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Preparation and Characterization of Polyurethane Foam Using a PLA/PEG Polyol Mixture

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Abstract: Polyurethanes are polymers with urethane linkages in their backbone. It is prepared by polyaddition polymerization between isocyanates and polyols, which produce different chemical, physical, and mechanical properties depending on their types and characteristics. Previous reports of polyurethane foams prepared by using PEG polyol indicated prominent features in the elasticity and recovery of the foams. However, it is necessary to improve the mechanical strength of these materials. In this study, polyurethane foams were prepared using a PLA/PEG polyol mixture and 1,6-hexamethylene diisocyanate. PLA polyol was synthesized by the direct condensation polymerization of lactic acid. The polyurethane foams were characterized using FE-SEM analysis, FT-IR spectroscopy, water absorbency measurement, and mechanical property measurement. In FE-SEM analysis, it was shown that the PLA content of polyol mixture significantly affected the porous structure. FT-IR spectra confirmed that urethane linkages formed between the PLA/PEG polyols and the isocyanates. The water absorbency decreased due to the hydrophobicity of PLA. With respect to the mechanical properties, the breaking stress and the Young's modulus increased with increasing PLA content. When the PLA content of polyols was 60 and 70 percent, the breaking strain was significantly higher than those of other polyurethane foams.

Keywords: PLA, PEG, Polyurethane foams, Water absorbency, Mechanical properties

Introduction

Polyurethanes (PUs) are polymers with urethane linkages in their backbone. It is prepared by polyaddition polymerization between isocyanates and polyols, which produce different chemical, physical, and mechanical properties depending on their types and characteristics [1]. The isocyanates and chain extenders compose a hard segment, and the polyols compose a soft segment [2]. Generally, polyols are divided into two main types: polyether and polyester [3,4]. Polyether polyol has hydroxyl reaction groups, while polyester polyol has carboxyl reaction groups.

Furthermore, the occurrence of carbon dioxide (CO_2) due to the reaction between water as a blowing agent and isocyanate enables the preparation of polyurethane foam (PUF). PUF is a versatile material because of its simple processing and various properties. It can be of practical use in the fields of industrial materials and biomaterials. Usually, rigid PUF is used in car bumpers, insulation, construction, facilities, and shipbuilding, while soft PUF is used in car seats, cushions, sofas, furniture, and biomaterials [5,6].

Hydrophilic polyurethanes are composed of soft segments which are water soluble [7]. The incorporation of hydrophilic polyols is considered an interesting method for the preparation of new biodegradable and biocompatible materials [8]. Thus, PUs based on fatty acid, polysaccharide, and polyethylene glycol (PEG) were studied [8-10]. Specifically, PEG, which is a linear non-ionic polymer, has extensive application to drug delivery and wound dressing because of nontoxicity, non-immunogenicity, and non-antigenicity [11].

Our previous reports on a hydrophilic soft PUF prepared by using PEG polyol indicated that it had prominent elasticity and recovery features when various characteristics were measured by tensile tests [10]. However, in comparison with rigid PUF, it is necessary to improve the strength and modulus from the viewpoint of the mechanical properties.

To overcome this problem, polylactic acid (PLA), which is a polymer derived from natural sources, was introduced. The studies to substitute existing materials by using excellent mechanical property and biodegradable property of PLA have been continuously progressing [12,13]. Moreover, PLA is widely used in sutures, implants, and tissue engineering because of its good biocompatibility and the low toxicity of its degradation product [14]. In PU material, PLA polyol was already used in some studies to increase mechanical property. For instance, the introduction of PLA into polyester PU increased the tensile strength and Young's modulus [15]. Additionally, PLA-based PUs such as rod-shaped memory material confirmed a change of T_g and mechanical properties of PU polymer [16,17].

Therefore, in this study, the PUF were prepared using a PLA/PEG polyol mixture and 1,6-hexamethylene diisocyanate.

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FT-IR spectra confirmed that the urethane linkages formed between the PLA/PEG polyol mixture and the isocyanate. Furthermore, a change in water absorbency was measured. Eventually, an improvement of mechanical properties of PUF using a PLA/PEG polyol mixture was investigated.

