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Research Article

Preparation and Characterization of Potato Crust-Based Polyurethane Foam-I

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ABSTRACT

Polyurethanes (PUs) are polymers obtained by reacting diisocyanates with a group of polyols. The first synthesized PU compounds were prepared using petroleum subproduct compounds. In this research study, biomass-containing polyols, which have been studied by other scientists, were prepared using potato crust and polymerized with diisocyanates to produce PU foam. Polyol reactions were carried out using the microwave heating method. Synthesis reactions and structural properties of polyols have been studied in many aspects. The most available polyol was used for PU synthesis. Different formulations were tried for PU synthesis and as a result, PU foam containing nearly 25% starch-polyol was synthesized. The chemical structure of PU polymer was identified by ATR-FTIR spectroscopy and crystallographic properties by WA-XRD analysis. The physical and mechanical properties of PU foam, which is used as a large number of building and construction materials, including thermal insulation materials, were evaluated by comparing them with a commercial PU foam.

According to the results of our research, it was detected that the incorporation of biomass into the structure of PU polymer improved its density, heat conduction coefficient, pressure based mechanical properties. PU foam derived from potato waste has a WA XRD-ray diffraction peak between 13.1-28.5°. This data is between 12.5-23° in synthetic commercial foam and has been positively improved in the product we synthesized as a result of combining biomass into the structure. Biomass-based PU foam has been synthesized with features that can be used as a thermal insulation material.

Keywords: Biomass, polyol, polyurethane foam, characterization

1. INTRODUCTION

Polyurethanes(PUs), is a group of polymer which had been synthesized by Dr. Otto Bayer in the 1930s and includes thermoset and thermoplastic types.[1,2] In daily life, many materials are used, including thermal insulation materials, plastic materials, adhesives, plastic paint, glass wool, sheets, floor and wall coverings, PU spray, water-based paint, filling materials and wooden materials.[3,4,5,6] In addition, PU foams are used as adsorbents in health, agriculture and environmental technologies.[7,8,9]

PUs are synthesized as a result of the exothermic reaction of polyol and diisocyanate/polymeric isocyanates in the presence of various catalysts, silicones and a wide variety of additives (flame retardants, phosphorus, humic acid, etc.) added to the final structure.[10]

Polyols are polymeric structures containing many hydroxyl groups and the majority of polyols used in the

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polyurethane industry are derivatives of petroleum products. Increasing fossil raw material prices and decreasing oil resources have redounded the studies on the research and industrial development of biopolyols syntheses.[11] In this context, scientists have conducted research on combining biomass with many different compositions, including wheat straw (cellulose-hemicellulose)[12], peanut shells (lignocellulose)[13], pine bark (lignocellulose)[13], turpentine resin (starch)[14,15,16,17], corn residue resin (bark of Acacia mearnsii-starch)[18] and etc. into the structure of polyols. Again, different pure vegetable oils have been used in large quantities in the synthesis of biopolyols.[19,20] Isocyanates used in the production of commercial polyurethanes are generally aromatic in nature. Typical diisocyanates used in polyurethane production are MDI (diphenylmethane-4, 4-diisocyanate), NDI (naphthalene-1,5-diisocyanate) and TDI (toluene diisocyanate)[21].

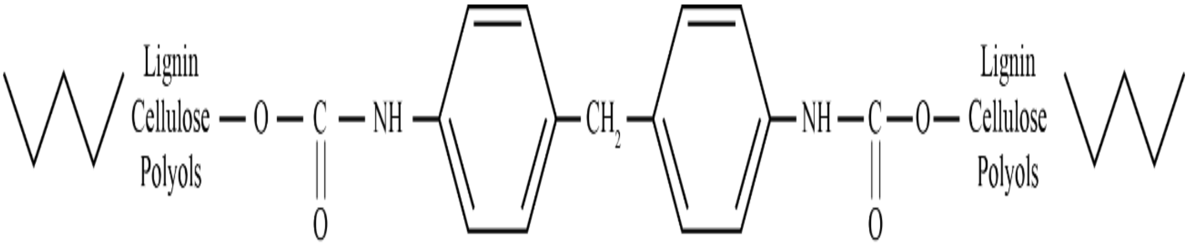

Figure 1. Scheme for the formation of polyurethane from the reaction diphenylmethanediisocyanete (MDI) and synthetic/natural polyols.[1]

The objectives of this study are: (1) to liquefy potato crust waste under different reaction conditions (2) to characterize biopolyols (3) to evaluate the microwave heating method (3) to measure the usability of biomass-containing PU thermal insulation materials; and (4) generate insight into the preparation of composite materials containing starch substances from the research results.

