

THERMAL AND INFRARED ANALYSIS OF DIFFERENT POLYOL MOLECULAR WEIGHT FROM EMPTY FRUIT BUNCH FIBRE (EFBF)

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ABSTRACT

Preparation of low cost polyol from abundant and renewable biomass resources has long been an interesting subject in the polyurethane industry. The oil palm empty fruit bunch fiber (EFBF) is one of the important lignocellulosic waste. EFBFs are a major by product of the oil palm industry. Recently the utilization of EFBF has become appealing because of it's environmental friendly, cheap, easy to get and cost of petroleum was increased. The first step involved chemically modified EFBF using isopropanol and sodium hydroxide (NaOH) to produce hydroxypropylated-EFBF (HP-EFBF). This reaction take 20 minutes and after that cooling it in room temperature for one hour. Then, propylene and polyethylene glycol (PEG) in a different molecular weight (6000, 8000 and 10,000) was added into the mixture. The reaction was performed 80°C for two hours. The next stage is to produce polyol whereas HP-EFBF was reacted with phenol and distilled water at temperature 110-120°C for one hour. Later, formaldehyde was added into the mixture and it was reacted at temperature 80-90°C for one hour and fifteenth minutes. The techniques used for characterizations were infrared analysis (FTIR) and thermogravimetry analysis (TGA). TGA result was analyzed to monitor the composition and structural dependence on thermal degradation of natural cellulose fiber and to calculate the kinetic activation energy, E_a of polyol. Meanwhile, FTIR was analyzed to measure the change of surface compositions of fibres after treatment. TGA analysis showed that activation energy of polyol slightly increasing with molecular weight of polyol. Molecular weight of polyol is high so E_a also high. If activation energy is higher, the thermal stability for that sample is more stable. Based on infrared analysis, after chemical reaction, the composition of the sample slightly different with untreated EFBF.

INTRODUCTION

Oil palm or it scientific name (*Elaies guineensis*) which is grown in mass plantation in tropical countries such as Malaysia, Nigeria and Indonesia. In Malaysia, EFB is one of the biomass materials which is by-product from oil palm. EFB waste generated by the industry is estimated to be about 10 millions tons per year. EFB consist of 65% hemicellulose and cellulose and 25% lignin. This lignocellulosic have lots of hydroxyl groups which is OH group could serve as reaction sites with various functional group in

the thermoset system (H. D. Rozman et al. 2003). According to Hatakeyama et al. 2005, natural polymer having more than two OH groups per molecule could be used as a polyol for polyurethane preparation if the groups could be reacted with isocyanate. Preparation of low-cost polyol from abundant and renewable biomass resources has long been an interesting subject in the polyurethane industry (Mizutani et al. 2006). Polyol is important material of PU which has wide application in furniture, packing, automobile, aviation, ship building and aircraft manufacturing (Hui et al. 2007). Polyol contains multiple hydroxyl (-OH) groups and ranges in molecular weight from 400 to 7000 Da. Usually polyol is produced from reaction of alkylene oxide (ethylene oxide or propylene oxide) and initiator (e.g. ethylene glycol, glycerin) in a necessary catalytic environment. It further reacts with isocyanate ($-N=C=O$) via the addition polymerization reaction to produce polyurethane products (Soohwa et al. 2005). For elastomer synthesis, molecular weight of polyol that usual use is variety, but for industry synthesis, molecular weight of polyol that they use is in range 600 to 2000 (Hepburn. 1992). The two main classes of polyols are polyesterols and polyetherol. Eighty to ninety percent of polyol used today are polyetherols. The polyetherols are produced by the alkali-catalysed polymerization of ethylene oxide propylene oxide using a triol as initiator (Lefebre et al. 2005). There are several research studies of using palm oil for polyol preparation. (Siwayanam et al.1999) have reported the preparation of polyols from palm oil by epoxidation for polyurethane production. By their method, Tri-G molecules were converted to polyols by the reaction with polyhydric alcohols. (Tanaka et al. 2008) reported the preparation of polyols by glycerolysis. Using this polyol, polyurethane foams were prepared. (Hui et al. 2007) have reported in their research, wheat straw was liquefied in mild condition and the liquefaction product was used as polyol.