Experimental

Materials

PLA, PEG, and glycerol were used as polyols in PUF. The PLA polyol was synthesized from the direct condensation polymerization of lactic acid (Junsei Chemical Co., Ltd., Japan.). PEG (molecular weight=2000) was purchased from Samchun Pure Chemical Co., Ltd., Korea. Glycerol which was used as a crosslinking agent was purchased from Junsei Chemical Co., Ltd., Japan. 1,6-Hexamethylene diisocyanate (HDI; Wako Pure Chemical Industries Ltd., Japan) was used as diisocyanates. Distilled water and dibutyltin dilaurate (DBTDL; Sigma Aldrich, Inc, USA) were used as a foaming agent and a catalyst, respectively.

Polymerization of Lactic Acid

The polymerization of lactic acid was performed in the absence of any catalyst by distilling water out. An aqueous lactic acid solution, 1000 m*l*, was placed in a three-necked flask that was fitted with a four-winged impeller, a water-cooling condenser and a capillary inlet for nitrogen gas [18]. The vessel was heated to 120 °C for 5 hours. Next, the temperature gradually rose to approximately 180 °C for 5 hours. An aspirator was used to accelerate water evaporation. Eventually, the formation of viscous lactic acid polymers was observed.

Preparation of PUF

PUFs were prepared with various polyol mixing ratios. First, polyols were added to a 1000 m*l* Teflon molding and vigorously stirred by a four-winged impeller at 100 °C for 40 minutes to blend the polyols. The polyol mixture was cooled to 70 °C for 20 minutes, and DBTDL and distilled water were then added under continuous stirring. After 1 min, HDI was added and vigorously stirred until a foaming reaction occurred. Finally, the viscous PUF was cured at 90 °C for 24 hours. Table 1 shows the ingredient compositions that were used in the preparation of the PUF. The expected reactions in the process are as follows:

$$\text{R'-OH}_{(\text{hydroxyl groups of PLA, PEG, and glycerol})} + \text{R-NCO} \rightarrow \text{R'-COONH-R}$$

$$\text{R'-COOH}_{(\text{carboxyl groups of PLA})} + \text{R-NCO} \rightarrow \text{R-COOCONH-R'} \rightarrow \text{R'-CONH-R} + \text{CO}_2$$

$$2\text{R-NCO} + \text{H}_2\text{O}_{(\text{blowing agent})} \rightarrow \text{R-NHCOOH} + \text{R-NCO} \rightarrow \text{R-NHCONH-R} + \text{CO}_2$$

Table 1. The ingredient compositions for the preparation of the PUF

Sample code	PLA (g)	PEG (g)	Glycerin (g)	Water (g)	NCO/OH index	HDI (g)
PLA0	0	72	8	0.8	1.1	38.98
PLA25	17.25	51.75	8	0.8	1.1	40.65
PLA50	34.5	34.5	8	0.8	1.1	42.31
PLA60	43.2	28.8	8	0.8	1.1	42.98
PLA70	50.4	21.6	8	0.8	1.1	43.64
PLA80	57.6	14.4	8	0.8	1.1	44.31
PLA90	64.8	7.2	8	0.8	1.1	44.98
PLA100	72	0	8	0.8	1.1	45.64

Characterization

PUF Morphology Analysis

FE-SEM (SUPRA 55VP, Carl Zeiss, Germany) was used to observe the PUF cell structure. Before specimen preparation, the PUFs were dried in an auto-desiccator (SANPLY DRY KEEPER, SANPLATEC Corp., Japan) for 24 hr. The specimens were coated with platinum and observed with a 70x magnification. The apparent density of the PUF was measured according to ASTM D1895 [19]. To measure the porosity, PUF in powder was prepared with a mincer. The porosity was calculated by

$$\phi = 1 - (W/W_0) \tag{1}$$

where ϕ is the porosity of PUF, W is the volume of PUF in powder, and W_0 is the volume of PUF.

FT-IR

An FT-IR spectrometer (Nicolet 6700 series, Thermo Scientific, USA) was used to confirm the reaction between the isocyanates and polyols. Before specimen preparation, the PUFs were dried in an auto-desiccator (SANPLY DRY KEEPER, SANPLATEC Corp., Japan) for 24 hr. The specimens were analyzed with a 4 cm^{-1} resolution and 32 scans between 400 and 4000 cm^{-1}.