2.EXPERIMENTAL

2.1.Materials

Potato crusts were dried under atmospheric pressure. Potato crust meal (Solanum Tuberosum L., 177 micron) was dried again for 12 hours in an oven at 103 ± 2 ^{o}C before being put into the reaction. Polyethylene glycol # 400 (PEG#400, Merck Company/Germany), glycerin (Merck Company /Germany), sulfuric acid, hydrochloric acid, phosphoric acid and sodium hydroxide were supplied from commercial company (Sezlab Chemical Mate. Paint Ind. Commence Ltd. Company). Other ingredients included polymeric diphenylmethane diisocyanate (PMDI 92140), triethylenediamine catalyst (93040), silicone surfactant (Silicone Glycol Copolymer, Chemika 81.170, M_A=380g.mol^{-1}), silicone PEG #400 were used as received. Water was used as the foaming agent.

2.2.Synthesis of Biopolyols

PEG#400/Glycerin 4/1 w/w reagents were used as solvent for the first step polymerization process. The first step polymerization reaction is referred to as the liquefaction reaction in many literatures. H_2SO_4, HCl and H_3PO_4 were preferred as catalysts. The polymerization reactions were carried out with the total equipment of a microwave heating oven with an independent backcooling system and a dependent temperature sensor.

The process decided for the biomass liquefaction polymer reaction is as follows; biomass/PEG#400/Glycerol 5/12/3 w/w/w 500 ml N/S 500 ml glass flask was placed. For each reaction, 3-21% x total amount of solvent was added separately and premixed.

A normal heating program of 350 watts/minute and a stirring speed of 300 rpm were found sufficient for the reactions. The reagents were left to react separately for 15 and 30 minutes. It was allowed to cool for half an hour and the acid catalyst in it, was neutralized with sodium hydroxide solution (40% w/w).

2.3.Measurements of the Un-liquefied Potato Crust Parts

As a result of the first step polymerization reaction, 10 g of the liquefied reactant mixture was dissolved in 40 ml of methanol and filtered using filter paper with a pore size of 125 mm with the help of a vacuum water pump. The unreacted biomass fractions were kept in an oven at 100±3 °C until their mass stabilized and were calculated according to the following equation (1):

$$R(\%) = \left(\frac{m_1}{m_0} \right) x100 \tag{1}$$

In equation (1), R is the unliquefied biomass in percent (%), m_1 is the mass of the unreacted biomass fractions, and m_0 is the initial potato crust amount in mass (g).

2.4.Measurements of the Specific Gravity, Viscosity and Surface Tension of Biopolyols

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The density and viscosity of starch-containing biopolyols under normal conditions were measured in accordance with ASTM D 4969 and ASTM D 4878 standards, respectively. Viscosity measurements were taken at 50 rpm/min stirring speed conditions with a Brookfield DV-IV viscometer with S05 spindle. Again, the surface tension of biopolyols was measured according to the Drop Counting Method under room conditions expressed as 25 ^{o}C.

2.5.Measurement of the Acid Number of the Biopolyols

The acid number of biopolyols was measured using the titration process according to ASTM D 4662-08.

2.6.Total Acid Value

The acid number of biopolyols was determined as follows.

1. Ethyl alcohol (120 mL) and toluene (120 mL) are mixed in a total 240 mL flask (Reagent).

2. Indicator; It is formed by dissolving 0.5 g of phenolphthalein in 50 mL of ethyl alcohol and 50 mL of pure water solution.

3. For 0.1N KOH; it is prepared by adding 10 mL of water, 5.61 g of KOH and the remaining ethyl alcohol in a 1000 mL flask.

4. 40% (w/w) NaOH solution is required for the neutralization process. Prepare 40 g of NaOH by completing the volume to 100 mL with pure water.

5. 40% (w/w) solution containing an equivalent gram of NaOH equal to the equivalent gram of acid catalyst in the liquefied sample is added to the liquefied sample and mixed well with the help of a baguette.
6. The process is carried out by taking 0.5 g of liquefied polyol, previously neutralized, with 25 mL of reagent. Then, 0.25 mL of indicator is dropped into this mixture, then 0.1 N KOH placed in the burette continues to be added until a color change is observed (The volume used is then noted down, this is the A value in the formula).

