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Curing Analysis of Lignin Reinforced Polyurethane by Fourier Transform Infrared Spectroscopy

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The second-most prevalent polymer in nature, lignin has a complicated structure made up of various amount of aliphatic and phenolic hydroxides. In recent years, extensive research was conducted to explore lignin's potential as a polyol source for the synthesis of polyurethanes (PUs), in an effort to improve the sustainability of polyurethanes by substituting renewable resources for petroleum-based ones. However, the curing process of lignin reinforced polyurethanes posed a crucial challenge in understanding and optimizing their final properties. The complex structure of lignin, with its variety of functional groups, could affect the polyurethane's overall performance and curing performance. Therefore, synthesizing lignin reinforced polyurethane with vary lignin content and effect towards curing analysis of the resulting lignin reinforced polyurethane were investigated. In this study, reinforced polyurethane was made by reacting lignin ranging from 0, 10, 20, 30, 50 and 100% with polyethylene glycol and isophorone diisocyanate. All lignin reinforced polyurethane uncured and cured samples were evaluated and characterized using FTIR. The research results indicated that polyurethane with 50% lignin content with 60 minutes curing time were discovered to have the best qualities overall. The outcome of this study emphasized lignin's potential as a sustainable renewable resource for polyurethane synthesis and demonstrated that an optimal balance of lignin content and curing time could enhance the performance and sustainability of polyurethane.

Keywords: Lignin, polyurethane, curing performance, FTIR, biocoating

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Polyurethane (PU) is a highly versatile polymer known for its mechanical strength, flexibility, and chemical resistance, making it suitable for applications such as foams, adhesives, coatings, and elastomers. PU is synthesized through the reaction between isocyanate groups (-NCO) and hydroxyl groups (-OH) from polyols, where the properties of the final material are largely influenced by the type and ratio of polyol and isocyanate used [1]. Despite its wide applicability, conventional PU relies heavily on petroleum-based polyols, which contributes to environmental pollution and the depletion of fossil resources. The rising cost and limited availability of petroleum further emphasize the need for sustainable alternatives.

Recent studies have explored renewable raw materials such as plant oils, sugars, starch, and lignocellulosic biomass to substitute fossil-based polyols. Lignocellulosic biomass, composed mainly of cellulose, hemicellulose, and lignin, is one of the most abundant and renewable resources available. Among its components, lignin stands out as a promising reinforcement material due to its complex aromatic structure, low cost, and abundance in plant cell walls [2]. Incorporating lignin into PU matrices has shown potential to enhance thermal and mechanical properties while promoting environmental sustainability. However, despite these advantages, the curing behaviour of lignin-containing PU system insufficiently studied, particularly regarding how varying lignin concentrations influence isocyanate conversion, crosslinking kinetics, and network formation during polymerization.

Fourier Transform Infrared Spectroscopy (FTIR) is a widely applied technique to monitor chemical conversions during polymer synthesis, particularly useful for evaluating the curing process of PU. It enables the tracking of characteristic absorption bands associated with functional groups such as isocyanate, indicating the degree of reaction and crosslinking. The curing behaviour of lignin-reinforced polyurethane depends on factors such as lignin concentration, NCO:OH ratio, lignin–matrix interactions, and solubility of lignin in solvents [3].

This study aims to systematically investigate the curing behaviour of polyurethane reinforced with different lignin concentrations using FTIR analysis. By correlating changes in functional group absorption with lignin loading, this work provides new insights

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into the role of lignin in PU network formation and curing kinetics. The findings are expected to contribute to the rational design of sustainable, lignin-based polyurethane materials with optimized performance and reduced environmental impact.

EXPERIMENTAL

Chemicals and Materials

Lignin with average molecular weight of 1513.58 g/mol were supplied from Sigma Aldrich. Polyethylene Glycol of molecular weight 600.00 g/mol were obtained from Sinopharmaceutical Chemical Reagents Co., Ltd. N, N-dimethylformamide (DMF) and acetone were bought from Sigma Aldrich. All chemicals were directly used without further purification.

Methodology

Preparation of Lignin Reinforced Polyurethane Sample

PEG and lignin with varying weight ratios were dissolved in a mixed solvent with a DMF/acetone ratio of 3:2 (v/v). The liquid was stirred for 30 minutes on a hot plate. Then, the liquid was continued to sonicate for another 30 minutes. The liquid was continuously stirred at 60°C in a water bath. IPDI was added and the temperature increased to 75°C. Then, the reaction will be continued for 30 minutes. Table 1 provides the sample and experimental conditions for producing lignin reinforced polyurethane film.