Water Absorbency

The water absorption test was performed according to ASTM F726 [20]. The water absorbency was calculated using the following equation.

$$\text{Absorbency} = (S_{ST} - S_O) / S_O \tag{2}$$

where S_{ST} is the weight of the PUF after 24 hours of water absorption and S_O is the initial weight of the dried PUF.

Mechanical Test

A mechanical test was performed for each PUF with a UTM (LRX plus, Lloyd Instruments, Ltd., UK). Tensile and compressive tests were performed under dry and wet conditions. The specimen dimensions for the tensile and compressive tests were 55 mm (length)×13 mm (width)×10 mm (thickness) and 25 mm (length)×25 mm (width)×15 mm (thickness), respectively. For dry condition, the specimens were pre-conditioned at 20 °C and 50 % RH for

24 hours. For wet condition, the specimens were soaked in distilled water for 24 hours. After immersing, the samples were cut into above-mentioned dimensions and blotted with a paper towel to remove excess water on the surface. The tensile test for each PUF was performed according to KS M ISO 1798 with a gauge length of 20 mm and a strain rate of 20 mm/min [21]. The compressive test for each PUF was performed according to ASTM D1621 with a strain rate of 20 mm/min [22].

Results and Discussion

PUF Morphology Analysis

As mentioned above, the hydroxyl groups of PLA, PEG, and glycerol form urethane linkages through a reaction with isocyanates. However, the carboxyl group of PLA forms unstable intermediates through a reaction. As a result, carbon dioxide is generated and amide linkages are formed [23]. In short, an increase of the PLA polyol causes additional carbon dioxide generation by decomposition of intermediates.

These differences of blowing degree were confirmed by PUF cell structure observations with FE-SEM analysis. As shown in Figure 1, the cell size gradually increased depending on the PLA content of polyol mixture. A dramatic increase in the cell size began at PLA 70. Additionally, Figure 1 showed the difference of PUF cellular structure. Generally, the closed-cell foam presents a structure separated by a cell wall, whereas the open-cell foam has the interconnected networks through large or small holes [24,25]. The factor to determine cellular structure is the degree of polyurethane formation before blowing occurred by carbon dioxide [4,25]. Actually, most PUFs resulted in open-cell structure through a balance of polymer formation and blowing. However, the PLA 90 and PLA 100 PUFs showed that about 91 % of all

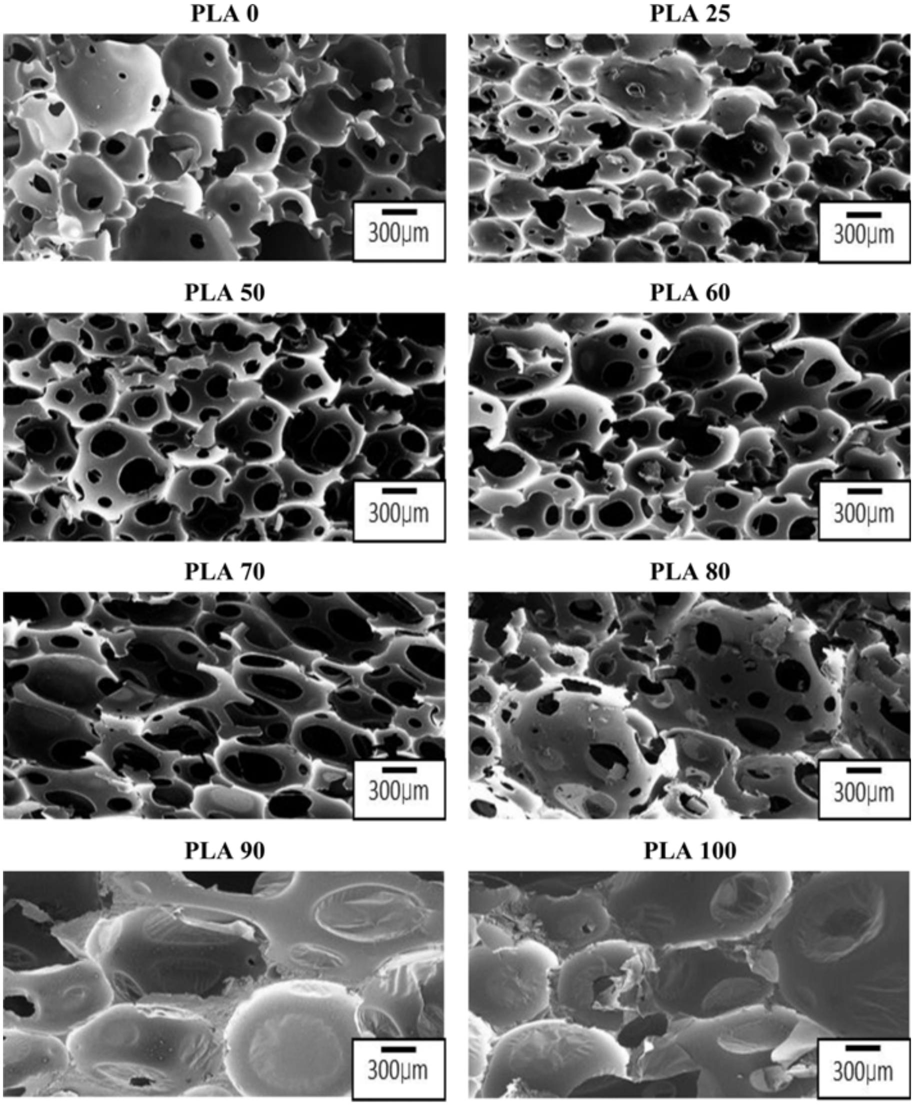
PLA 0 PLA 25 PLA 50 PLA 60 PLA 70 PLA 80 PLA 90 PLA 100