7. After adding 0.25 mL of indicator to 25 mL of reagent, titration is performed with 0.1 N KOH (The amount of KOH spent is recorded, it is the B value in the formula).

As a result, the acid value is calculated according to the formula below.

$$AD = \frac{(A-B)\text{x}N\text{x}56{,}1}{W} \quad \text{mg KOH/g polyol} \qquad (2)$$

2.7.Measurement of the Hydroxyl Numbers of the Biolyols

The hydroxyl number of biopolyols was measured according to ASTM D 4274-05.

2.8.Total Hydroxyl Value

The hydroxyl value of the biopolyols was determined as follows.

1. Prepare 0.5 M NaOH from a mixture of two 2 g NaOH and 100 mL of pure water.

2. Seven hundred (700) mL pridine and 111 g phthalic anhydride are mixed with the help of a magnet at 110^{o} C for 2 hours (in a dark colored balloon). (reagent)

3. For the indicator; A mixture of 50 mL of pyridine and 0.5 g of phenolphthalein is required.

4. Forty percent (40%) NaOH solution is required for the neutralization process (40 g NaOH is prepared by making up its volume to 100 mL with pure water.

5. 40% (w/w) solution containing an equivalent gram of NaOH equal to the equivalent gram of acid catalyst in the liquefied sample is added to the liquefied sample and mixed well with the help of a baguette.

6. After adding 0.25 mL of phenolphthalein to 25 mL of reagent, it is titrated with 0.5 M NaOH (aqueous) (The volume of NaOH spent is recorded and is the A value in this formula).

7. The procedure is carried out by taking 0.5 g of biyopolyol with 25 mL of reagent. Then, 0.25 mL of indicator is dropped into this mixture and the addition is continued until a color change is observed with 0.5 N NaOH solution placed in the burette (Then the volume used is noted and it is the B value in the formula).
As a result, the hydroxyl value is calculated according to the equation below.

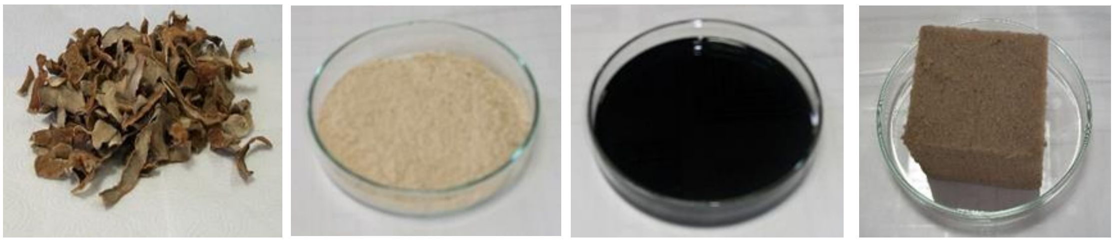
$$HD = \frac{(B-A).N.56.1}{w} \quad \text{mg KOH/g polyol} \qquad (3)$$

2.9.Preparation of the PU Foams

After the acid catalyst contained in the synthesized biopolyols is neutralized, it is used for the PU foam reaction. Biopolyol, catalyst, surfactant and water were used as reagents in the second polymerization reaction. Tried and preferred formulations were applied. Pre-mixing was done in a plastic container and MDI (isocyanate index 90) was added and mixed rapidly for 15-20 seconds at mixing speed of 8000 rpm/min. It was left to rise freely under reaction conditions about 10-20 seconds. The crystal structure of the foams was waited for two days to settle within itself. They were then removed from the plastic container and cut to be used as test samples.

Table 1. Foam formulations for the biyopolyol-contained PU foam

	Ingredients	**Parts by Weight**
1. Liquid	Biyopolyol	100
	Catalyst	3
	Surfactant	2.5
	Blowing agent	6.25
	PEG 400	20
2. Liquid	MDI	130



Biomass Biomass miles Biopolyol Biopolyol-contained foam

Figure 2. Photographs of biomass, biomass particles, biopolyol and biopolyol contained-PU foam

2.10.Measurements of Properties of the Rigid Foam Samples

2.11.Density of Foam

The density of the synthesized rigid foam's samples and commercial ones were measured according to ASTM D 1622-08. Both synthesized and commercial ternary foam samples were 1x1x1 cm in size. The specimens were conditioned for 2 days at 23 ^{o}C and 50% relative humidity and then were calibrated and weighted to calculate densities.