After the polymerization, the solution was placed on a silicone mold lying horizontally and cured on a hot plate for 45 minutes, 60 minutes and 75 minutes at 85°C in an open-air condition.

Characterization of Lignin Reinforced Polyurethane

The uncured and cured samples (PU, LPU1, LPU2, LPU3, LPU4 and LPU5) were analysed using Fourier Transform Infrared (FTIR) Spectrometer brand Bruker ALPHA, Germany. The measurements were conducted with an attenuated-total-reflection (ATR) probe within the wavenumber range of 4000–600 cm^{-1}, employing a resolution of 4 cm^{-1} with average of 32 scan. The whole process can be represented as flowchart in Figure 1.

Table 1. Experimental condition to prepare lignin reinforced polyurethane sample.

Sample	Lignin (wt%)	PEG (wt%)	[NCO/OH] Ratio
PU	0	100	1:1
LPU1	10	90	1:1
LPU2	20	80	1:1
LPU3	30	70	1:1
LPU4	50	50	1:1
LPU5	100	0	1:1

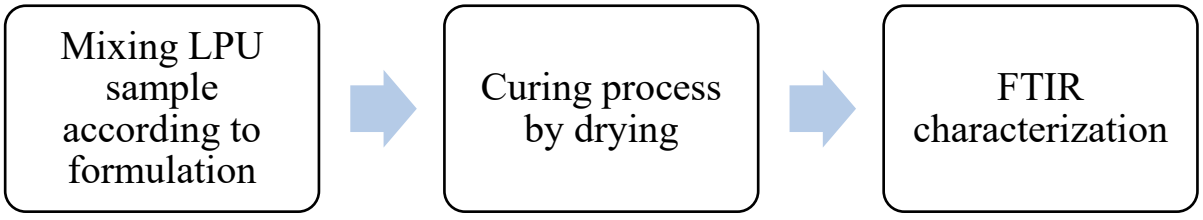


Figure 1. Flowchart for preparation of lignin reinforced polyurethane (LPU).

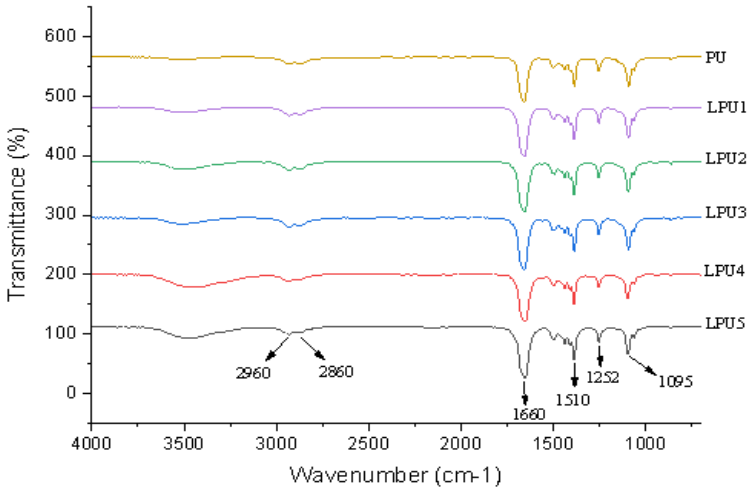


Figure 2. FTIR spectra of PU, LPU1, LPU2, LPU3, LPU4, LPU5.

