

Synthesis and Characterization of Lignin-Based Polyurethane as a Potential Compatibilizer

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Received August 1, 2017; Accepted December 5, 2017

ABSTRACT

Lignin is one of the most abundant biopolymers on earth. It has polar and non-polar sides due to its hyperbranched structure, but the polarity of lignin has a higher tendency than non-polarity. Lignin has potential to be compatibilizer if the portion of non-polar can be increased. This research is focused on investigation of the synthesis of lignin-based polyurethane to enhance the non polar portion in lignin. Lignin-based polyurethane was prepared by reacting 4,4'-Methylenebis(cyclohexyl isocyanate) (HMDI) and polyethylene glycol (PEG), then lignin was added to the reaction. In this study, the structure of lignin-based polyurethane was confirmed by NMR and FTIR spectrometers. The NMR and FTIR analyses showed that lignin was successfully grafted. NMR, also used to investigate the effects of molar mass of PEG and isocyanate contents to polarity of lignin-based polyurethane. The polarity of lignin-based polyurethane decreased as the composition of HMDI and molecular weight of PEG increase. This result also occurred on the sessile drop test that used to determine surface tension of lignin-based polyurethane. The thermal properties of lignin-based polyurethane was also investigated using STA. Based on STA, enhancement of composition of HMDI and PEG increase thermal degradation and resistance of lignin-based polyurethane.

Keywords: synthesis; lignin; polyurethane

ABSTRAK

Lignin adalah salah satu biopolimer terbanyak di dunia. Lignin memiliki sisi polar dan nonpolar akibat struktur yang bercabang. Namun, berdasarkan penelitian sebelumnya, tendensi kepolaran lignin lebih besar dibandingkan kenonpolarannya. Lignin berpotensi sebagai kompatibiliser yang baik apabila kenonpolarannya dapat ditingkatkan. Penelitian ini bertujuan untuk mensintesis hibrida poliuretan berbasis lignin (HPL) untuk meningkatkan kenonpolaran lignin. HPL dihasilkan dari reaksi 4,4'-Metilenebis(sikloheksil isosianat) (HMDI), polietilen glikol (PEG) dan lignin. Struktur HPL dikonfirmasi menggunakan nuclear magnetic resonance spectroscopy (NMR) dan fourier transform infrared spectroscopy (FTIR). Berdasarkan NMR dan FTIR, HPL berhasil dihasilkan. NMR juga digunakan untuk meneliti efek variasi masa molar PEG dan komposisi diisocianat terhadap kepolaran HPL. Kepolaran HPL menurun seiring meningkatnya komposisi HMDI dan masa molekul PEG. Hasil ini juga dikonfirmasi oleh pengujian sessile drop yang digunakan untuk menentukan tegangan permukaan. Sifat termal HPL juga diuji menggunakan STA. Berdasarkan STA, suhu degradasi (T_d) dan ketahanan suhu semakin meningkat seiring dengan meningkatnya komposisi dari HMDI dan PEG.

Kata Kunci: sintesis; lignin; poliuretan

INTRODUCTION

Compatibilizer has important part in immiscible polymer blends. It can develop the high-performance materials with enhancement in thermodynamic compatibility and interphase strength. In a previous study, biodegradable blends of poly(D,L-lactide) and poly(ϵ -caprolactone) found to be immiscible [1]. Addition L-lysine-diisocyanate and L-lysine-triisocyanate as

compatibilizer to the mixed of poly(D,L-lactide) and poly(ϵ -caprolactone) was reported be able to maintain their biocompatibility and increase the fracture toughness of materials [2]. The other general compatibilizers are poly(butylene succinate) (PBS), poly[(butylene succinate)-co-adipate] (PBSA), and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) [3-5].