2.12.Mechanical Properties of Foam

The pressure-based mechanical properties of PU thermal insulation material test samples were measured using the Universal Test Instrument (Zwick (Roell 2010)) according to JIS (Japan Industrial Standard) K7220. Both samples synthesized from biopolyol and commercially supplied ones were cut into dimensions of 5 cm x 5 cm x 5 cm. Samples were conditioned as mentioned above. Measurements were taken at a constant speed of 1 mm/min in the direction perpendicular to the rise of the PU material. In all measurements, compressive strengths were determined as stresses at which the sample deformation was compressed to approximately 15% of its volume.

2.13.Heat Conductivity Value of Foams

The thermal conductivity coefficient value was measured with the device called Quick Thermal Conductivity Meter Instrument according to the Hot Wire Method and ASTM C 1113-90. A method based on the principle of heat dissipation sent to the center both of the synthesis and comparison samples which are measuring 2 cm x 5 cm x 10 cm was used.

2.14.Fourier Transform Infrared Spectroscopy (ATR-FTIR)

ATR-FTIR (Attenuated Total Reflectance Fourier Transform Infrared spectroscopy) spectroscopy is used to identify the bonds in the structure of molecules in solid, liquid and amorphous phases. It was used to characterize the functional groups of potato crust meal, unliquefied potato crust residue, the prepared polyurethane foam and synthetic foam. Analyzes were performed with a Thermo Fisher Scientific mark, Nicolet İS10 model spectrometer. Single-beam spectra of the samples were obtained after averaging 16 scans in the range from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1}. All spectra were obtained in the transmittance mode at the temperature of 23 ± 2 ^{o}C.

2.15.X-Ray Diffraction (XRD)

Wide Angle X-ray Diffractometer analysis of synthesis thermal insulation material and commercial comparison thermal insulation material which were grounded into coarse-grained particles were made by Philips X' Pert PRO brand device. For irradiation, the CuKα line was selected at λ= 0.154056 nm, 40 kV cathode potential difference and 30 mA current were applied. Scattering was recorded in the range of 2ϕ=10-70^{o}.

2.16.Biodegradability of PU foams synthesized from biopolyol

The synthesized PU foams were cut into cubes of equal size and buried in organic soil in triplicate samples. Test samples were removed from the soil after a period of three months, it was lightly calibrated with deionized water from soil elements and then dried in the oven at

50^{o}C temperature for about one day. Mass loss due to biodegradation was calculated with Equation (4).

$$Weight\ loss\ (\%) = \frac{W_0 - W_S}{W_0}\ X\ 100 \qquad (4)$$

where W_0 is the initial quantity of the PU material and W_S is the quantity of the PU material after biodegradation.

3.RESULTS AND DISCUSSION

3.1.Effect of Reaction Conditions on the Liquefaction

Table 2 shows the effects of reaction conditions on liquefaction of potato components.

Table 2. Effects of the reaction conditions on liquefaction reactions

Biomass	Catalyst	Acid catalyst concentration %	Reaction time (min)	PPIP (%)	Reaction Completion Temparature (^{o}C)
Biomass	H_2SO_4	3	15	9.25	86.6
Biomass	H_2SO_4	4	15	6.04	88.2
Biomass	H_2SO_4	9	15	4.99	90.3
Biomass	H_2SO_4	3	30	5.74	94.2
Biomass	H_2SO_4	4	30	4.70	100.4
Biomass	H_2SO_4	9	30	0.60	107.0
Biomass	HCl	9	15	8.37	56.0
Biomass	HCl	12	15	7.99	117.3
Biomass	HCl	18	15	6.80	103.9
Biomass	HCl	9	30	6.07	87.0
Biomass	HCl	12	30	4.56	84.0
Biomass	HCl	18	30	4.22	88.1
Biomass	H_3PO_4	9	15	25.85	156.7
Biomass	H_3PO_4	15	15	21.40	123.5
Biomass	H_3PO_4	21	15	7.20	123.5
Biomass	H_3PO_4	9	30	25.85	140.6
Biomass	H_3PO_4	15	30	21.40	109.4
Biomass	H_3PO_4	21	30	7.75	123.4

Conditions: Biomass/PEG400/Glycerin = 5/12/3, 350 watt/min microwave-heating energy, 300 rpm/min mixing speed; PPIP (Percent of PEG#400 insoluable part)