METHODOLOGY

Materials

Empty fruit bunch fiber was supplied from Sabutek Sdn Bhd at Teluk Intan, Perak. Natrium hydroxide, isopropanol, propylene oxide, formaldehyde and phenol was supplied from Merck. Polyethylene glycol (6000, 8000 and 10000) was supplied from Fischer Scientific. All of the chemicals were used without further purification.

Preparation of hydroxypropylated-EFBB (HP-EFBB)

Isopropanol act as a solvent for this mixture. EFB fiber were soak in this solvent together with 32% natrium hydroxide (NaOH). The mixture was stirred using magnetic stirrer for 20 minutes. After 20 minutes, it was cool down under room temperature for one hour. Then propylene oxide and polyethylene glycol (PEG) with different molecular weight (6000, 8000 and 10000) were put into the mixture. The mixture were charged into three necked glass flask (1000ml) furnished with a reflux condenser, thermometer and stirrer. The reaction carried out at temperature 80°C for two hours to prepare hydroxylpropylated-EFBB. After two hours, the HP-EFBB were cool at room temperature, filtrated using glass filter and oven dried for 24 hours at temperature 80°C.

Preparation of polyol

Phenol with ratio 1:1 to EFBF were used. First, phenol was melted at temperature become 50°C. Later, HP-EFBF were mix with the molten phenol and distilled water were added into the mixture. The heating reaction was done at temperature 110-120°C for one hour. The mixture then cooled until temperature 35°C. At 35°C, formaldehyde were added into the mixture at a ratio 1:1 to phenol. The reaction was perform at temperature 80-90°C for one hour and fifteenth minutes. Then, the mixture was cooled down under room temperature and was filtrated using glass filter.

Thermogravimetry analysis (TGA)

TGA analysis were performed using Metler Toledo 220 TGA instrument. Temperature programs for thermal degradation analysis were from 35 to 700°C at a heating rate of 2.5-30°C/min. The measurement were conducted under nitrogen (20mL/min) and switched to air at 700°C.

Fourier transform infrared (FTIR)spectroscopy measurements

Infrared spectrum analysis was performed using a Perkin-Elmer 2000 spectrometer. Resolution of 2cm⁻¹ was taken for each sample with total of 100 scans. A mixture of 5.0 mg of sample and 200 mg of KBr was pressed into a disk for FTIR measurement.

Calculation of the kinetic activation energy, E_a

Thermogravimetry was used to calculate the kinetic activation energy of polyol. From the thermogravimetry data, graph ln (ln 1/y) versus 1/T was plotted to get E_a value.

From activation energy equation,:

$$\ln (\ln 1/y) = (-E_a/R \times 1/T) + \ln (R/E_a \times Z/R_H \times T_m^2)$$

Where E_a = activation energy (kJ/mol)

T = Temperature (K)

R = Gas constant (8.314 J/molK)

From equation:

$$y = mx + c$$

where y = ln (ln 1/y)

$$m = -E_a/R$$

$$x = 1/T$$

$$c = \ln (R/E_a \times Z/R_H \times T_m^2)$$

RESULTS AND DISCUSSION

Infrared spectrum analysis

The aim of using FTIR is to measure the change of surface composition of fibres after treatment. Infrared spectra of untreated EFBF are shown in Figure 1. Vibration peak at 3434.81cm⁻¹ attributed to the hydroxyl (OH) stretching. This indicated the OH stretching maybe consist of variety compound such as water, primer and secunder

