization with FTIR, GC (Gas Chromatography), and NMR (Nuclear Magnetic Resonance) spectroscopy.

*2.3. Synthesis of Polyurethane (**P1**)*

The polymerization reaction in this study were performed in the vacum reactor. **M1** product from the previous synthesis was used in this reaction. 1 mmol eq of **M1**were mixed with *cis*-2-butene-1,4-diols (1 mmol equiv.). The reaction was hold at 80 ^{O}C with the medium presure (400±5 mbar) until viscous solution succesfully achieved. The temperature was slowly raising to 120 ^{O}C, and holded until polycondensation reaction were completely achieved. In this reaction, TBD organocatlyst also used. The **P1** polymer was purified by precipitation of a concentrated THF solution of **P1** product into cold ethanol.

2.4. Characterization

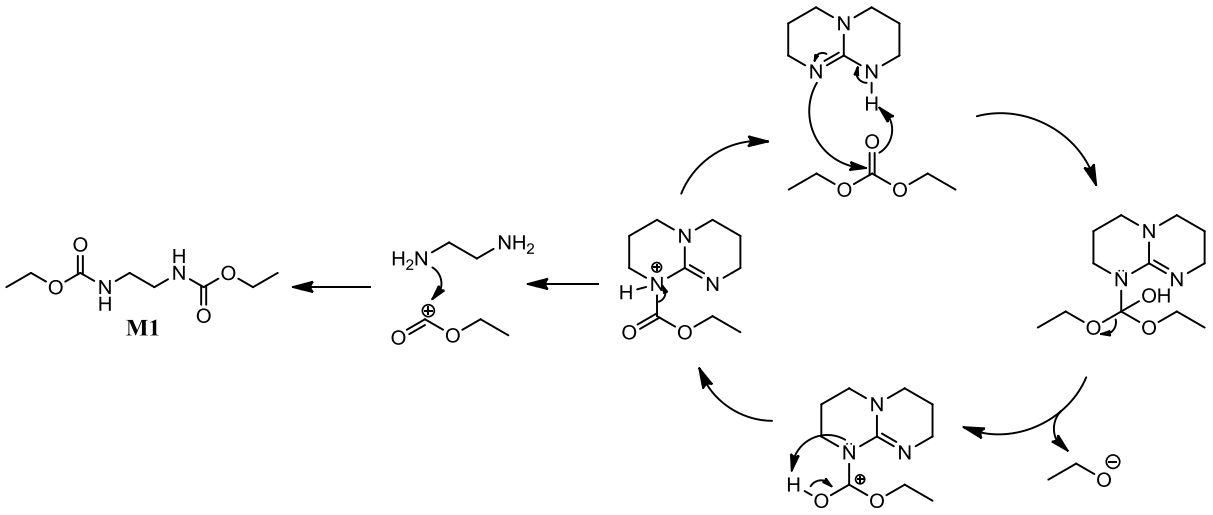
All of reagents in this study were characterized with FTIR Prestige 21 SHIMADZHU to confirmed the functional groups of each reagent. Also, the M1 and P1 synthesis products were characterized. In this study, we used KBr as background and set the scaning up to 45 times of scan.

^{1}H-NMR and ^{13}C-NMR were used in this study was Agilent with frecuency of 400 MHz. In the caracterized of M1, we used $CDCl_3$ as solvent and for P1 product used warm DMSO solvent. GC-MS analysis were perfomed in Chemistry laboratory of UII. For M1 compound analysis, we used chloroform as solvent and heating up to 350 ^{O}C.

3. Result and Discussion

3.1. Synthesis of dicarbamates

Diethyl ethane-1,2-diyldicarbamate (**M1**) was dicarbamate compound that sucessfully synthesized in this study. **M1** was prepared by reacting diethyl carbonate (DC) with ethylene diamine (ED) in the presence of TBD catalyst (Scheme. 1). TBD catalyst was reported as selective organocatalyst in the forming of carbamates compounds [16,23]. This organocatalyst was able to prepare carbocation as electrophilic, so make it easily to reaction with ethylene diamine or nucleophilic. TLC was used to monitored the reaction. After 4 hours reaction, according to TLC observation showed the disappeared of ethylene diamine spot which indicates the **M1** product has been form.



Scheme 1. Possible chemical reaction on synhesis of Diethyl ethane-1,2-diyldicarbamate (**M1**)

M1 product was obtained after settling for 12 hours at room temperature. The **M1** product were solid like crystal and white form. The solid form of **M1** product was very beneficially, due it was easy to separated from the exess of dimethyl carbonate. In the other side, it was also minimizing in energy consumtion. This fact made **M1** product categorized as green compound. In this work, **M1** product has high yield, up to 92% just for 4 hours reaction. This was attributed of TBD organo catalyst, where this catalist was reported as selective catalyst to forming carbamate compound [16,22,23]. This study also investigated of synthesis **M1** product without TBD organo catalyst and these compound was obtained about 4 days. This investigation was evidenced that TBD organo-catalyst plays an important role in the formation rates of **M1** compound.