Figure 1. The FE-SEM images of PUFs with various PLA/PEG mixing ratios.

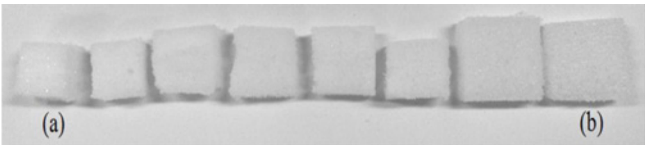

Figure 2. The arranged polyurethane foams in order of the PLA polyol content; (a) PLA 0 and (b) PLA 100.

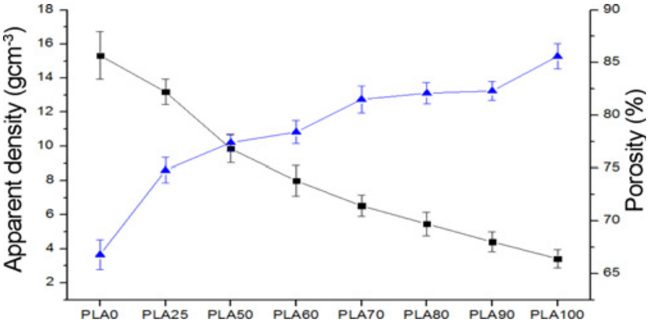

Figure 3. The apparent densities (black square) and porosities (blue triangle) of PUFs with various PLA/PEG mixing ratios.

cells were closed-cell structure because the cream time and gel time for polyurethane formation were very rapid compared to other PUFs.

To measure the apparent density of PUFs, as shown in Figure 2, the prepared PUFs were cut into cuboids. Each specimen was the same weight (0.5 g) and height (1 cm), but volume was different by blowing degree. In short, the difference of bottom area in each specimen determines the volume and apparent density of PUF. Figure 3 shows the results of the apparent density. The maximum value was 0.15 gcm^{-3} for PLA 0 and the minimum value was 0.06 gcm^{-3} for PLA 100. The PUF porosity was measured through a preparation of PUF powder. The maximum value was 86 % for PLA 100 and the minimum value was 67 % for PLA 0. The porosity was inversely proportional to the apparent density. Therefore, it was shown that the PLA content of polyol mixture significantly affected the porous structure.