aliphatic alcohol which is got in cellulose, hemicellulose and lignin structure. The existence of methyl and methylene group in EFBF was showed at wave number 2917.91cm^{-1} which is it was aliphatic C-H stretching. Aromatic stretching from =C-H bonding was showed at wave number 1507.64cm^{-1} . This is because of benzene ring aromatic stretching from lignin. At wave number 1034.70cm^{-1} is C-O-C stretching which is existing of eter. The existing of eter maybe from type of aliphatic eter in cellulose and lignin and aromatic eter in lignin also. However, the existence peak at wave number 892.92cm^{-1} because of β -glycosidic bonding in EFBF. Figure 2 showed infrared spectrum of different polyol molecular weight which is reaction with phenol and formaldehyde. The vibrational peak at 3400cm^{-1} in the FTIR spectrum of polyol was regarded as a proof that the polyol also has hydroxyl band. From the results, hydroxyl stretching vibration of OH band is more higher than OH stretching vibration for EFBF without treatment. This is due to chemical reaction in polyol which is more chemical was used to produce polyol. Chemical reaction in polyol give this polyol additional OH value and other functional group which is not exist in EFBF without treatment. However, before phenol and formaldehyde reaction, vibrational band at 2923.51cm^{-1} still appear but after reaction this band fully disappear but strong band at 1633.28cm^{-1} exist in polyol. This is due to CH_3 and CH_2 bonding become less after the reaction. The strong band exist around 1600cm^{-1} . This vibrational peak was carbon double bond stretching from aromatic $\text{C}=\text{C}$ and alkena group. It was assumed that carbon aromatic ring from phenol structure was formed in polyol. 1250cm^{-1} existed again in this reaction with high intensity. Existence of this peak was regarded as the proof that the existence of phenol because of this peak due to benzene aromatic ring from phenol which is their intensity band in EFBF is low intensity in polyol due to benzene aromatic ring or phenol is one of lignin. The existence band 1472.67cm^{-1} because of $\text{C}=\text{C}$ stretching from phenol and benzyl alcohol structure. The existence of C-O-C stretching because of eter group exist in cellulose and lignin. The vibrational band around 757cm^{-1} also due to phenol structure. This peak exist because of C-H tortion (Siverstein et al. 1991).

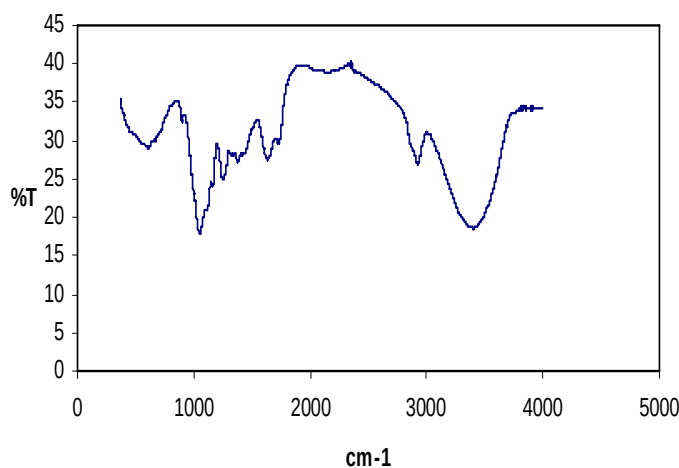


Figure 1: FTIR spectrum for untreatment EFBF

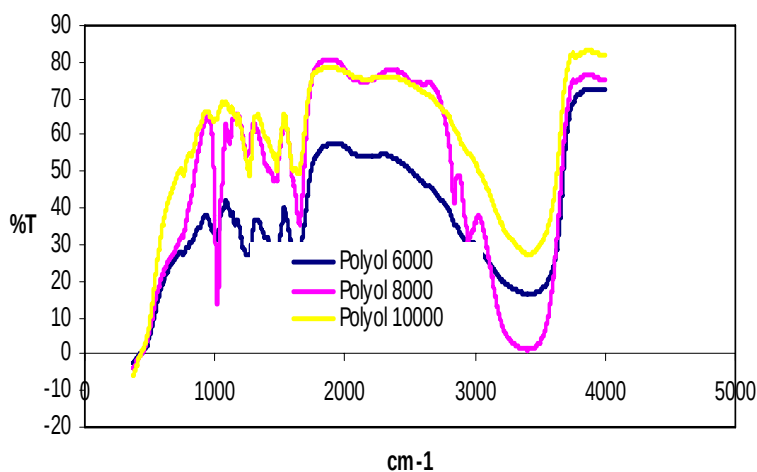


Figure 2: FTIR spectrum for different polyol

Table 1: Vibrational peak of FTIR for untreated EFBF

Wave number (cm ⁻¹)	<i>Bonding movement</i>
3434.81	Hydroxyl (OH) stretching
2917.91	C-H stretching from CH ₃ and CH ₂
1507.64	Aromatic stretching from =C-H bonding
1024.70	C-O-C stretching
892.92	β -glycosidic from carbohydrate