RESULTS AND DISCUSSION

Synthesis Characterization of Lignin Reinforced Polyurethane

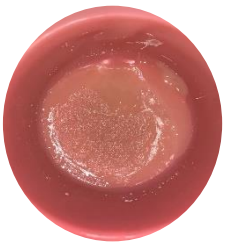
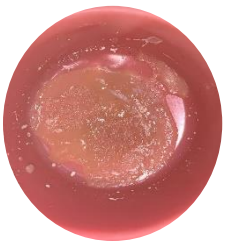
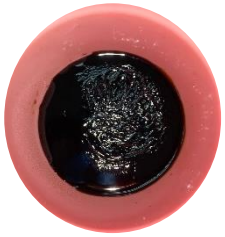
The molecular structures of lignin reinforced polyurethane samples were firstly determined. In Figure 2, the ATR-FTIR spectra of uncured sample PU, LPU1, LPU2, LPU3, LPU4 and LPU5 were shown. Based on the figure, all lignin reinforced PU presented similar profiles. Urethane linkages (-NH-(C=O)-O-) were primarily identified by the stretching vibrations of the C=O groups at peak 1660 cm^{-1}. These linkages were formed through the reaction of polyethylene glycol with the aliphatic hydroxyl (OH) groups of lignin [4]. Besides that, the hydroxyl peak (OH) of lignin was also observed at 3400 cm^{-1} which signifies the incorporation of lignin into the polyurethane synthesis. The other characteristic bands of PU were observed at 2860 cm^{-1} and 2960 cm^{-1} associated with the alkane C–H stretching vibration, N–H bending vibration (1510 cm^{-1}), C–N stretching (1252 cm^{-1}), and C–O stretching (1095 cm^{-1}). All of the samples exhibited these features, indicating the occurrence of chemical reaction between isocyanate groups (N=C=O) of IPDI and OH groups of polyol, and lignin. The consistent molecular structures and characteristic bands observed in the ATR-FTIR spectrum of PU, LPU1, LPU2, LPU3, LPU4 and LPU5 affirmed the successful synthesis of lignin reinforced polyurethane with the effective incorporation of lignin and the formation of urethane linkages through chemical reactions with polyethylene glycol and isocyanate groups.

Physical Observation Curing Analysis of Lignin Reinforced Polyurethane Samples

Table 2 shows the sample physical appearance of PU, LPU1, LPU2, LPU3, LPU4 and LPU5 cured at room temperature for 30 minutes, 45 minutes, 60 minutes and 75 minutes. Based on the first 30 minutes of curing, all the samples (PU, LPU1, LPU2, LPU3, LPU4, LPU5) were still in a watery state. These conditions explained that the 30 minutes of exposure at room temperature was not sufficient to complete the polymerization reactions for the transformation of liquid formulation into solid. As the curing time increased to 45 minutes, less watery sample were observed which reflected to significant curing process in which evaporation of the high volatile compound in the samples such as DMF and acetone had happened. The mixture's viscosity rises as the solvents evaporated, which helps explain the observable change from a watery to a less watery and slowly hardening state for all samples. After 60 minutes being cured, PU, and PU-lignin samples: LPU1 (10% lignin), LPU3 (30% lignin) and LPU4 (50% lignin) were completely dry which indicates the complete curing process. The complete drying and hardening indicates successful polymerization and crosslinking, resulting in a solid and dry polyurethane matrix [5]. However, crack occurred for LPU1, while sample LPU2 (20% lignin) was still moist after being cured for 60 minutes. These results might be due to the imbalance in ratio of lignin to the polyurethane components which affected their curing and cross-linking properties. At 10% lignin content (LPU 1), the significant crosslinking is taking place through the hydroxyl group of 90% PEG. PEG is a simpler compound with low steric hinderance as compared to lignin in which polymerization is preferred. Thus, 60 minutes heat exposure curing led to over drying sample and resulted in brittleness of the sample [6]. While the moist sample observed after 60 minutes curing in 20% lignin (LPU2) inclusion may be due to the trapped volatile organic compound in the system. This phenomenon suggested that the polymerization at 60 minutes is mostly contributed by the 80% PEG

content while some of the complex lignin structure remain in the system without contributing to crosslinking and polymerization process during curing disturbing the curing process. As compared to polymer network formation in 30% (LPU3) and 50% (LPU4) lignin samples [7], the dry film observed reflecting to fully cured properties at 60 minutes curing. This phenomenon suggested that 30 to 50% lignin to PEG showed the optimum curing phenomenon at 60 minutes. However, for 100% lignin sample (LPU5), the sample remains watery after cured for 60 minutes reflecting to slower the curing process. This is due to complex structure and high steric hinderance of lignin-hydroxyl group as compared to PEG for the isocyanation process to complete [5]. Among these samples, LPU4 (50% lignin) showed the most effective curing process as the sample observed is completely dry and smooth surface after 60 minutes of curing. This phenomenon explained that 50% lignin concentration may represent an optimal balance in the formulation, allowing for sufficient interaction with other components in the formulation.

Table 2. Physical appearance of lignin reinforced polyurethane samples after curing for 30 minutes, 45 minutes, 60 minutes and 75 minutes.