FT-IR Analysis

FT-IR analysis was performed to confirm urethane linkages formation between the PLA/PEG polyol mixture and the isocyanate. Figure 4 shows the FT-IR spectra from 400-4000 cm^{-1} for the PUF. The peaks related to urethane linkages were detected at 1740-1750 cm^{-1} (hydrogen bonded C=O stretching in urethane) and 1525-1536 cm^{-1} (N-H bending in urethane). When the NCO groups in diisocyanate reacted with water, not only urethane groups but also urea groups (-NH-CO-NH-) were generated. Therefore, a peak was detected at approximately 3330-3400 cm^{-1} due to the N-H of urea [26]. At 2250 cm^{-1}, HDI has a specific spectrum of NCO groups. However, FT-IR spectra showed that no NCO peaks were detected in this area. This result confirms that urethane linkages between the polyols and isocyanates successfully formed without unreacted NCO groups.

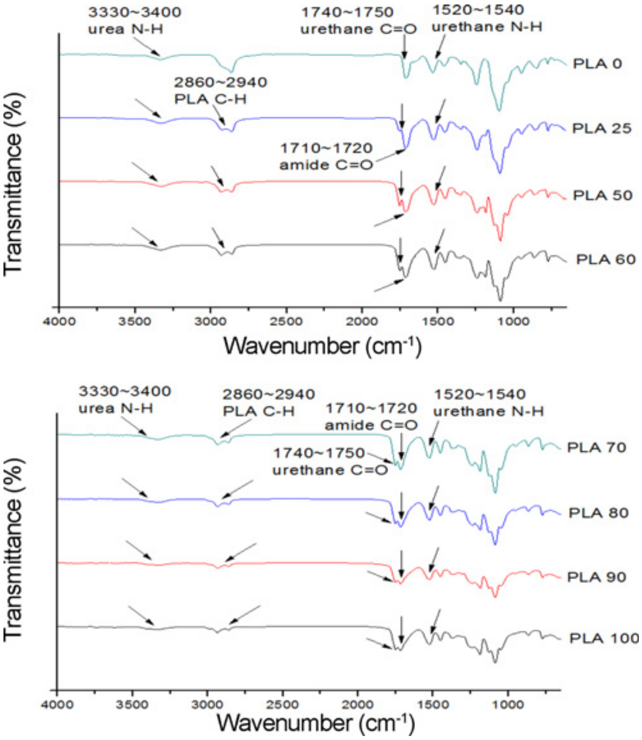

Figure 4. The FT-IR spectra of PUFs with various PLA/PEG mixing ratios.

In addition, Figure 4 showed the spectra related to PLA polyol. The FT-IR spectra of PLA 0 didn't have amide C=O peak at 1710-1720 cm^{-1} and revealed a single peak by PEG (-CH$_2$ linear chains) at 2860-2940 cm^{-1}. However, an introduction of the PLA polyol changed the FT-IR spectra. First of all, the double peaks were detected at 1710-1750 cm^{-1} due to urethane C=O peak (1740-1750 cm^{-1}) and amide C=O peak (1710-1720 cm^{-1}). Moreover, the spectra from 2860-2940 cm^{-1} showed a splitting shape by PLA (-CH$_3$ side chains) [27].

Water Absorbency

The water absorbency of the PUF was calculated after soakage for 24 hours. Generally, a major factor to determine the water absorbency is the polyol and the cell structure of PUF. Specially, the open-cell structure provides direct tunnels for water to diffuse in [28].

As shown in Figure 5, the absorbency decreased with increasing PLA polyol content. The absorbency of PLA 0 and PLA 100 PUFs were 15.3 and 3.4 times its weight, respectively. Although the cell size and porosity of PUF was increased with PLA polyol content, the water absorbency was not proportional to the porosity. This is due to intrinsic polymer structure. Hydrophilic PEG has a long end-to-end distance of linear aliphatic chains, whereas hydrophobic

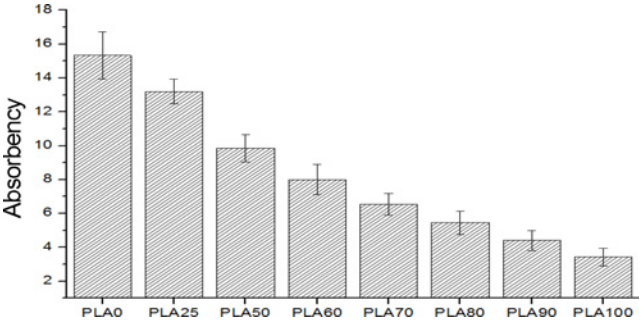

Figure 5. The water absorbency of PUFs with various PLA/PEG mixing ratios.

