

FTIR SPECTROSCOPY ANALYSIS OF THE PREPOLYMERIZATION OF PALM-BASED POLYURETHANE

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ABSTRACT

The palm kernel based polyurethane (PU) was synthesized by prepolymerization method with various isocyanate/ polyol group ([NCO/OH]) ratio in ambient temperature under nitrogen gas. The presence of the urethane bond was observed in all the FTIR spectra of the PU. The carbonyl peak was identified at 1700 cm⁻¹ while the disappearance of isocyanate peak (-NCO) was observed around 2270 cm⁻¹, indicating a complete usage of the diisocyanate. However, the absorption peak of the carbonyl group (-C=O) in the urethane bond shifted to the left when the diisocyanate content decreased. The FTIR spectroscopy analysis justified that the diisocyanate was the main contributor in the formation of the hard segment of the PU. When the diisocyanate content is decreased, the formation of hard segment of PU will be affected and lowered the extent of polymerization of urethane bond in the PU system. Hence, PU1 may have the strongest urethane bond compared to others.

INTRODUCTION

Since the year of 2000, a lot vegetable oil based polyurethane products have been produced because the cost of petrochemical was increased drastically. Many researches were carried out to replace the petroleum based PU. In this research, the polyol was produced by using palm kernel oil via the method which described in the studies of Badri and her partners [1]

The PU been produced in this research undergo prepolymerization method which involve the use of specially designed prepolymers, namely structoset prepolymers. Structoset prepolymers are usually polymerized in the second step by the addition of a catalyst or other reactant and this polymers are highly advantageous because it generally offer greater control of polymerization and crosslinking reaction. Generally, there is 2 categories in structoset prepolymers which are structoterminal prepolymers and structopendant prepolymers. Structoterminal prepolymer is the prepolymer which its functional groups are located at the ends of the prepolymer chains whereas structopendant prepolymer is the prepolymer which its functional groups located along the prepolymer chain. Hence, the structoterminal prepolymer been produced and utilized to form PU in this research as below [3]:

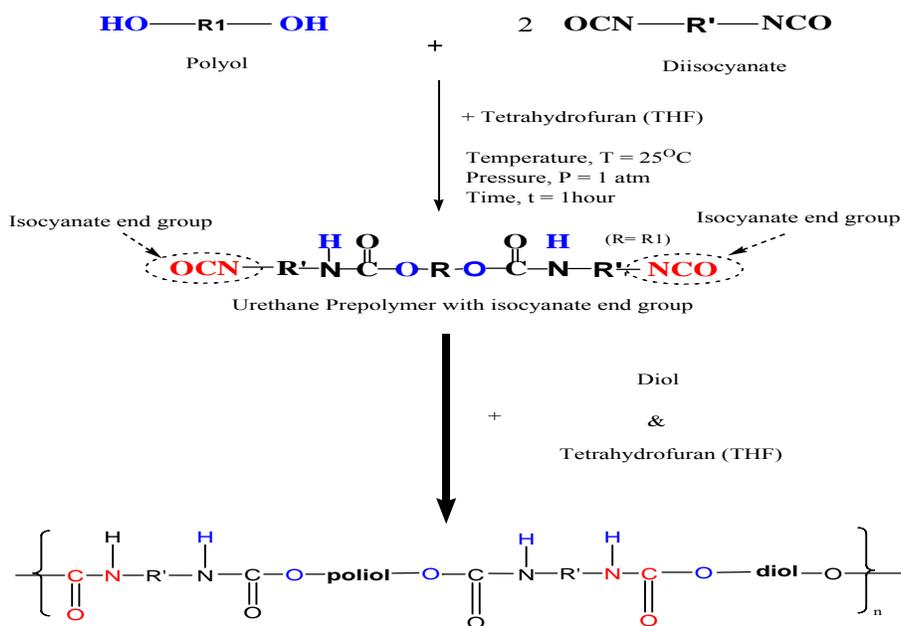


Figure 1: PU via prepolymerization method

There are several reasons to make PU through prepolymerization method as opposed to the single step polymerization. These include lower isocyanate vapour levels and reduce the exotherm of final reaction. During the process of making urethane prepolymer, the diisocyanate will react to polyol to form urethane prepolymer. Although the prepolymer is strictly contain isocyanate end group, but the molecular weight of urethane prepolymer will increase as the time proceed and hence its vapor pressure will reduced to be very low. The polyurethane which produced via single step polymerization will gives off heat when urethane bonds are formed and this will cause shrinkage in the final part. The production of urethane prepolymer will allow part of the exotherm to be dissipated prior to the formation of the final polyurethane. This will result in a lower final exotherm and lower shrinkage [2].