Table 2: Vibrational peak of FTIR for polyol

Wave number (cm ⁻¹)	<i>Bonding movement</i>
~3400	Hydroxyl (OH) stretching
~1600	C=C stretching (aromatic and alkena groups)
~1400	C=C stretching (phenol and benzyl alcohol groups)
~1200	C-O- stretching
~1000	C-O-C stretching

Thermal degradation analysis

Thermal degradation analysis was showed some degradation which is mainly under temperature ranging 200°C is the evaporation. At temperature 140°C it was carbon monoxide degradation. Meanwhile in temperature ranging from 200-280°C was cellulose degradation and 400-500°C is lignin degradation (M. V. Pandya et al. 1998). Figure 3 showed thermal degradation for untreated EFBF. The first stage degradation of

untreated EFBF is at temperature below 100°C it was evaporation which is their weight loss around 5.41%. Second stage is at temperature ranging from 220-390°C which is their weight loss around 74.58%. This is caused primarily component of EFBF which is cellulose was decomposition at this stage. Therefore, endothermic peak appeared at temperature 355°C and fully decomposition occurred at temperature 390°C. Figure 4 showed thermal degradation for different polyol. Five thermal degradation stage appeared in this sample. First stage is water molecule decomposition at temperature range below 100°C. Second stage is carbon monoxide decomposition below 140-340°C. Weight decreasing in this temperature give big effect to primer component of cellulose which is due to dehydration and depolymerization of cellulose. While last decomposition occurred at temperature ranging from 340 – 410°C which is caused of decomposition of lignin which is their losing weight around 17.63% to 18.93%. Fully degradation occurred at temperature 440°C. Figure 6(a, b and c) is to calculate the kinetic activation energy for different polyol molecular weight. From a plot of $\ln(-\ln 1/y)$ versus $1/T$, the kinetic of E_a can determined. The results showed that E_a increasing slightly with increasing of molecular weight of polyol. If molecular weight of polyol is high so E_a also is high. The activation energy at various molecular weight is shown in Table 1. Polyol 10000 indicated E_a value is 2.9423×10^4 kJ/mol, polyol 8000 and polyol 6000 is 1.5975×10^4 kJ/mol and 1.3575×10^4 kJ/mol respectively.