Beside the desire to develop new high-performance materials, there has also significant

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interest in the recycling and reuse of waste due to environmental and economic concerns. Lignin as one of the waste content in pulp industrial has potential to be used as compatibilizer. It is because lignin has polar and nonpolar side due to benzene rings and hydroxyl groups. Rozman et al. studied lignin as compatibilizer between polypropylene and coconut fiber [6]. It is reported that hydroxyl groups in lignin have dominant influence over the others functional group and result in decline tensile properties. Therefore, it is believe that lignin has a higher tendency to polarity than non-polarity [7]. So it is important for lignin to decrease polar side in order to become a good compatibilizer by reacting the hydroxyl group.

Synthesis of polyurethane is the solution to decrease polar side of lignin because requiring hydroxyl groups in the reaction. It is produced from the reaction between the polyol and the diisocyanate. The properties of the polyurethane can be altered by changing the type of the diisocyanate, diol, polyol and crosslinker precursors [8-10]. Cross-linked polyurethanes have better thermal and thermomechanical properties and a good shape memory effect than linear polyurethane [11-12]. Comparison between linear PU and pentaerythritol cross-linked PU connected by polyethylene glycol (PEG-200) spacer result in the improvement of stress and strain for the combination of both pentaerythritol and PEG-200 [13].

The objective of this study was to evaluate the effect of composition of 4,4-methylenebis(cyclohexyl isocyanate) (HMDI) and molecular weight of polyethylene glycol (PEG) on polarity of lignin-based polyurethane. To study the polarity, polyurethanes were made by reacting HMDI, PEG (Mw 4000 and 6000) first and then lignin was added as crosslinker. Lignin-based polyurethanes were characterized by FTIR, NMR spectrometers and sessile drop. The thermal properties of lignin-based polyurethane were also studied using STA.

EXPERIMENTAL SECTION

Materials

Lignin, 4,4-Methylenebis(cyclohexyl isocyanate) (HMDI), Polyethylene glycol (PEG) (Mw 6000, 4000), and Dibutyltin Dilaurate catalyst (DBTL) were obtained from Sigma Aldrich. Research variables are listed in Table 1. Lignin was dried at 70 °C prior to polymerization.

Instrumentation

To confirm the structure of molecules and reactions, lignin-based polyurethane was characterized by

Table 1. Variables

Sample	PEG, g	HMDI, mL	Lignin, g
HPL6B	15	1.2	0.5
HPL6C	15	1.8	0.5
HPL6D	15	2.4	0.5
HPL6E	15	3	0.5
HPL4C	10	1.8	0.5
HPL4D	10	2.4	0.5
HPL4E	10	3	0.5

Nuclear Magnetic Resonance (NMR) type JEOL JNMECA 500 and Fourier Transform Infra-Red Spectroscopy (FT-IR Spectroscopy) type PerkinElmer spectrum two. The polar and nonpolar ratio can be also calculated by the equation integration spectrum from H-NMR analysis [14]. Sessile drop was used to calculate surface tension using Zisman equation [15]:

$$\cos\theta = 1 - \frac{\gamma - \gamma_c}{\gamma}$$

where γ_c is Critical surface tension of the sample. Simultaneous Thermal Analysis (STA) type PerkinElmer STA-500 was used to know the thermal properties and morphology of the product. The heating rate was 20 °C/min under nitrogen gas.

Procedure

Synthesis of lignin-based polyurethanes

Lignin-based polyurethanes were synthesized by two-step polymerization in DMF solution, using HMDI, PEG (Mw 6000 and 4000), catalyst DBTL and lignin as crosslinker. The reactor Schlenk tube with nitrogen gas inert was prepared for the first step of synthesis polyurethane. The first step was preparation of prepolymer by reacting variation PEG, diisocyanate and added two drops catalyst DBTL in the solvent DMF at 80 °C under stirring for 1 h. In the same system, the second step was done by adding variations composition of lignin as crosslinker at 80 °C under stirring for 1 h. The reaction was then terminated by water to produce lignin-based polyurethane.