3.2.Effect of Reaction Times on the Liquefaction

The unreacted percentage amount of liquefied biomass catalyzed by three different acids and using three different catalyst concentrations within two reaction times using the microwave heating method is shown in Table 2. The most striking and important point of the results is the rapid decrease in the amount of biomass during the initial period of the reactions catalyzed by all three acids. This revealed that microwave energy heats the reagents in the reaction flask in a very short time, causing the biomass to polymerize very quickly, and as a result, the percentage of unreacted biomass content decreases rapidly.[26]

3.3.Evaluation of Completion Temperature of the Liquefaction Reaction

Table 2 shows the completion temperatures of liquefaction of potato plant's crust according to microwave heating method. These results showed that microwave heating liquefied potato crust at an average reaction temperature and liguefaction reaction was a thermochemical process under mild organosolvolysis terms.[27] Thus, for liquefaction of potato crust, reaction temperature must not be very high and 100 ^{o}C degree is sufficient.

3.4.Effect of Catalysts and Catalyst's Concentrations on the Liquefaction

Figure 2 shows the effects of catalyst strains and catalyst's concentrations on the liquefaction of potato crust in PEG#400/Glycerin solvent mixture under microwave heating. In the experiments, sulfuric acid, hydrochloric acid and phosphoric acid were added as the catalyst of the liquefaction reaction 3% to 21% under microwave heating within 15 and 30 min. At 9% x $m_{solvents}$ of three kinds of catalyst quantities, unreacted residue percents of potato crust were 0.6, 6.07 and 25.82, respectively. These phenomena can be explained with different catalytic activity and content of organic acid catalysts.[28] Under microwave liquefaction, a small amount of sulfuric acid provided superior yield on liquefaction. In addition, due to low catalytic activity of phosphoric acid, recondensation reaction took place in liquefaction of potato crust, and the residue percent increased. So, 9% sulfuric acid for liquefaction reaction of potato crust could be recommended in practical production of polyurethane foams.

3.5.Characterization of Biopolyols

Table 3 shows some physical and chemical properties of the synthesized starch-parent composition biopols. Due to all these features and the highest reaction rate, biopolyol synthesized at 9% concentration of sulfuric acid catalyst can be used in the synthesis of PU composites.

Table 3. Properties of the liquefied biopolyols

Catalyst	Organic acid concentration [%]	Reaction Time [min]	Apparent Density [g/cm^3]^a	Viscosity [Cp]^a	Surface Tension [dyn /cm]^a	Acid Value [mg KOH/g]	Hydroxyl Value [mg KOH/g]
H_2SO_4	3	15	1.32	586	218.7	38.9	385.8
H_2SO_4	4	15	1.34	589	223.7	40.0	388.0
H_2SO_4	9	15	1.35	744	347.6	43.8	407.9
H_2SO_4	3	30	1.16	877	193.9	50.3	407.9
H_2SO_4	4	30	1.21	880	199.5	43.7	381.8
H_2SO_4	9	30	1.26	893	334.2	33.4	372.5
HCl	9	15	1.34	722	162.1	44.3	382.3
HCl	12	15	1.28	701	173.8	34.2	385.9
HCl	18	15	1.27	680	304.2	21.5	447.8
HCl	9	30	1.22	705	221.9	45.7	419.0
HCl	12	30	1.22	713	146.5	34.8	442.7
HCl	18	30	1.12	1.036	115.2	33.5	455.5
H_3PO_4	9	15	1.28	1.046	305.5	28.1	317.6
H_3PO_4	15	15	1.38	1.058	218.9	53.0	356.9
H_3PO_4	21	15	1.53	1.090	406.3	31.2	255.6
H_3PO_4	9	30	1.30	1.054	352.2	24.0	341.9
H_3PO_4	15	30	1.40	1.080	242.4	54.2	352.8
H_3PO_4	21	30	1.62	1.180	475.8	35.1	232.5
PEG 400	-	-	1.12	140	-	-	280

Conditions: Biomass/PEG#400/Glycerin: 5/12/3 (w/w/w) T: 25 ± 0.2 °C

^{a}: Polyols don't contain unliquefied parts.

Potato crust-based polyols did not contain a residue component, therefore values of specific gravity, viscosity and surface tension increased with increscent liquefaction ratio.