Gas chromatography technique was performed to determine of **M1** compound purity. These product was recorded using chloroform as solvent. This analysis resulted that **M1** product has high purity, up to 99.18%. It was veru luckly to obtaine the product with high purity. To determine **M1**

chemical structure, some analysis has been conducted, such as FTIR technique, ^{1}H-NMR, ^{13}C-NMR and Mass spectroscopy.

Functional group analysis showed a shift of a wavenumber from the precusror material in M1 product indicate the carbamates has been formed. From curve A (spectrum of diethyl carbonat) can be seen that a carbonil group (>C=O) streaching vibration adsorption peak at 1761,08 cm^{-1}. After reaction, the >C=O streaching vibration peak shifted to 1685,86 cm^{-1}. It proved that carbamate group completely formed. Fleischer et al. [12] was confirmed that an urethane bands was obtained in 1680 cm^{-1} and disappeared of carbonate group band at 1700 cm^{-1}verified the complete conversion of all carbonate to carbamates or urethane group. Also, amine group (-NH) bending vibration shifted from 1599 cm^{-1} to 1546 cm^{-1} indicated that carbonil group from diethyl carbonate was interacted with amine group from ethylene diamine to formed carbamates group.

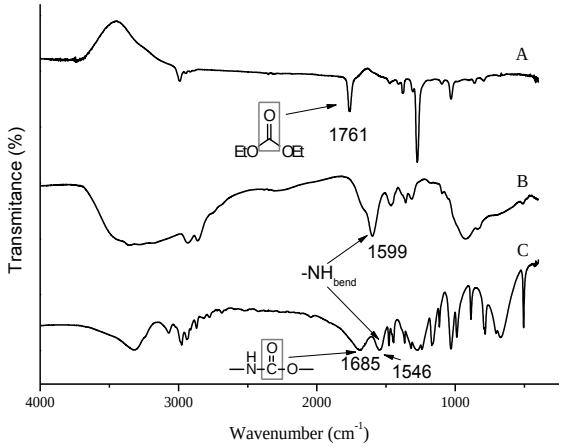


Figure 1. FTIR spectrum of (A) diethyl carbonate, (B) ethylenediamine and (c) M1 product

Figure 2. shows the ^{13}C-NMR spectrum of M1 product. Signal of ^{13}C-NMR was corresponding with chemical structure of M1 product, where a signal arround 14.9 ppm accordance to carbon atom in methyl group (-CH_3). Moreover, the signals at 40.1 ppm and 60.1 ppm were corresponded to carbon atoms in methylene (-CH_2-N-) and methylene (-CH_2-O-) groups, respectively. In Fig. 2 was investigated that only four signal which detected. This cause by a symetry chemical structure of **M1** compound. A peak at 157,06 ppm was assigned to the carbon atom on the carbamates groups. It was also found by Li et al [17].

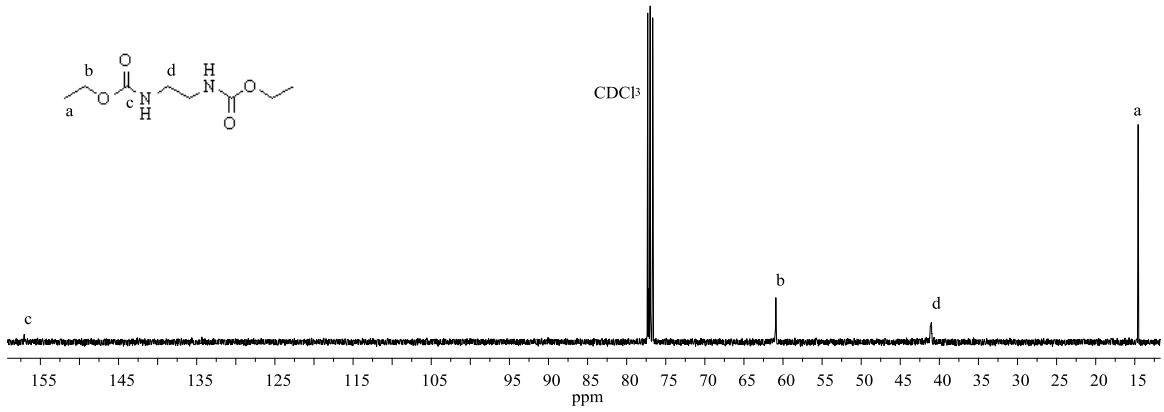


Figure 2. ^{13}C-NMR of M1 product

^{1}H-NMR also performed to strongly prediction of M1 chemical structure (Figure 5). The signal at 5.01 ppm was assigned to hidrogen atom at amide group (-C(O)-NH). The other signals such as 3.36