RESULT AND DISCUSSION

Synthesis of Lignin-Based Polyurethane

Lignin-based polyurethanes were successfully synthesized using lignin as crosslinker. Illustration of synthesise is shown in Fig. 1. The synthesise start from reaction between PEG (Mw 6000 or 4000) as polyol and HMDI as diisocyanate with catalyst DBTL to make prepolymers. Cyanate groups (N=C=O) in HMDI have electropositive carbon. This carbon is easily attacked by hydroxyl groups as nucleophile from PEG. The reaction will produce urethane bonds. The

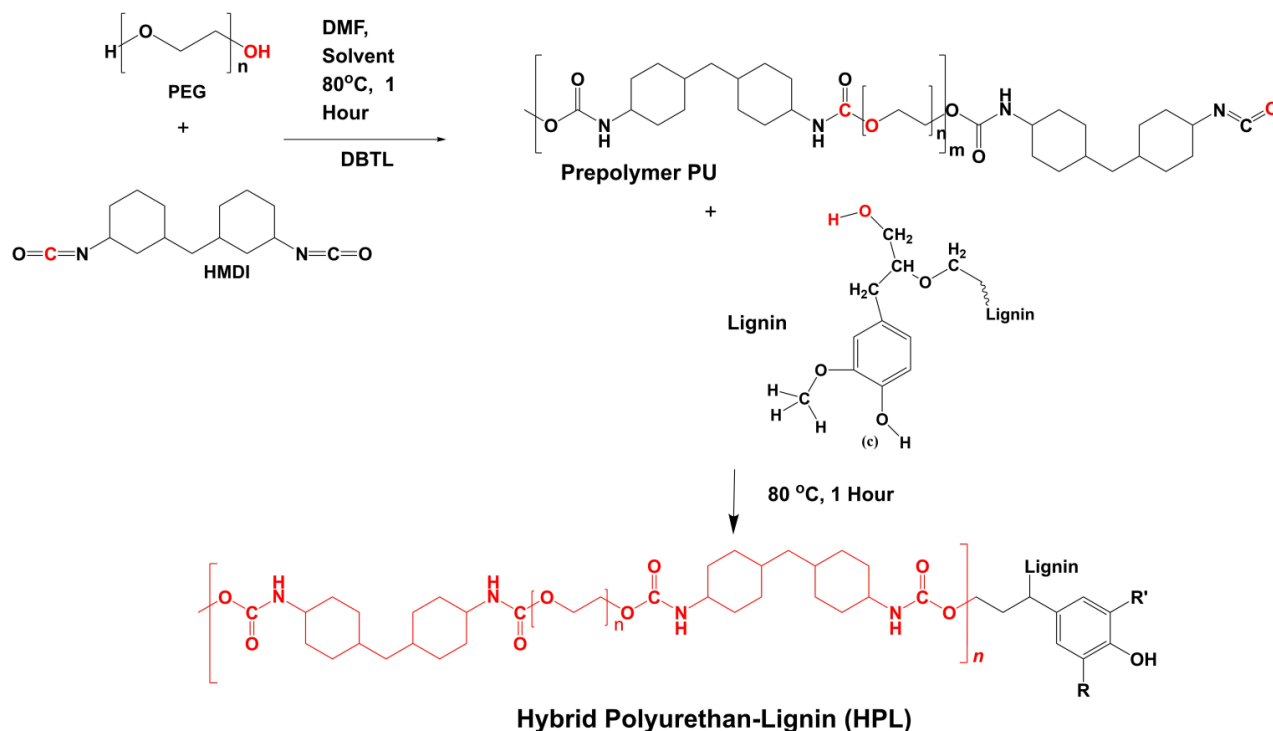


Fig 1. Synthesize of lignin-based polyurethane

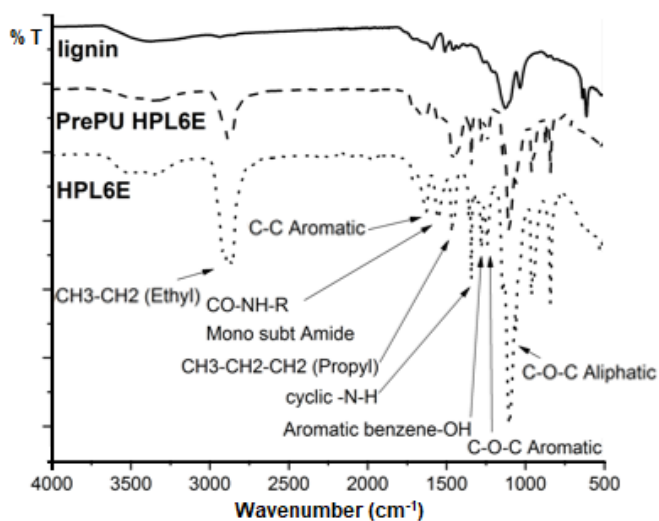


Fig 2. FTIR spectra of lignin, prepolymer PU (prePU) HPL6E and HPL6E

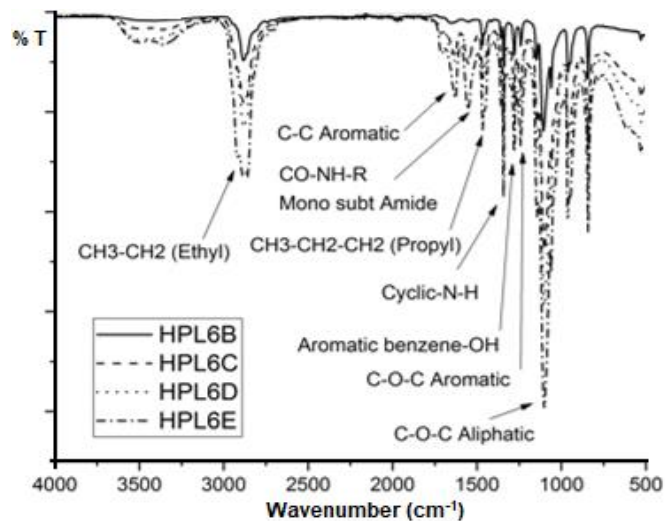


Fig 3. FTIR spectra of HPL6 with variation composition of HMDI

prepolymers are expected to be nonpolar segment because of the length of the chain from PEG. The nonpolar prepolymers were then grafted to the lignin to produce lignin-based polyurethane. FTIR was used to confirm the scheme and structure of lignin-based polyurethanes (HPL).

Fig. 2 depict the differences in spectra of lignin, prePU HPL6E and HPL6E. The reaction between hydroxyl group from polyol and diisocyanate from HMDI