Samples	30 minutes	45 minutes	60 minutes	75 minutes
PU	 Watery	 Less Watery	 Completely hard	 Hard and brittle
LPU1	 Watery	 Less watery	 Dry and crack	 Dry and completely crack
LPU2	 Watery	 Less watery	 Moist	 Moist

LPU3	 Watery	 Less watery	 Completely dry	 Completely dry
LPU4	 Watery	 Less watery	 Completely dry	 Completely dry
LPU5	 Watery	 Watery	 Watery	 Watery

Besides that, as the curing process continued for 75 minutes, neat PU become hard and brittle. This is because, in the absence of lignin, PEG and IPDI most likely dominate the polyurethane matrix and the extended curing time contribute to brittleness [8]. For LPU1, an excessive crack occurred. Prolonged curing time leads to a complete cross linking resulting in the sample becoming too rigid and prone to cracking [5]. As for other samples, it remains unchanged after 75 minutes cured. After observing the samples for 75 minutes, it can be concluded that the LPU4 sample is the best as evidenced by its dry and smooth surface, indicating successful curing and optimal physical characteristics.

Chemical Structure Analysis of Curing Analysis Lignin Reinforced Polyurethane Samples

The basic chemical structure analysis of curing process was conducted using Fourier-transform infrared (FTIR) spectroscopy. Figure 3 showed the ATR-FTIR spectra of (a) 45 minutes, (b) 60 minutes, and (c) 75 minutes curing of neat PU, LPU1, LPU2, LPU3, LPU4 and LPU5. In all the figures, it can be observed that the existence peaks of hydrocarbon from 2800 cm^{-1} to 3000 cm^{-1} peaks indicating the PU main chain, and the carbonyl group (C=O) at 1660 cm^{-1} which confirmed the immobilization of isocyanate urethane functional group [9]. Based on the results, as the lignin content increases from LPU1 to LPU5, the C=O peak intensities increase due to the increased presence of lignin-derived carbonyl groups. In addition, the peak at 1556 cm^{-1} can be observed indicates the presence of aromatic stretching vibrations of lignin [10] in which the intensity of this peak decrease in decreasing amount of PEG sample (higher lignin content, LPU5 to LPU 1). This phenomenon supported the analysis in observation which indicates, PEG was the main polyol contributed to the crosslinking and polymerization process of the sample as compared to lignin due to their compact and complex structures contributing to higher steric hinderance.