(t, Ha), 4.03 (q, Hb) and 3.27 (s, Hd) ppm was confirmed as methyl, methylene (CH_2-O-) and methylene (-CH_2-NH-). The existence of this signals was confirmed the M1 chemical structure as seen in Scheme 1. M1 products was high solubility in chloroform, thus, in ^{1}H-NMR analysis $CDCl_3$ used as solvent.

Figure 4 shows a MS signal and possible fragmentation mechanism of M1 product. The MS signals of M1 product was matched with the possible fragmentation which indicated the possible compound was diethyl ethane-1,2-diyldicarbamate (M1). The base peak of M1 can be seen at 115 m/z corresponding to cyclic carbamates. It was found that the cyclic carbamates be a stable structure than the other structures.

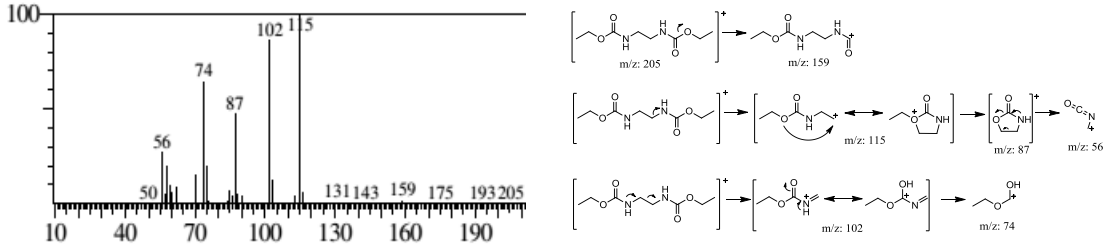
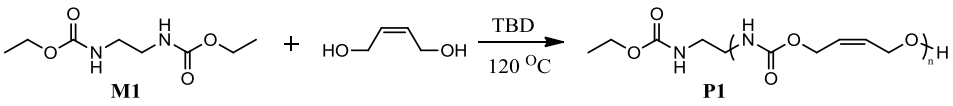


Figure 3. MS and possible fragmented mechanism of M1 product

3.2. Synthesis of Polyurethane

Synthesis of polyurethane was performed in the vacum reator to minimized the interaction with other compound in the polycondensation reaction. M1 product was reacted with 2-butene-1,4-diols (DO) with the presence of TBD organocatalyst. Unverferth et al. [23] reported that polycondensation of polyurethane which catalyzed by TBD organocatalyst become an efficient strategy to obtain renewable polyurethane. In this study, temperature of the reaction was raised with slowly from 80 ^{O}C to 120 ^{O}C. In the first step, the polycondenzation reaction was perfomed in 80 ^{O}C about 2 hours and then raised to 120 ^{O}C to completely the polycondenzation reaction. It was found that, at 120 ^{O}C the product was solid form so fastly indicated the polymerization was terminated. The obtained product was yellow and after precipitation process the colours was white to brown, indicated the TBD was dissolved in methanol and the product was pure.



Scheme 2. Polymerization reaction of P1 product

FTIR technique was one of simple methods to characterized of synthesis product by their fuctional group. Several researchers [18, 19, 24] has used this technique as supporting data to analyze and predict of chemical structure. Figure 4. showed FTIR spectrum of M1 and P1 product. The bands at 1645.35 cm^{-1} and 1483.32 cm^{-1} was corresponding to –C=C-H groups. It was indicated that the M1 and DO was reacted to form P1. Also, carbamates group band was shifted to 1722.51 cm^{-1} was clearly the P1 was form.

