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F U L L P A P E R www.ms-journal.de Effect of Lignin Content as Bio-Chain Extender in Polyurethane Foam Elvi Kustiyah, Dwiki Syahbana Putra, David Gerry, Dick Ferieno Firdaus, and Mochamad Chalid*

Polyurethane is a polymer compound that consists of a hard segment and a soft segment. Further modification of polyurethane makes it possible to make foam products with a variety of properties. Polyurethane foam has a tendency to be rigid and flexible by adjusting the segment ratio and adding chain extenders during the synthesis process. The basic precursors used in this research on bio-polyurethane foam are Polypropylene Glycol 2000, Toluene Diisocyanate 80, Amine catalyst, Tin catalyst, surfactant, and the addition of lignin biomass as a chain extender and as independent variables of this study with 1, 2, and 3 wt% variations with the synthesis method used is a one-shot method. In an attempt to investigate the effect of lignin chain extender addition to the macromolecular structures and morphology, FTIR and SEM are used, while the mechanical properties are analyzed using a tensile machine. From the synthesis carried out, bio-polyurethane foam with open pore shape is obtained. It has increased tensile strength, but the elongation tends to decrease with increasing lignin biomass addition.

1. Introduction Polyurethane is produced from synthesis polymer produced by means of a polyaddition reaction between polyols and polyisocyanates to form urethane chains. Polyurethane has a wide application ranging from automotive, furniture, packaging, medical devices to polyurethane foam. Polyurethane foam itself can be widely used for sound dampening or heat shock applications, [1] which is composed of materials such as diisocyanate, chain extender, polyol, foaming agent, and catalyst. [2] The structure was made from the reaction between main segmented copolymer that consists of hard segment:

diisocyanate and chain extender; and soft segment: polyols such as polyester[3,4] and connected with a functional compound called chain extender.

The chain extender has a high level of reactivity and lower molecular weight compared to the main compounds, which results in diverse

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functional abilities.

The chain extender molecular weight is vital for determining the mechanical properties of polyurethane; for example, the increasing amount of crosslinking can escalate rigidity, softening point, modulus of elasticity, and elongation.[5]

In the process of forming polyurethanes, to improve the mechanical properties such as yield stress, ultimate tensile strength, and thermal stability the hard segment

amount of bonding with the chain extender needs to be increased, especially from its

crosslinking rate with the chain extender.[6] On the other hand, chain extender itself with

hydroxyl functional end group during the processing must react with the iso-

cyanates from the main compound to form the complete polyurethane form, but it is

known that the reaction speed is slow. So, it is necessary to accelerate the reaction, such

as the addition of a catalyst. One of the strategies is to add more

hydroxyl groups into the system. The most promising candidate

is to add hydroxyl group from the biomass that is available abundantly

in nature, for example, lignin, starch, and cellulose, where there are hydrocarbon chains with massive population of hydroxyl groups.

With this method, the functional group $N=C=O$ by isocyanates will form a covalent bond with the OH hydroxyl group by biomass during pre-polymerization, hence increase the amount of bonding between the hard segment and the chain extender.[7,8]

In this research, lignin as a complex polysaccharide composed of abundant hydrocarbon compounds was used to initiate the

mentioned strategy. Lignin compounds are commonly found in

plant cell walls, or some types of algae. Variations in lignin synthesis can provide diversity in composition, size, a number of crossbonds, and functional groups[9,10] Hence, the

purpose of this study is to obtain the effect of lignin concentration which functions as a chain extender on polyurethane foam by characterizing using FTIR, FE-SEM, and

mechanical testing to see the modulus of elasticity.[11] 2. Result and Discussion

2.1. Structure Characterization Lignin-based biomass was expected to react with the

polyurethane foam during the polymerization process. To Macromol.

Symp. 2020,391,1900153 ©2020WILEY-VCHVerlagGmbH&Co. KGaA,Weinheim 1900153(1of4) www.advancedsciencenews.com www.ms-journal.de Figure1. FTIR Spectra of Polyurethane foam virgin and Polyurethane foam-lignin. investigate the content contained in polyurethane foam, tests were carried out using Fourier Transform Infrared Spectroscopy (FTIR). FTIR testing was used because polyurethane foam is an organic polymer-based material with a distinctive peak of the band at a wavelength of 3364 cm^{-1} as can be seen in Figure 1. From that, we can see that there is an O-H stretch group that indicates the hydroxyl group of lignin.

At a wavelength of 2938 cm^{-1} , it indicates the C-H stretching bond, which indicates the presence of an aliphatic chain in lignin. Then the $1600\text{--}1500\text{ cm}^{-1}$ waves susceptibility indicates a C-C chain. Figure 1 shows the comparison of the compound content obtained before and after the addition of biomass to the compound. Through this comparison, it can be concluded that there are inferences in the molecular structure when there is the addition of lignin to the compound.

The polyurethane-lignin has a significant characteristic in the C-N, N-H, and C=O groups that are explained through wavelength absorption of the FTIR data. [12] Referring to Figure 1, there is absorption at wave 3284 cm^{-1} that shows the bond N-H stretch. Then there is also the C-H stretch bond at the wave absorption of 2970 and 2868 cm^{-1} . There is also a C-N stretch bond at a wavelength of 2275 cm^{-1} that can be interpreted as a free isocyanate group.