When the acid and hydroxyl values of biopolyols synthesized under all reaction conditions are examined in Table 3, the equilibrium ratio in the liquefaction reactions catalyzed by sulfuric acid is forward and low. Equilibrium reactions occurred in the reactions catalyzed by the other two catalysts. Generally, with increasing reaction time, the number of hydroxyls in the reaction medium decreased and the number of acids increased.[29] These results indicate that dehydration and/or oxidation reactions occur during the liquefaction of potato crusts.[30]

3.6.Characteristic and Mechanic Properties of Biyopolyol-Contained Foam

When the synthesized biopolyols were examined in terms of density, viscosity, surface tension, liquefied biomass ratio, acid and hydroxyl value; biopolyol, in which 9% by mass x $w_{solvent}$ amount of sulfuric acid was used as a catalyst, was chosen to synthesize the PU thermal insulation material.

Table 4. Characteristic and mechanical properties of PU foams

Polyurethane Foam	Density [g/cm^3]	Compressive Strenght [kPa]	Apparent Modulus [Mpa]	Permanent Deformation [%]^a	Heat Conductivity Value [W/mK]
Biomass/PEG# 400/Gycerin 5/12/3 9% sulfuric acid t: 30 min	0.0544	301.4	1.48	2.24	0.0331
SynteticFoam	0.0456	212.6	2.03	5.98	0.0442

^{a}The permanent deformations of the foams after compression test (15% strain).

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The density of foams prepared from liquefied biopolyol was measured to be similar and slightly higher compared to those synthesized from petroleum-derived polyol. Because, when the synthesized biopolyol was chemically bonded to petroleum polyol, it reduced the average cell size and integrated the crystal structure. The similar result was achieved in the research of Wang and others.[30,31,32,33,34]

The strength of the biopolyol-containing PU thermal insulation material under pressure is calculated as 301.4 kPa. The compressive strength of the commercially supplied thermal insulation material is 212.6 kPa. The inclusion of biopolyol into the PU structure increased the compressive strength of the synthesized material.[24,35] The permanent deformation that occurs when compressing the test samples to 15% of their volume is 2.24% in the biomass-PU material and 5.98% in the comparison material. In other words, biopolyol PU increases the stability of the structure with the new internal and interface bonds it creates. On the other hand, the incorporation of biopolyol into the structure of PU thermal insulation material was reported by Pan et al. (2011) and Ugarte et al. (2014) caused a partial loss of elasticity, as previously reported.[24,26] This situation was also observed in this study. The improved pressure properties of the synthesized PU thermal insulation material was attributed to its biomass ratio and biopolyol structure.

Heat conductivity value of foams derived from biyopolyols was significantly lower (0.0331 W/Mk) than the petroleum-based ones (0.0442W/m.K). As a result, the synthesized PU thermal insulation material has better insulation properties due to its smaller cell size, mostly gated cells, closed and open cell number ratio and chemical internal structure. Our comparison material has a higher thermal conductivity coefficient value.[24,35]

3.7.Fourier Transform Infrared Spectroscopy Analysis (ATR-FTIR)

ATR-FTIR spectroscopy analysis was made to investigate the polymer structure of potato crust, the unliquefied potato crust residue with 9% sulfuric acid catalyst, PU foams from potato crust-based polyols and synthetic PU Foams. The goal was characterization of molecular bonds and identification of functional groups, aromatic or aliphatic units.