is indicated with the appearance of urethane bond. The bonds are represented by CO-NH-R Mono substituted amide and cyclohexane-N-H [16]. Based on Fig. 1, CO-NH-R Mono substituted amide showed at wavenumber 1553 cm^{-1} for sample prePU HPL6E and at 1560 cm^{-1} for HPL6E. While cyclohexane-N-H appears at 1341 cm^{-1} for both prePU HPL6E and HPL6E. Both functional groups do not appear in FTIR spectrum of lignin because lignin is the source of polyol and does

not have nitrogen. Lignin has aromatic functional group. The differences between prePU HPL6E and HPL6E are the content of lignin. prePU HPL6E does not have lignin, so the aromatic functional group (benzene and benzene -OH) do not appear for prePU HPL6E. They appear in HPL6E at wavenumber 1624 and 1280 cm^{-1} .

Fig. 3 represents the FTIR spectra of lignin-based polyurethane with different composition of mol HMDI. FTIR spectra for HPL6 with variation composition of HMDI show that all ethyl, C-C aromatics, CO-NH-R, N-H cyclic, aromatic/benzene-OH, C-O-C aromatics and aliphatic functional groups appear around wavenumber of 2883, 1630, 1657, 1344, 1275, 1245 and 1110 cm^{-1} . As seen from Fig. 2, peak at 2250 cm^{-1} is not visible at all which means that the product does not have active cyanate group because of the entire diisocyanate has reacted. Based on Fig. 2, FTIR spectra seem to rise as the increasing of composition HMDI. It is caused by the increasing of reaction between HMDI and lignin as crosslinker. The highest peak is owned by HPL6E.