Moreover, at a wavelength of 1711 cm^{-1} there are C=O bonds and 1223 and 1091 cm^{-1} that indicate the presence of C-O absorption. Referring to the results of the characterization of the polyurethane foam-lignin sample such as the graph in Figure 2 explained that there is a shift in the line that occurs in the polyurethane foam-lignin sample. The shifting of these lines can, among other things, indicate the reaction of urethane formation with biomass. When compared to the graph on Polyurethane-Virgin foam, there is a shift in the content of the Polyurethane foam-lignin graph.

The shift occurred at a wavelength of 1718 cm^{-1} which showed a shift in the C=O bond. Where the shift indicates a reaction that occurs between isocyanate and hydroxyl, this explains that there is an effect of adding biomass to the polyurethane reaction itself.

The value of $C=O$ wave absorption can be derived from the reaction of diisocyanate with hydroxyl groups in polyols and hydroxyl groups owned by biomass, through hydrogen bonds with $C=O$ [13,14]. In addition, there is also a shift in absorption at wave 1093 cm^{-1} which shows a shift in the $C-O$ stretch bond formed from the hydroxyl group in the reaction of biomass with isocyanate. [14] However, the addition of biomass did not affect the main polyurethane group which can be seen from the results of the FTIR test.

2.2. Morphology

Figure 2 shows the morphological differences between the polyurethane foam-virgin and polyurethane foam-lignin at $250\times$ optical magnification. Figure 2a, which indicates the polyurethane foam virgin images show that the shape of the open-cell structure is not neatly arranged and tends to be large, while Figure 2b can be seen that the morphology of polyurethane-lignin foam has an open-cell form and has a tendency to be smaller and neat.

The phenomena probably caused by the effect of adding lignin as a chain extender, where lignin can increase the gelling process time and inhibit the blowing process. Hence, polyurethane foam cannot expand properly during the blowing process and can result in the formation of thicker foam walls. In addition, the foam pores are hardly formed because the carbon dioxide forming is hindered by thick foam walls itself [15,16].

2.3. Mechanical Properties

The tensile resistance on the foam samples can be obtained using the tensile test. The information acquired is the maximum value of the test load to the sample, or commonly referred to as the Ultimate Tensile Strength (UTS).

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Figure 2.

Morphology of Samples. a) Polyurethane foam Virgin. b) Polyurethane foam-Lignin with $250\times$ magnification. Figure 3. Graph of the relationship between lignin concentration and mechanical properties in polyurethane foam.

of the test load to the sample, or commonly referred to as the Ultimate Tensile Strength (UTS). The addition of lignin biomass to the polyurethane foamable to increase the tensile strength of the compound, According to Jinpeng, et al., [14] addition of lignin biomass $<1\%$ can influence the increase mechanical foam along with the addition of foam density. But in Figure 3, Polyurethane foam with $1\text{ wt.}\%$ of lignin there is a decrease in the value of tensile strength of about 57% , it can be caused by the clumping of lignin in foam during the mixing process. According to the graph shown in Figure 3 it can

been that the highest elongation value reached 196% elongation obtained by the polyurethane virgin sample while the lowest elongation value is 65% elongation obtained by polyurethane foam with 3 wt% of lignin sample. Through these data it can be explained that the addition of lignin can affect the elongation value of polyurethane foam. This can be caused by the presence of lignin which has rigid properties that disrupt the structure of the macromolecules of polyurethane foam which reduce the elongation properties naturally.[5] According to Jinpeng, et al.,[5] the elongation value will decrease with the addition of lignin above 1% because it allows hydrogen bonding to form in large, in which can increase the modulus but decrease the maximum elasticity value of polyurethane foam.[17,18]

3. Conclusion

From the morphological test, the results showed that pore growth is not perfect, and seem to have an open pore shape. From this study, it can be concluded that the addition of lignin in certain values can increase the tensile strength of the compound, which caused by the increase of the number of hydrogen bonds between surfaces (cross bonds) formed in the compound via intermolecular force. The addition of lignin also can increase foam density, pore size in the foam, frame thickness, and pore stability of the polyurethane foam.[19,20]

4. Experimental Section

Materials and Instrumentation:

The lignin used was in a powder form purchased from Sigma–Aldrich. Polypropylene glycol as the soft segment in this research has a molecular weight of 2000 with trade name Voranol 8010 produced by DOW. Methylene Chloride obtained from Samsung Fine Chemical Co. Ltd.,

whereas the toluene diisocyanate 80 used was Cosmonate T-80 produced by Mitsui Chemicals & SKC Polyurethane Inc. This research also used Silicone from OSI Specialties Singapore PTE Ltd as a surfactant and the Catalyst Amine used was Niox Catalyst A-230 from Momentive Performance Materials and Tin catalyst kosmos 29 by Evonik Industries AG.

To confirm the structure of molecules and reactions, lignin-based polyurethane characterized by Perkin Elmer's Fourier transform infra-red spectroscopy (FT-IR Spectroscopy) and Field Emission Scanning Electron Microscope (FE-SEM). Test specimen for mechanical properties ASTM D-882, the samples were analyzed using Gottech AI-7000S Method: Polypropylene Glycol 2000, water, silicon surfactant, amine catalyst as a blowing agent, methylene chloride as a solvent, toluene diisocyanate, tin catalyst as a gelling agent, then lignin as chain extender are Macromol.

added. To find out the effect of lignin concentration on polyurethane properties, different lignin concentrations were made 1, 2, and 3 pbw. Conflict of Interest
The authors declare no conflict of interest. Keywords

chain-extender, foam, lignin, polyurethane [1]

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