PLA contains -CH_3 side chains in the main backbone [29]. Therefore, it can be stated that the PLA hydrophobicity is significant factor in terms of water absorbency. In addition, the closed-cell structure of the PLA 90 and PLA 100 PUFs affected water resistance.

Mechanical Properties

The mechanical properties under dry condition were investigated to ensure an improvement in the strength and modulus of PUF through PLA polyol. Specially, the mechanical properties under wet condition was investigated because PEG-based PUF can be easily affected by humidity or wetting. The introduction of hydrophobic PLA polyol was expected to prevent weakening of mechanical properties under wet condition.

Figure 6 shows the breaking stress, breaking strain, and Young's modulus from the tensile test under dry condition. Breaking stress and Young's modulus of the PUFs increased with increasing PLA content. This result shows that the more PLA polyol, the more stress is needed to break the PUF.

Considering the brittleness of PLA and the flexibility of PEG, it was predicted that the breaking strain would decrease with increasing PLA polyol content. However, the tendency of breaking strain was different from those of breaking stress and Young's modulus. When the PLA content of polyol mixture was below 50 %, the PUF breaking strain was less than 87 % because the weak strength of PEG-dominant PUF makes it difficult to achieve higher strain. When the PLA content of polyol mixture was above 80 %, the PUF breaking strain was less than 35 % due to the high strength and stiffness of dominant PLA.

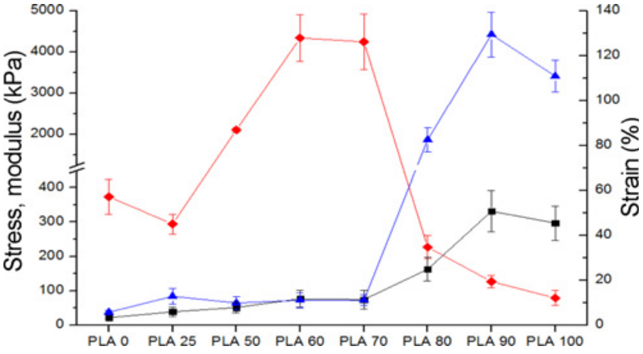

Figure 6. The tensile properties of various PUFs under dry condition: breaking stress (kPa, black square), breaking strain (%, red diamond) and Young's modulus (kPa, blue triangle).

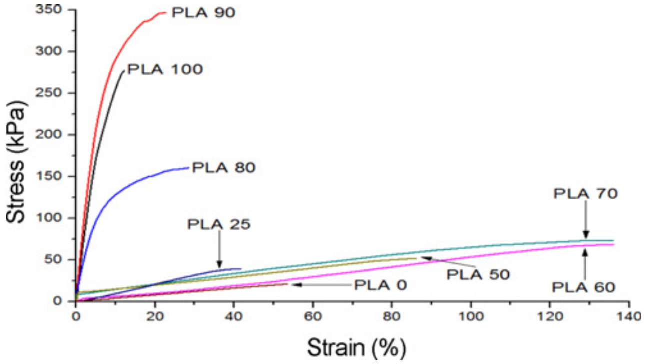

Figure 7. The tensile S-S curve of various PUFs under dry condition.

Interestingly, the breaking strain of PLA 60 and PLA 70 PUFs increased to 128 % and 126 %, respectively. It shows that the PLA polyol not only improve the PUF strength but also contribute to achievement of higher strain. According to Nakayama [30,31], homo PLA and PLA-based PU are hard and brittle polymers with high tensile strength (32 MPa and 34.3 MPa, respectively) and low breaking strain (14 % and 23.8 %, respectively). In contrast, the incorporation of tetra ethylene glycol units as polyols led to much higher breaking strain (918 %). According to Shen [32], when up to 30 % of PEG, in total weight, was introduced into PU, the breaking stress decreased to 16 MPa compared to that of PLA-based PU (52 MPa). But the breaking strain increased from 5 % to 160 %. Through these results, it was confirmed that introduction of PLA polyol reinforced the tensile properties of the PEG-based PUF.