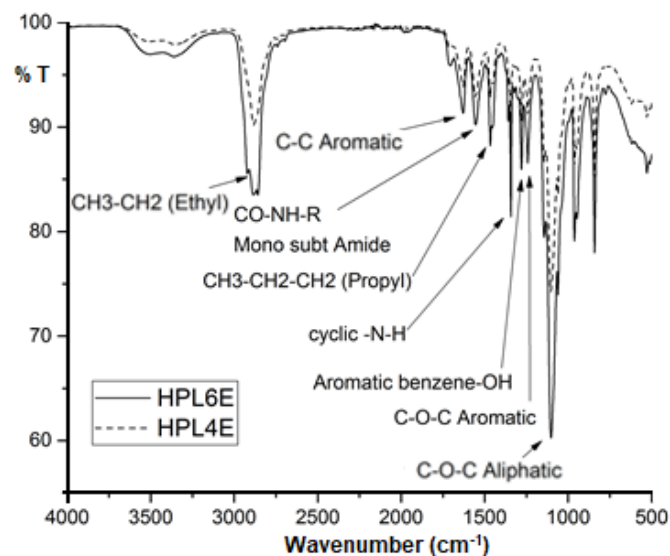


Fig 4. Comparison FTIR spectra of HPL6E and HPL4E

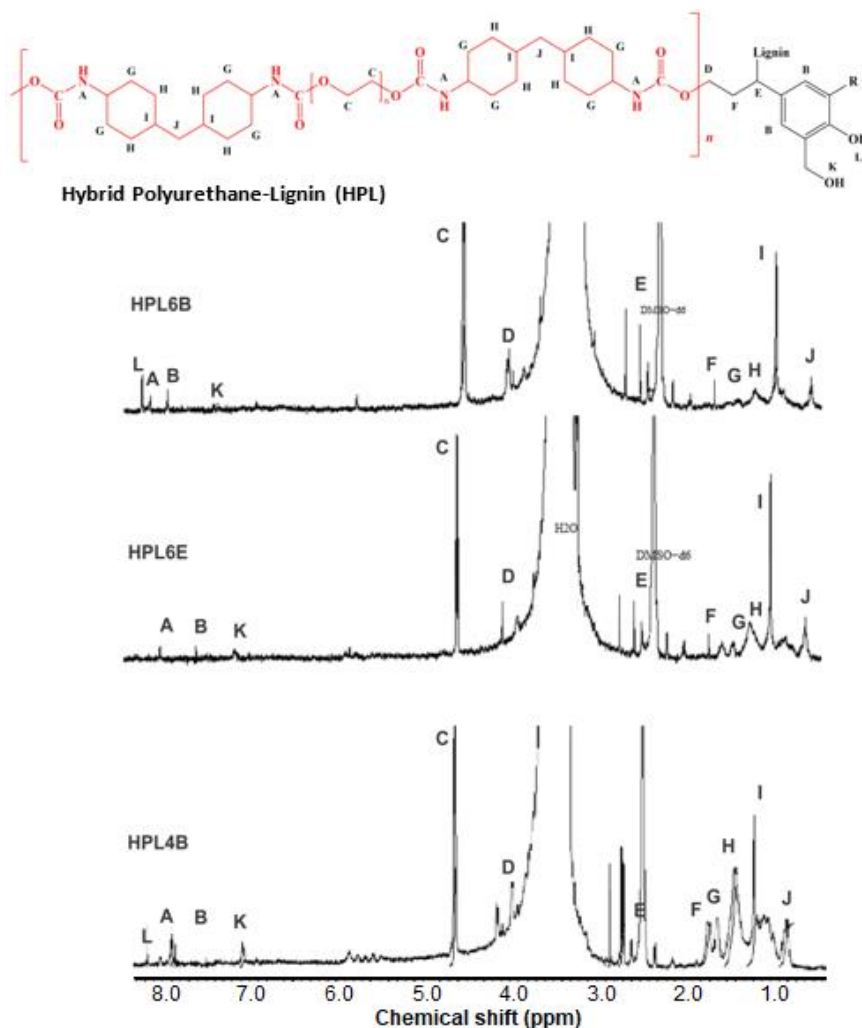


Fig 5. H-NMR spectra of HPL6B, HPL6E and HPL4B

Table 2. Ratio polarity lignin-based polyurethane

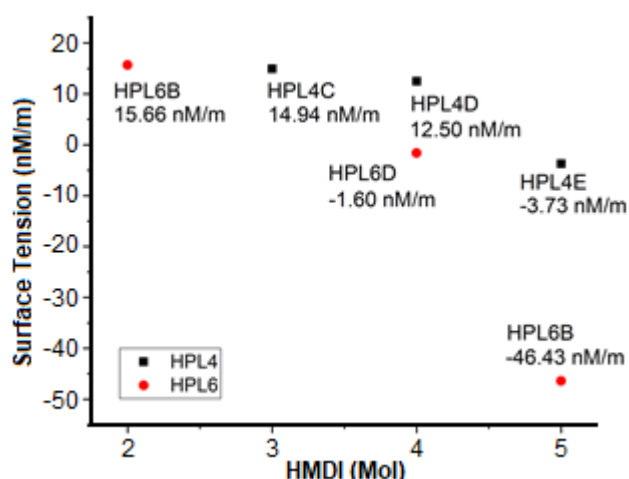
Samples	Polarity comparison	Polarity Index
	p : np	p/ np
HPL6B	2.063 : 29.878	0.69
HPL6E	1.270 : 30.727	0.041
HPL4B	2.495 : 28.006	0.089

Table 3. Contact angle and surface tension of HPL4 and HPL6 from various composition of HMDI

Samples	Θ water	Θ ethylene glycol	Surface Tension (nM/m)
HPL6B	62.82	46.02	15.66
HPL6D	57.74	47.68	-1.60
HPL6E	33.44	29.63	-46.43
HPL4C	38.69	28.93	14.94
HPL4D	37.48	28.45	12.50
HPL4E	36.25	29.79	-3.37

Table 4. Comparison of the Td of lignin-based polyurethanes

Sample	Tm (°C)	Tg (°C)	Td (°C)
HPL4B	60	75	365.6
HPL6B	61	76	413.8
HPL6E	64	84	414.5

**Fig 6.** Surface tension of HPL4 and HPL6 for various compositions of HMDI

FTIR was used to know the influence of molecular weight of PEG in HPL. All functional groups of ethyl, C-C aromatics, CO-NH-R, N-H cyclic, aromatic/benzene-OH, C-O-C aromatics and aliphatic in FTIR spectra for HPL6E and HPL4E are shown in Fig. 4. They appear around wavenumber of 2887, 1650, 