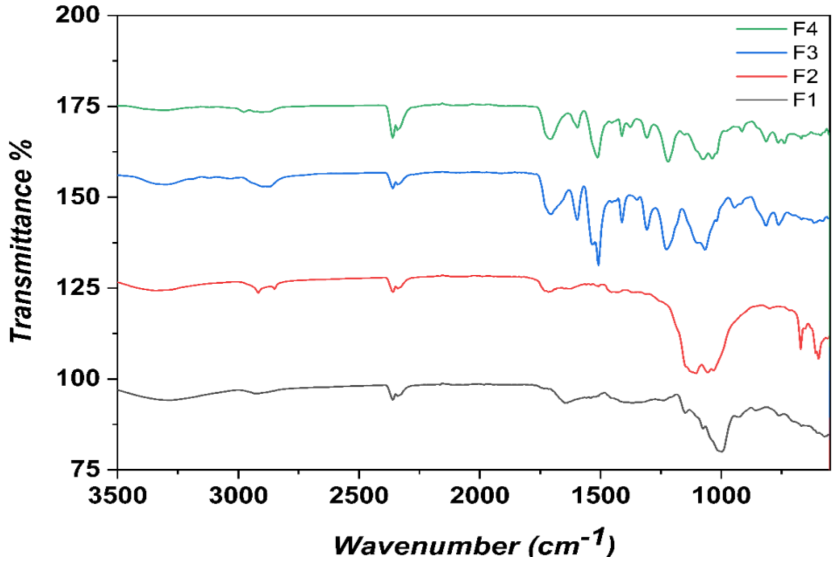

Figure 3. ATR-FTIR spectra of the potato crust (F1), the residue of unliquefied potato crust (F2), rigid PU foam prepared from liquefied potato crust polyol (F3) and syntetic foam (F4). (Potato crust/ PEG#400/Glycerin:5/12/3 (w/w/w), sulfuric acid concentration: 9%)

FTIR spectra of potato crust (F1) and unliquefied potato crust (F2) at 3847, 3790, 3728 cm^{-1} and more than twenty vibration bands are similar to each other. This revealed that liquefied potato crust didn't dissolve and/or react in PEG 400/Glycerin binary solution. The vibration band at 3790 cm^{-1} was the characteristic band of –CH in glucose and starch found in the structure of potato crust. The vibration bands were about 3348 and 3600 cm^{-1} showed the –OH groups of starch and had excess intensity. They had reacted with PMDI and converted into –NCO groups. The vibration bands at 1172 cm^{-1} were attributed to – C-O chain bands of glucose.[36,37]

Figure 3 also illustrates the typical ATR-FTIR spectrum of polyurethane foam (F3) prepared from mixture of potato crust-polyol with commercial polyol and methylene diphenyldiisocyanate. The FT-IR spectrum verified the presence of the polymer structure. The wide absorption band at 3294 cm^{-1} represented stretching

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vibration of N-H urethane hydrogen bonded. Hydrogen bonded –C=O of urethane was located domain at 1637 cm^{-1} between 1696 cm^{-1}. The bands at 1315, 1231, 1201 cm^{-1} confirmed that urethane linkages were formed between hydroxyl groups in the liquefied potato crust and NCO. The bands at 1410, 1657 and 1696 cm^{-1} were derived from aromatic rings of starch and cellulose. Transmittances at wavenumbers 1231 and 1690 cm^{-1} were assigned to the ester asymmetric absorbance and internal ester groups, respectively.[32] -NCO groups attached to MDI, which do not react with the hydroxyl groups of the biopolyol, created vibration bands at 2138 cm^{-1} and 2166 cm^{-1}. Huang et al. (2017b) assumed that isocyanate completely reacts with hydroxyl groups in PU synthesis when the [NCO]/[OH] ratio is less than 1.0.[37] Since these vibration bands were found in the spectroscopic analysis, there is an excess of -NCO that did not react.[35]

Other absorption peaks were attributed to asymmetrical and symmetrical stretching vibration of CH, CH_2, CH_3 at 813, 923 and 2971 cm^{-1}. In addition to these, aliphatic –CH_2 groups which were degraded showed a stretching vibration at 1448 cm^{-1}. Characteristics bands of CO_2 were also observed at 2138 and 2166 cm^{-1}.

From FTIR spectra of synthetic foams (F4), transmittances at wavenumbers 3224, 1607 and 1507 were assigned to the N-H (urethane bonded), N-H (Amide I) and N-H (Amide II) respectively. In addition, the bands at 1069 cm^{-1}, 1216 and 832 were attributed to C-O-C, C-N and C-H of pre-polymer polyol and PMDI. The bands of the excess –NCO group of diisocyanate were not observed.

3.8.X-Ray Differaction Analysis of Biyopolyol-Contained Foam

Polymer structure of PU foam (S1) and synthetic foam (S2) in molecular level were studied with wide-angle X-ray diffraction technique. Another aim was to investigate the crystalline structural changes of the potato crust components.