The significant of this research was synthesis the PU without heating compared to other previous research such as Truss [4] and Lynda Merlin [5] because they used polytetramethylene ether glycol (PTMEG) as their polyols which act as solid at ambient temperature and must be heated to allow further processing [2]. On the contrary, the polyol been used in this research were liquid at ambient temperature.

In this paper, it describes a significant investigation of isocyanate/ hydroxyl group ([NCO/OH]) ratio on the FTIR spectrum of PU films.

MATERIALS AND METHODS

Materials

Polyol was prepared which was described in the studies of Badri and her partners.⁷ 4,4-diphenylmethane diisocyanate (MDI) gained from Cosmo polyurethane (M) Sdn. Bhd., Klang, Malaysia. Tetrahydrofuran (THF) were from Merck Sdn Bhd, Malaysia. Diethylene glycol (DEG) was purchased from Fluka Chemie Sdn. Bhd,

Methods

Preparations of PU film

The polyol dissolved in THF was mixed with MDI in different ratio (2, 1.5, 1 and 0.75, respectively denoted as PU1, PU2, PU3 and PU4) in the round-bottomed flask under nitrogen atmosphere at ambient temperature as described by Clemitson 2009 to form urethane prepolymer and then added with DEG. Then the solution was agitated at 200 rpm in 1 hour for the polymerization without catalyst and surfactant. Then the mixture was cast on Teflon plate. The cast film was dried in vacuum oven at 55°C for 24 hours. All the PU films thickness obtained were about 50 microns and were transparent. No gel particles or bubbles were observed.

FTIR of PU films

Fourier Transform Infrared Spectrum recorded were obtained from FTIR spectrum Perkin Elmer Spektrum BX Spectroscopy model. This analysis is important to detect the functional groups of PU and identify the differences between the functional groups of PU with various [NCO/OH] ratio and the isocyanate end group of urethane prepolymer.

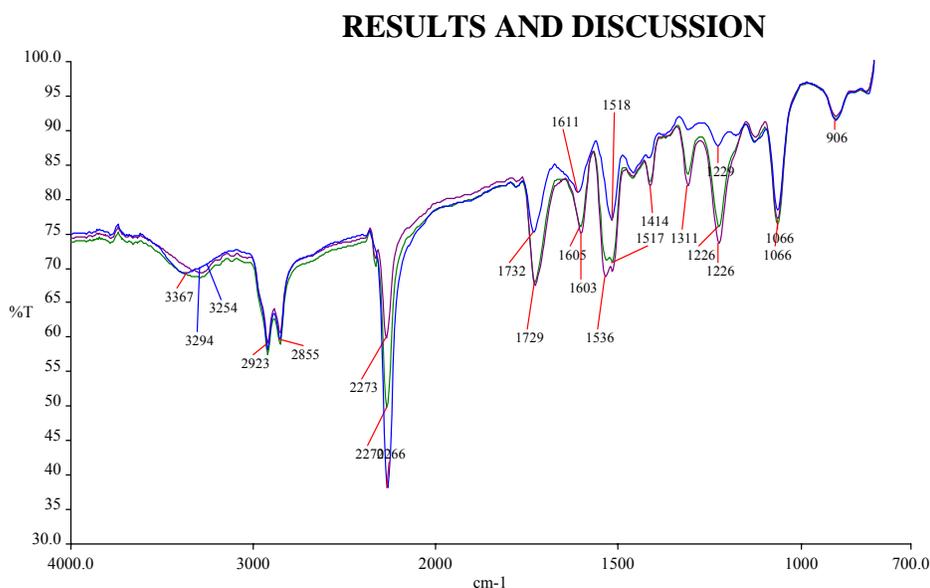


Fig. 2. IR spectrum of Urethane Prepolymer in 1 minute (blue), 15 minutes (green) and 30 minutes (purple)

From Figure 2, the IR spectrum of the urethane prepolymers displayed several similar characteristics. On the other hands, the presence of main characteristic peaks at around 2270 cm⁻¹, which corresponds to the stretching of NCO group. The IR spectrum of all urethane prepolymer show similar bands.