1657, 1344, 1275, 1246 and 1110 cm^{-1} . The FTIR spectra show the %T increase as the increasing of molecular weight. The significant increasing is shown at ethyl and aliphatic wavenumber around 2887 and 1465 cm^{-1} . It is caused by a lot of ethyl and aliphatic in PEG 6000 structure than PEG 4000.

H-NMR was used to confirm the structure of samples. Fig 5 shows H-NMR spectra of HPL6B, HPL6E and HPL4B. Based on previous study [17-20], peak for urethane and benzene will appear at chemical shift at 8.4 and 7.5–8 ppm. Chemical shift at 4.31 ppm is for ethyl from PEG. Based on Fig. 5, all chemical shift of structure of hybrid lignin-based polyurethane appear. There are differences for HPL6B and HPL6E in chemical shift H-NMR above 8 ppm. It is because the hydroxyl benzene in lignin for HPL6B did not react with cyanate groups from HMDI, while react in HPL6E. It did not react because HPL6B has less HMDI than HPL6E. In HPL6B, excess of cyanate group from prePU react with aliphatic hydroxyl group in lignin, because it has less interference than benzene hydroxyl group. PrePU in sample HPL6E has more excess of cyanate group, so it will react with both aliphatic hydroxyl group and benzene hydroxyl group from lignin.