Under wet condition, Figure 8 shows that the mechanical strength and stiffness of the PUF decreased compared to

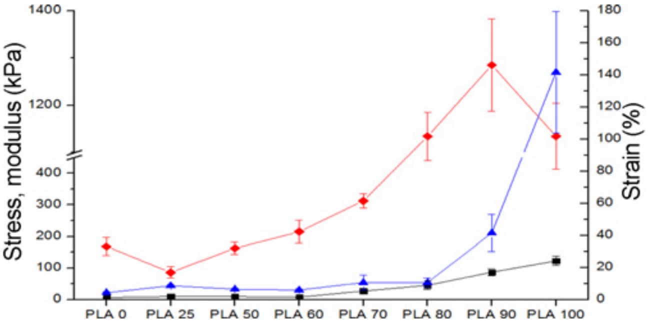

Figure 8. The tensile properties of various PUFs under wet condition: breaking stress (kPa, black square), breaking strain (%, red diamond) and Young's modulus (kPa, blue triangle).

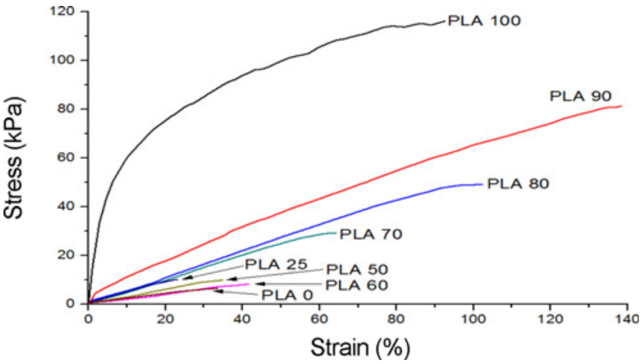

Figure 9. The tensile S-S curve of various PUFs under wet condition.

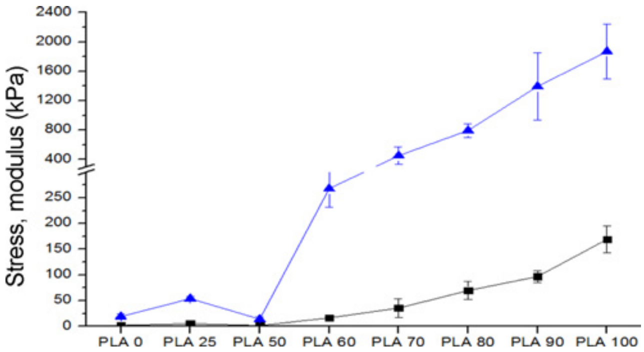

Figure 10. The compressive properties of various PUFs under dry condition: compressive stress at a 10 % deformation (black square), compressive modulus (blue triangle).

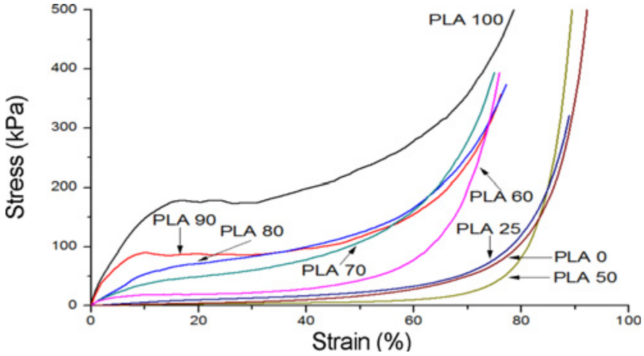

Figure 11. The compressive S-S curve of various PUFs under dry condition.