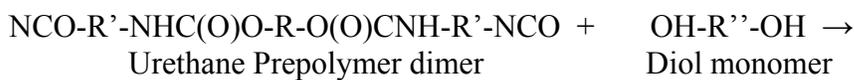
Functional group	Wavenumber (cm ⁻¹)
C=O	≈1730
C=C	≈1520
N=C=O	≈2270
C-O-C	≈1220

Table 1 FTIR characteristic peaks for urethane prepolymer

The NH group was formed with the presence of N-H peak at 3294cm⁻¹. Hence, it proved the prepolymerization reaction was happen to form urethane prepolymer. The prepolymerization of the PU is a step polymerization. Step polymerization proceeds by a slow increase in the molecular weight of the polymer. The first step of the polymerization of PU is the reaction of polyol and diisocyanate monomers to form dimer [6]:



Then, the dimer reacts with another unreacted low molecular weight diol monomer to form trimer:



The trimer proceed to react with others monomer, dimer or each other. Hence, the molecular weight of the polymer continuously increasing. Step polymerizations are characterized by the disappearance of monomer in the reaction [9]. Hence, the general reaction can be expressed as:



Figure 3 showed the IR spectrum of MDI, urethane prepolymer and PU. In Figure 4, the wavenumber of NCO peak of MDI and urethane prepolymer were around 2270-2250 cm⁻¹ but the NCO peak of MDI was sharper than the urethane prepolymer because the polyol reacted with diisocyanate to form urethane prepolymer in order to remove the

free diisocyanate of MDI. Besides that, there is no NCO peak in PU. Hence, it showed that the diisocyanate completely react with polyol to form PU. Generally, free NH stretching band, hydrogen bonded NH groups with ether oxygen and bonded NH groups with carbonyl oxygen are observed at 3450 cm⁻¹, 3290-3310 cm⁻¹ and 3300-3350 cm⁻¹ [7]. Hence the NH peak of PU in IR spectrum was observed at 3290 cm⁻¹ and it proved that hydrogen bond been formed in PU chain.

The reaction mechanism of the urethane bond formation in prepolymerization of PU is nucleophilic substitution. The nucleophile of oxygen will attack the carbonyl group of diisocyanate and forms 2 types of intermediate complexes resonance structure (A & B) as below. It was found that the intermediate complex B is more intend to react with polyol compared to the intermediate complex A. It is because the carbonyl bond (C=O) of intermediate B is stronger than the C=N bond of intermediate complex A. Hence, the intermediate complex B is more stable than intermediate complex A. On the other hand, nitrogen atom (N) is more electropositive than oxygen atom, so the -CN bond is prior to attract cation (H⁺) compared to -C-O [8]. Hence, the intermediate complex B will react to form urethane bond. The mechanism of urethane bond formation is as Figure 4.