Polarity of Lignin-Based Polyurethane

The index of polarity from HPLs can be determined based on the integration from H-NMR characterization. Polarity of HPLs is represented by hydroxyl functional group and nonpolarity by PEG. The index of polarity from HPLs can be determined based on integration from H-NMR characterization and they are shown at Table 2. Based on H-NMR characterization, index polarity decrease as the increasing of composition HMDI and molecular weight, it indicated that the nonpolarity side of HPLs was decreased.

Sessile drop was used to know the surface tension of HPLs. Water and ethylene glycol were used to know the contact angle. Zisman equation then used to determine surface tension from contact angle. Table 4 show the contact angle and surface tension of HPLs. Based on sessile drop test (Fig 6), surface tension decline as the increasing of composition HMDI and molecular weight PEG. It also showed the relationship of decreasey polar in HPLs.

Thermal Properties

HMDI has cyclic structure where it can enhance the thermal properties. It also can be caused by the increasing of urethane bond and crosslinking between prePU and lignin. The phenomena can be seen on Table 4. HPL6B has less HMDI. It caused less urethane bond and crosslinking between prePU and lignin than HPL6E. Therefore, sample HPL6B to HPL6E show the increasity of Tm, Tg, and Td along with the increasing of composition HMDI. The increasing trend also appear between HPL4B to

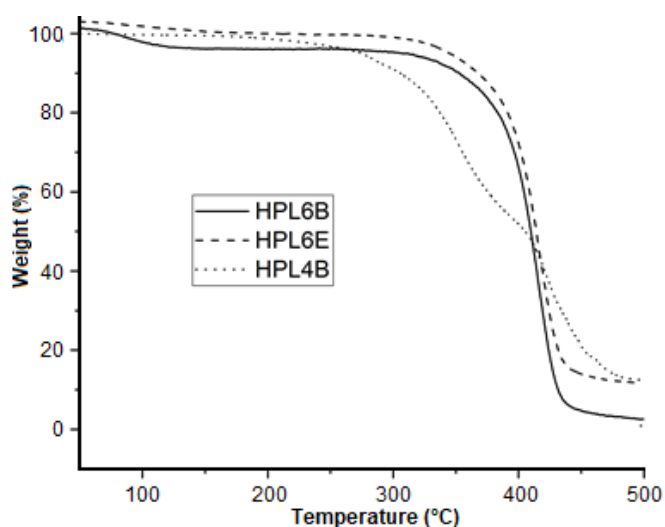


Fig 7. Curve TGA of HPL with variation of HMDI composition and Mw PEG

HPL6B. It caused by escalation of molecular weight of PEG.

TGA analysis based on Fig. 7 shows that HPL6E has better thermal stability than other HPLs because it has more HMDI, molecular weight and crosslinking than others. Crosslinking make the structure more rigid and cause better thermal stability [21]. HPL4B, HPL6B and HPL6B degraded at temperature 365.5, 413.8 and 414.5 (°C). They are decomposition of urethane bonds between hydroxyl and cyanate groups. The aliphatic segments of polyol and aromatic ring also degraded at 320 and 565 °C [22-23].

CONCLUSION

Lignin-based polyurethanes (HPLs) were successfully synthesized based on FTIR and NMR characterizations. Polarity of lignin was successfully decreases. Reduction of polarity in HPLs reported that the influence of enhancement HMDI and molecular weight of PEG with the best index polar and surface tension were 0.041 and -46.43 nM/m for HPL6E. HPL6E has the best stability heat with Td 414.5 °C. Thermal stability increased as the increasing of HMDI and molecular weight of PEG.

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