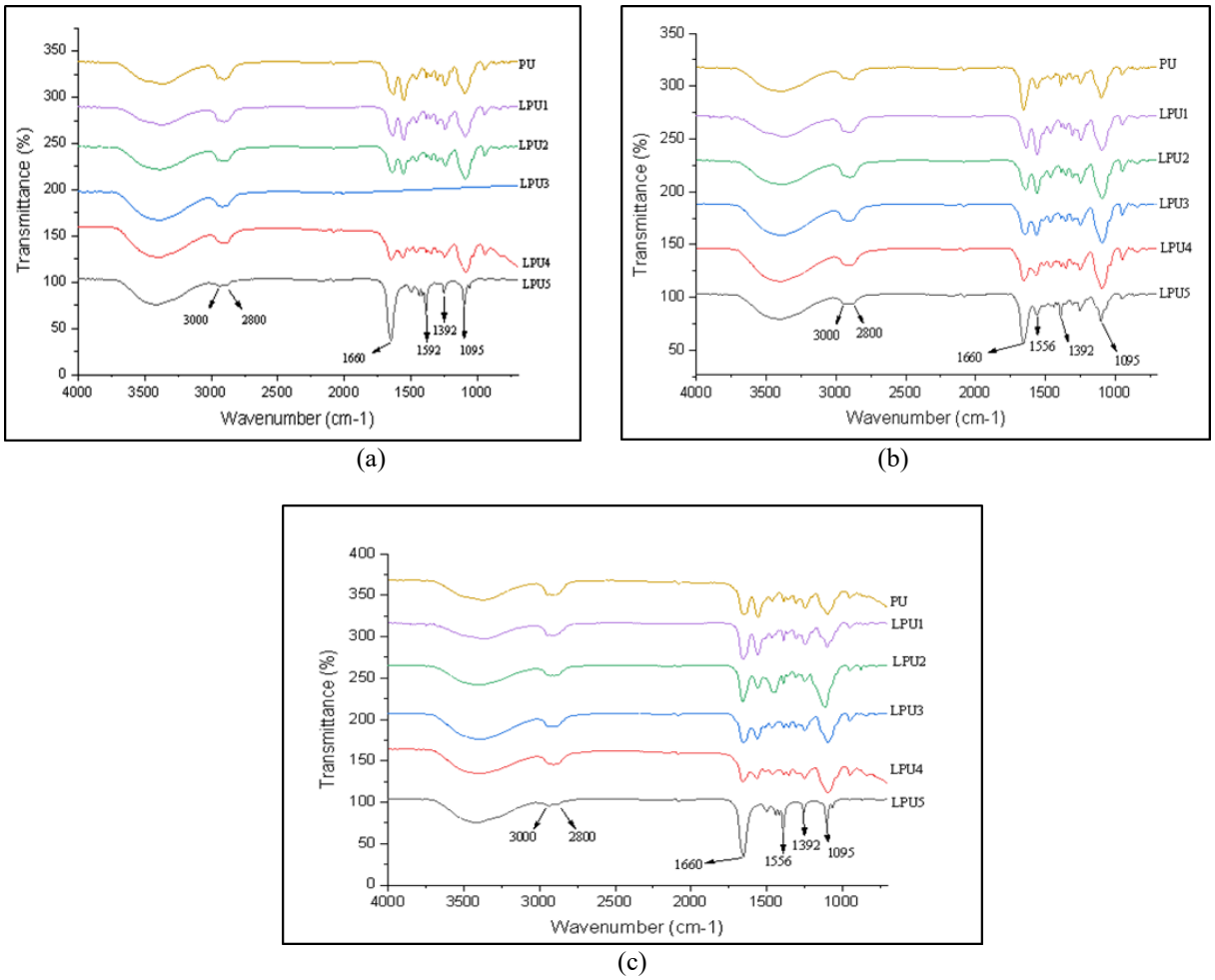


Figure 3. FTIR spectra of cured PU, LPU1, LPU2, LPU3, LPU4 and LPU5 at (a) 45 minutes curing (b) 60 minutes (c) 75 minutes.

At the other hand, peak at 1392 cm^{-1} for LPU5 (100% lignin) was clearly observed in all curing time which corresponds to the C=C stretching vibrations within the aromatic rings of lignin. The presence of this peak becomes more pronounced at LPU5 sample as it reflects the higher concentration of lignin in PU [5]. In addition, the C-O peak at 1095 cm^{-1} for LPU5 sample also showed the most narrowed as compared to other samples. This is because, as the lignin content increase, crosslink density increases contributed to a more rigid structure and a narrower peak in the C–O stretching region [11].

CONCLUSION

The synthesis and curing behaviour of lignin-reinforced polyurethane were investigated through FTIR spectroscopy and visual observation. This study explored the effect of varying lignin and polyethylene glycol (PEG) content serving as hydroxyl group sources on the crosslinking density and curing performance of PU, while maintaining a constant NCO/OH ratio of 1:1. All samples were cured at 85°C in an oven. The viscosity of the reaction mixture was shown to be significantly impacted by an increase in lignin content, which resulted in slower crosslinking and longer curing periods. Because PEG-rich formulations had lower steric hindrance and increased hydroxyl accessibility, they cured more quickly and uniformly, producing smoother surfaces and greater flexibility. On the other hand, high-lignin samples tended to generate brittle and broken films (as observed in sample LPU1) and required longer curing times (> 60 min), indicating uneven or incomplete crosslinking. Although balanced lignin–PEG compositions (such LPU2) showed moderate curing behavior, their total curing effectiveness was decreased due to their susceptibility to VOC entrapment. The successful chemical interaction between isocyanate and hydroxyl groups from both lignin and PEG was supported by FTIR analysis, which verified the creation of urethane linkages through distinctive peaks of -NCO, -OH, and -C=O groups. Higher lignin loadings, however, indicated partial crosslinking and phase separation due to the presence of unreacted hydroxyl groups. Overall, adding lignin in tiny amounts increased PU's thermal stability and rigidity without significantly reducing its flexibility,

but adding too much lignin caused mechanical embrittlement and slower curing. The study was restricted to a set NCO/OH ratio and a single curing temperature of 85 °C. Long-term stability, heat resistance, and mechanical strength were not quantitatively assessed. To further improve lignin–PEG compositions for useful polyurethane applications, future research should incorporate tensile testing, differential scanning calorimetry (DSC), and changing isocyanate indices.

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