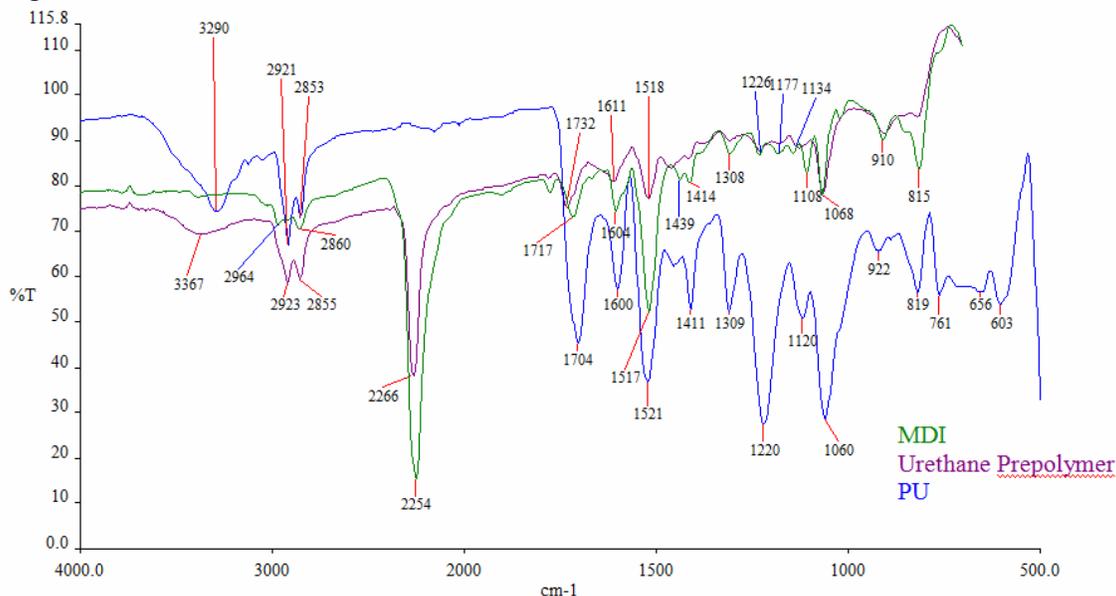


Figure. 3. IR spectrum of MDI (green), urethane prepolymer (purple) & PU (blue)

Functional groups	MDI	Wavenumber (cm-1)	
		Urethane prepolymer	PU
N-H	-	3367	3290
C=O	1717	1732	1704
C=C	1517	1518	1521
C-N	1604	1611	1600
N=C=O	2254	2266	-

Table 3 FTIR characteristics peaks of MDI, urethane prepolymer and PU

From Figure 5, we can found that the existance of the peaks of amide group -N-H, carbonyl urethane group -C=O, carbamate group -CN and -C-O-C proved the urethane formation in the PU above. On the other hand, the FTIR spectra showed the wave number for the carbonyl peak -C=O of these 4 PU were around 1700 cm-1 and ini it proved that the hydrogen bond was formed in PU as in below:

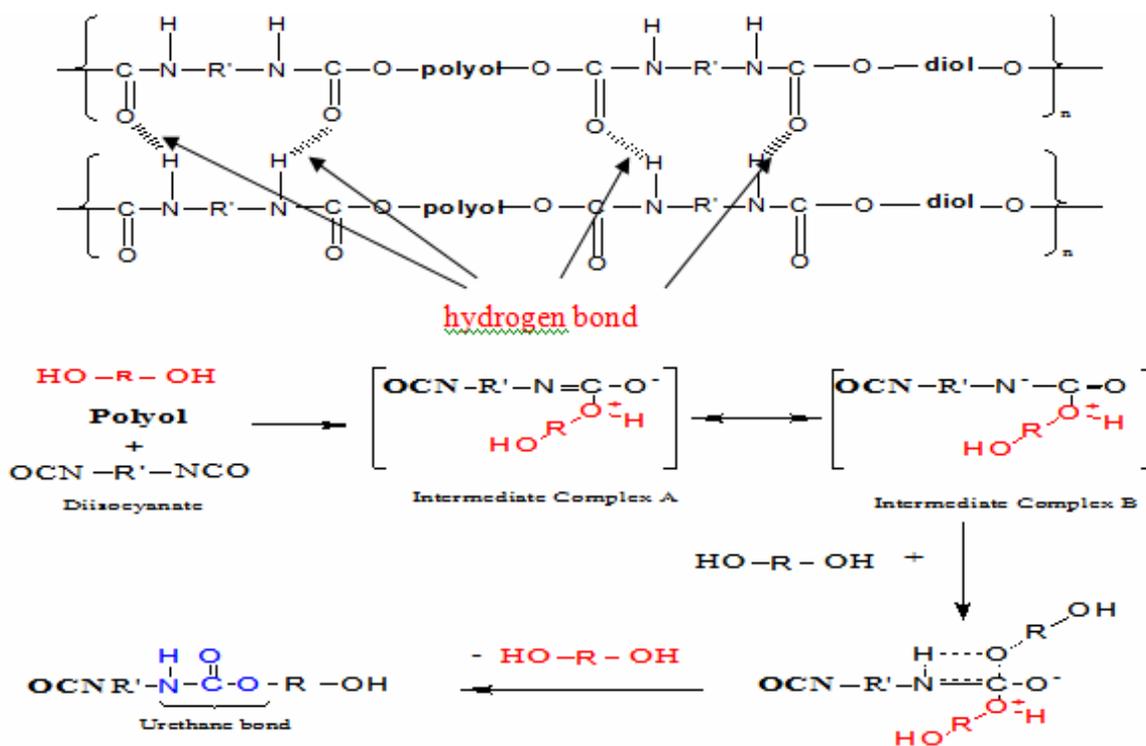


Figure 4. Mechanism of Urethane bond formation

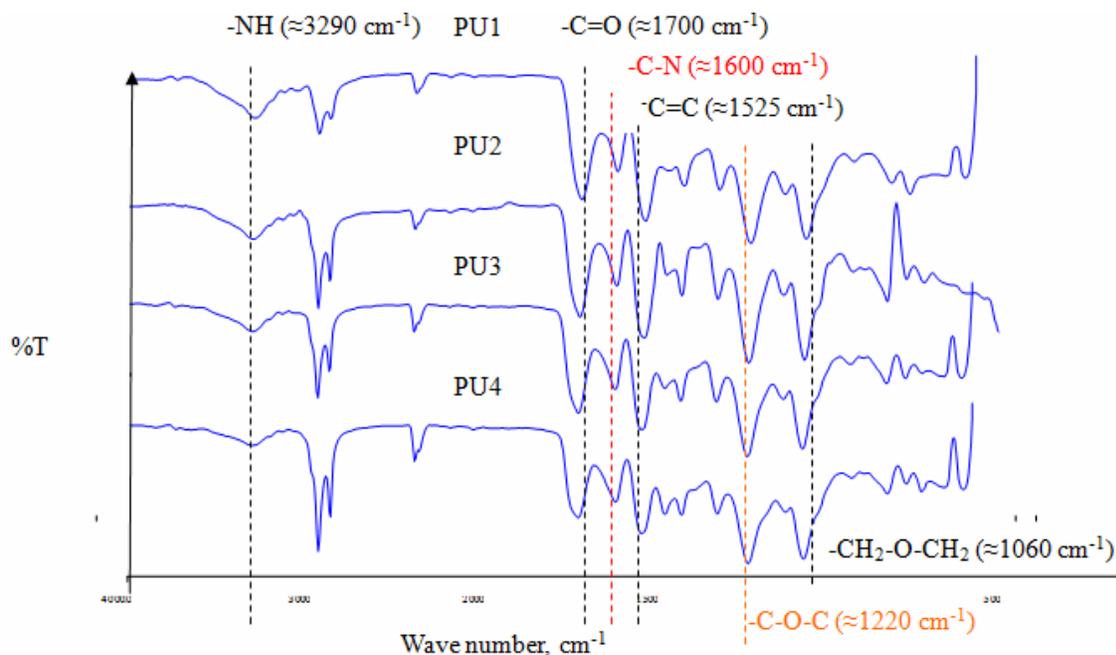


Figure 5: IR spectrum of PU with 4 types of different [NCO/OH] ratio

According to Clemitson (2008), the existence of the peak at 1730 cm^{-1} was a non hydrogen bonded carbonyl urethane group -C=O where the peak around 1700 cm^{-1} was a hydrogen bonded carbonyl urethane group. Hence, the FTIR spectra proved that the hydrogen bonding was occur in this prepolymerization method.

Following the Figure 5 as above, when the isocyanate content was decreasing by the descending of [NCO/OH] ratio from PU1 to PU4, the carbonyl urethane group -C=O were shiefting to the left. A hypothesis can be made that when the isocyanate content of PU was decreasing, the lesser urethane group been formed in PU and the interaction between the PU chain became weaker. So, PU1 had strongest urethane bond with wave number of carbonyl urethane group at 1704 cm^{-1} where PU4 had weakest urethane bond with wave number of carbonyl group at 1709 cm^{-1} . From the Figure 5, we can see that the peak become broader when the isocyanate content was decreasing. Besides that, all isocyanate groups were react with hydroyl groups in polyol to form urethane groups also can explained the disappearance of the peak of isocyanate group around 2270-2250 cm^{-1} for the above FTIR spectrum

CONCLUSIONS

The FTIR results proved the prepolymerization of PU happened. The polymerization of urethane bond were proved by the disappearance of the peak of isocyanate group around 2270-2250 cm^{-1} in FTIR results. When the isocyanate content was decreasing, the carbonyl urethane group -C=O were shiefting to the left. Hence, PU1 had stongest bond with wave number of carbonyl group at 1704 cm^{-1} .

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