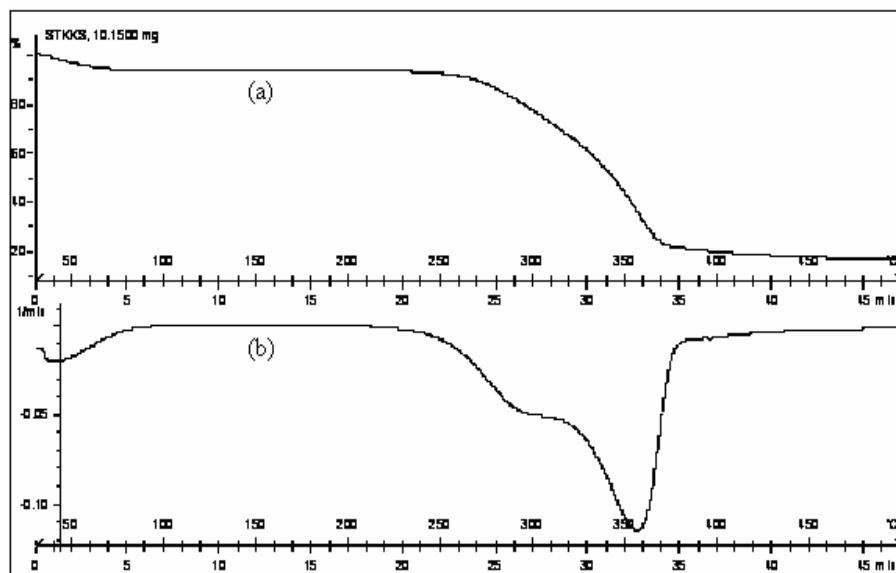


Figure 3 The thermogram of TGA and DTG and DTG for untreated EFB

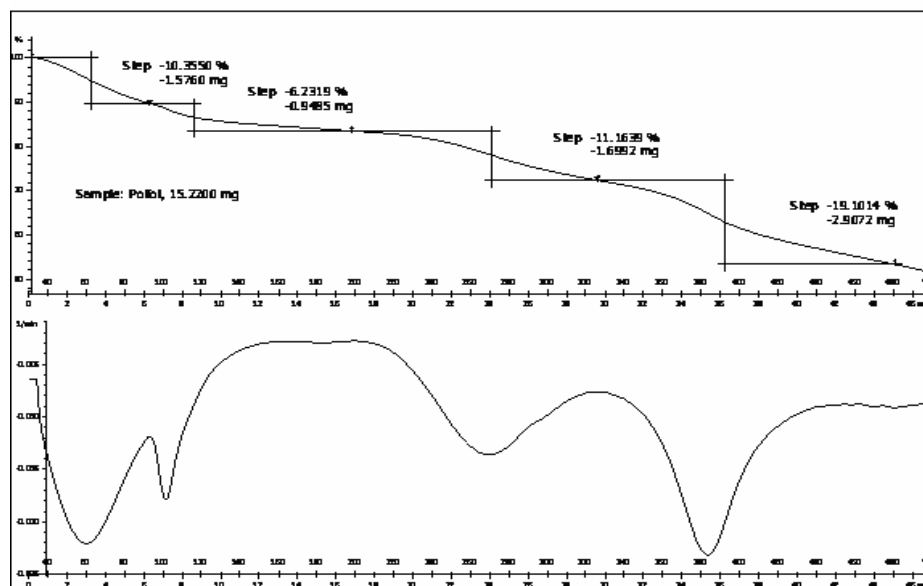


Figure 4 The thermogram of TGA for polyol

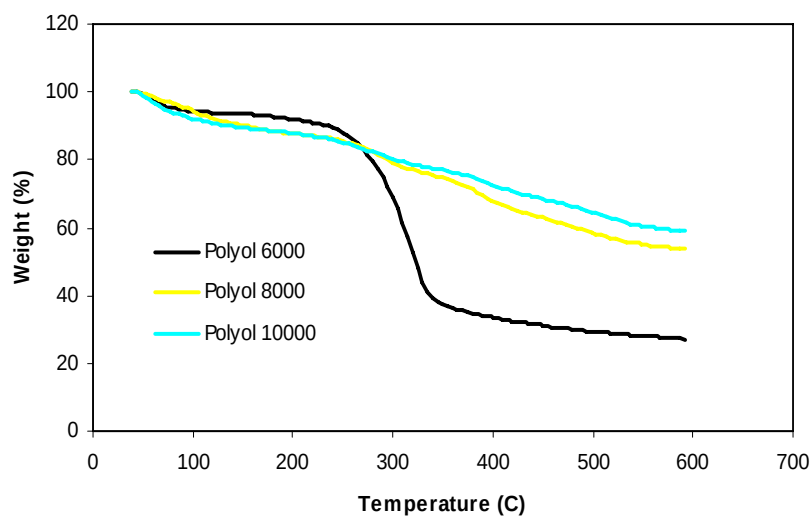


Figure 5 Weight (%) versus Temperature (C) for different polyol

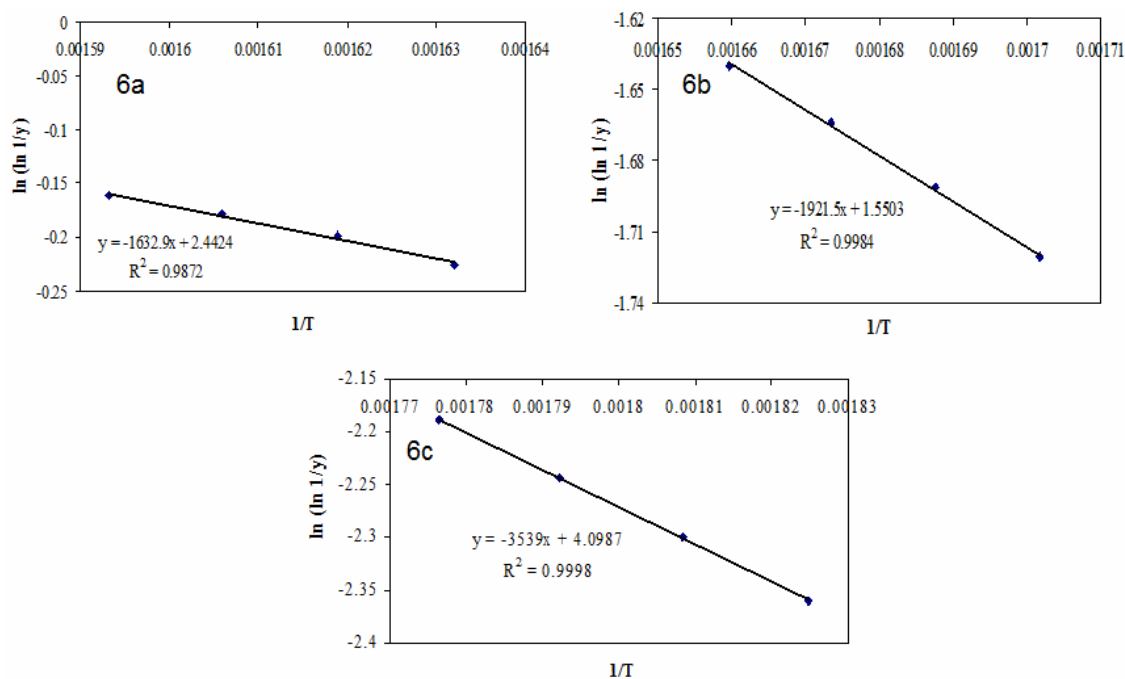


Figure 6: a) $\ln(\ln 1/y)$ versus $1/T$ for polyol 6000, b) $\ln(\ln 1/y)$ versus $1/T$ for polyol 8000 and c) $\ln(\ln 1/y)$ versus $1/T$ for polyol 10000.

Table 1: Activation energy, E_a value for different polyol molecular weight

Type of polyol	Activation energy, E_a (kJ/mol)
Polyol 6000	1.3575×10^4
Polyol 8000	1.5975×10^4
Polyol 10000	2.9423×10^4

CONCLUSION

The FTIR results indicated a change of bonding movement for untreated EFBF and polyol are quite different their functional groups whereas after chemical reaction, polyol was showed additional functional groups which is not appear in untreated EFBF. The existence of other functional groups in polyol proof that after chemical reaction, new functional groups exist in the sample. Thermogravimetry revealed that thermal degradation of EFBF depend mainly on cellulose, hemicellulose and lignin that were present in the fibre. Meanwhile, thermal degradation of polyol depend on the fiber in EFB and also depend on chemical that use in experiment which is when chemical reaction was done, more degradation happened. The kinetic activation energy of thermal degradation of the polyol varied with different molecular weight of polyethylene glycol. Polyol with molecular weight 10000 shown the highest E_a than polyol 8000 and polyol 6000. Hence, it showed that E_a increasing with increasing of molecular weight of polyol. It also showed, thermal stability of the sample depend on E_a

value, if E_a value is high, so more stable the thermal stability of the sample.

ACKNOWLEDGEMENT

The authors would like to thank the Malaysian Government for the support through Science Fund Grant UKM-ST-06-FRG0010-2007 and gratefully thank Universiti Kebangsaan Malaysia (UKM, Bangi) for a PhD scholarship.

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