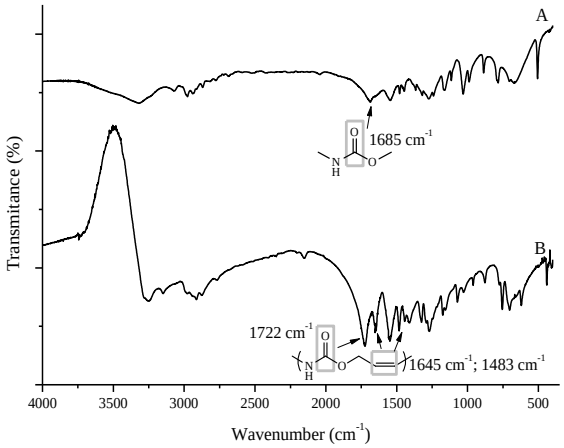


Figure 4. FTIR spectrum of (A) M1 and (B) P1 products

^{1}H-NMR investigated of Polymerizations confirmed the expected structure of P1 products. The ^{1}H-NMR of dicarbamates compound showed a decreasing of signals intensity at 1.11 and 3.95 ppm corresponding to the methyl (Ha) and methylene (Hb), respectively in ^{1}H-NMR spectra of P1 as shown in Figure 5. Not only decrease, the signal also shift, where in M1 products ^{1}H-NMR spectra Ha and Hb has appear in 1.21 and 4.09 ppm, respectively. This was caused by the presence of diol compounds as polymerizing agent which has vinyl group, so the signal has shift but not to much. The P1 products has low solubility in several solvent, such as $CDCl_3$, THF, and DMSO. However, in warm DMSO solution was found that P1 product has good solubility. Thus, before ^{1}H-NMR test, P1 products was dissolved in warm DMSO (40-50 ^{O}C, approximately).

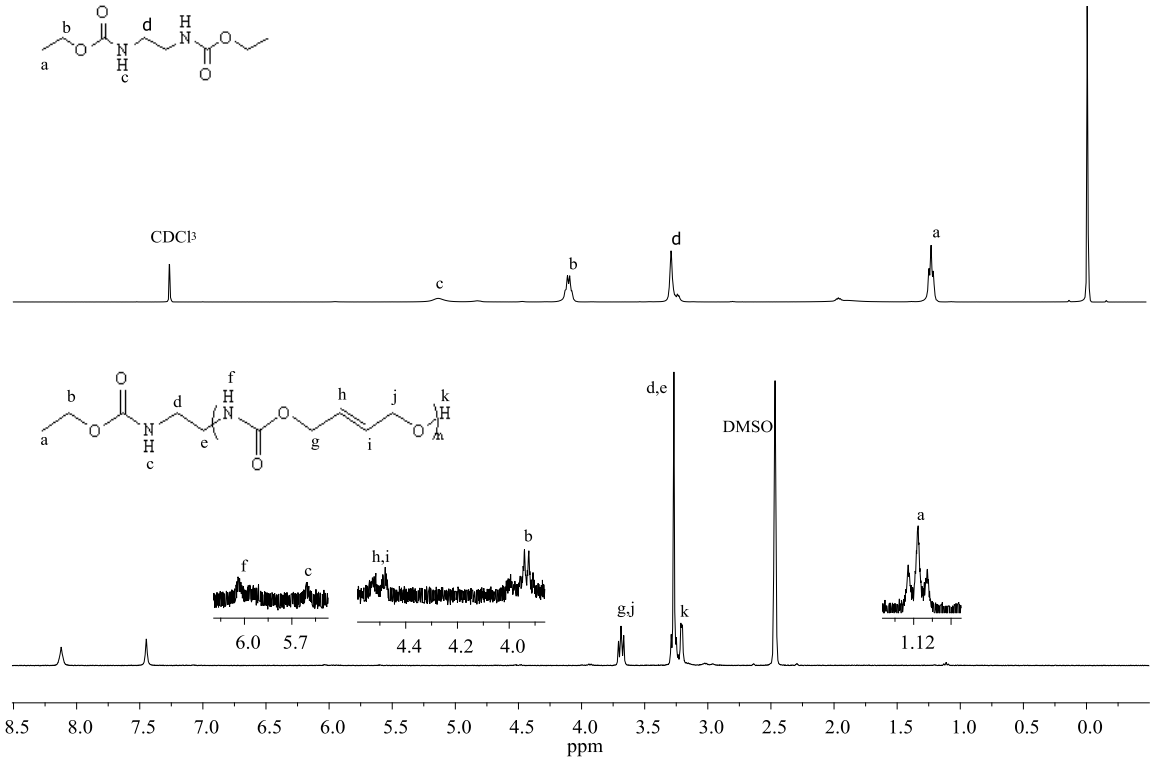


Figure 5. ^{1}H-NMR spectra of M1 and P1 products

4. Conclution

FTIR and NMR technique has confimed that the M1 and P1 product was succesfully form. The purity analysis with GC was confirmed the M1 product has purity up to 99,18%. Also, the MS analysis showed a corresponding signals with the possible fragmentation of M1 product indicated the M1 product surely formed. The polymerization of P1 was confimed using FTIR and ^{1}H-NMR technique. An invistigated showed that both in FTIR and ^{1}H-NMR spectra was prove of P1 structure.

Acknowledgement

Author gratefully acknowledges the Indonesian Directorate General of Higher Education (DIKTI) for financial support of this research by *Program Kreatifitas Mahasiswa* (PKM).

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