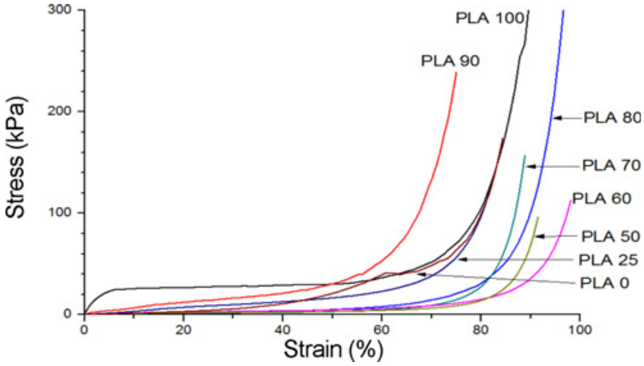

Figure 12. The compressive S-S curve of various PUFs under wet condition.

those under dry condition. However, the breaking stress and Young's modulus increased with increasing hydrophobic PLA polyol. It was remarkable that the breaking strains of the PLA 80, PLA 90, and PLA 100 specimens under wet condition were 102 %, 146 %, and 102 %, respectively. The result was caused by the mobility of polymer chains. When the PLA content of polyol mixture is below 70 %, the water absorption of PUF helps to increase the flexibility of hydrophilic PEG chain. Thus, the overall mechanical properties of PUF decrease dramatically. When the PLA content of polyol mixture is above 80 %, relatively less water permeates into the PUF and extends the distance between the polymer networks. The -CH_3 side chain of PLA accelerates this phenomenon [33]. Thus, the polymer crosslinking chain has more flexibility but less strength compared to that under dry condition. Therefore, the breaking stress decreased but the breaking strain increased dramatically within the failure limitations.

Figure 10 shows the compressive stress (at a 10 % deformation) and the compressive modulus for the compressive test under dry condition. The PUF compressive stress and compressive modulus increased with increasing PLA content. The strain-stress curve (Figure 11) clearly shows that the rigid property of PUF is changed into the soft property at a certain point. When the PLA content of polyol mixture was above 70 %, the PUF had a yield point at 10-20 % deformation, and the stress gradually increased until the deformation reached 50-60 %. This result is a typical compressive S-S curve of a rigid PUF. Conversely, when the PLA content of polyol mixture was below 60 %, an increase of the stress was low until the deformation reached 50-70 %. Afterwards, a dramatic increase in the stress was observed. This result is a typical behavior of a soft PUF.

Figure 12 shows the strain-stress curve under wet condition. Similar to the results under dry condition, the PUF compressive stress (at a 10 % deformation) and compressive modulus generally increased with increasing PLA content. However, the experiments for the PLA 0 and PLA 25 PUFs showed different results. The stress of PLA 0 dramatically increased after 30 % deformation and the stress of PLA 25 was relatively high. These results are based on the hydrophilicity and pore structure of the PUF. When water permeates into the many pores of these samples, the distance between PU polymer chains is extended and water is trapped by pores. This phenomenon is similar to the formation of a chain-water-chain layer structure. Therefore, in the case of the wet condition, the compressive properties of PLA 0 and

PLA 25 increased compared with those of the other specimens with relatively low water absorbency.

Conclusion

It was shown that various PUFs were successfully fabricated using a PLA/PEG polyol mixture. During the reaction with isocyanates, the PLA polyol caused more carbon dioxide generation. The differences of blowing degree due to carbon dioxide generation were confirmed by PUF cell structure observations using a FE-SEM analysis. The PUF cell size increased depending on the PLA content of polyol mixture. The FT-IR analysis confirmed that the PLA/PEG polyols reacted with HDI. Additionally, peaks related to amide linkages were detected by the reaction between the PLA carboxyl groups and the HDI isocyanate groups. A decrease in the water absorbency was caused by hydrophobicity when PLA was the major polyol.

In the tensile test under dry condition, the PUF breaking stress and Young's modulus increased with increasing PLA content. Interestingly, the PLA 60 and PLA 70 PUFs exhibited remarkable increases in their breaking strains because PLA reinforced the weak strength of the PEG-based PUF. In tensile test under wet condition, the breaking stress and Young's modulus of the PUF decreased compared with those under dry condition. However, the breaking strains of the PLA 80, PLA 90, and PLA 100 specimens under wet condition were similar to those of the PLA 60 and PLA 70 under dry condition. The result was due to the mobility of PU polymer chain networks.

For the compressive test under dry condition, the PUF compressive stress and compressive modulus increased with increasing PLA content. When the PLA content of polyol mixture was below 60 %, the rigid property of PUF was changed into the soft property. For the compressive test under wet condition, the PLA 0 and PLA 25 PUFs exhibited interesting properties. These results were based on the formation of a chain-water-chain layer structure in the PUF.

Acknowledgements

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