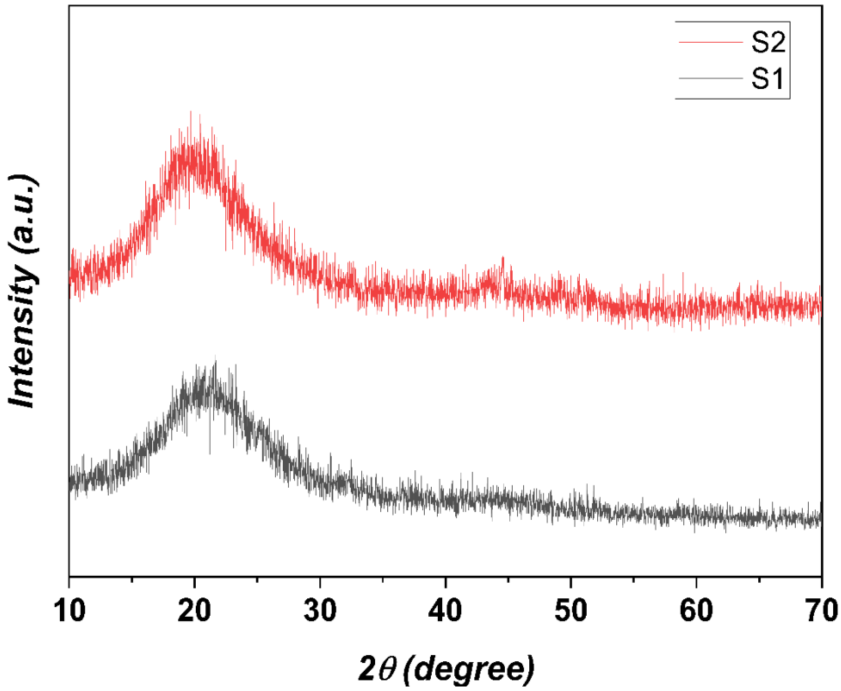

Figure 4. WA X-RD pattern of potato crust-based PU foam and synthetic PU foam, potato crust (S1) foam and synthetic (S2) commercial foam

As shown in Figure 4, there was no diffraction peak observed for the potato crust-based PU foam (S1). This phenomenon could be ascribed to polyurethane foam prepared from potato crust-based polyols as soft segments. It showed no crystallinity. It was reported that starch was a semi-crystalline polymer by Wang et al. (2010) which presented in potato-crust and correspondingly this condition, potato crust components had been degraded completely.[39] The sharp, high diffraction peak of the potato crust starch at a 2θ value close to 20.6° and was assigned to the lattice plane of starch and the second diffraction peak of the potato crust cellulose at a 2θ value was close to 19.4° and was assigned to the lattice plane of cellulose. However, the intensity of these characteristic peaks decreased or disappeared in the diffractogram obtained for potato crust-starches.[39] This was an indication that the

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interaction between potato crust and PU prepolymer changed the main crystalline form of potato crust.[40]

From the total diffractogram, it can be seen that the potato crust-based PU foam has a unique and amorphous structure and correspondingly some excellent mechanical properties. Atomic structure is irregular but compatible with polymer structure. Potato crust-based PU foam has a wide-angle X-ray diffraction pike in the range of 10-27.5°.[41,42,43]

Syntetic PU foam (S2) showed a diffuse peak located at 18.5° of 2θ, in spite of the fact that –C=O- based hydrogen bonds constructed a small scale ordered domain in the PU matrix. In this case, -NH in the hard segment was hydrogen bonded with the-C=O of the hard segments and the ester –C=O of the glycerin soft segments.[41]

When the holistic diffraction chart was examined, it was seen that the comparison material, the commercial PU thermal insulation material, also had a holistic and amorphous structure. It has a characteristic wide-angle X-ray diffraction peak in the range of 12.5-23.8°. When evaluated in terms of the Bragg equation, with the increase of biopolyol chemically incorporated into the PU structure, the X-ray diffraction peak angle increased and the intensity of the total X-ray vibration peaks decreased.[44]

3.9.Biodegradability of PU foam synthesized from biopolyols

Cubic test samples, which were removed from moisture, were buried in organic soil in the form of triplicate test samples. It was then incubated for 3 months under temperature conditions varying between 15-30°C. By adding water from time to time, the water content of the soil was kept at 60%. At the end of the incubation period, the test samples were calibrated from the soil elements and dried in an oven for one day. As a result of the procedures, mass loss was calculated as a percentage.[22,35]

A ratio of 178.4/1.1 times was determined between the degraded mass amounts of biomass-containing PU and synthetic foams. This amount suggests that biomass-containing PU foam will degrade more with increasing test time, considering that it contains approximately much more biomass. The biodegradability of the synthesized material is related to the plant components such as starch and cellulose it contains.

4.CONCLUSION

In this experimental study, potato crust waste with starch main composition was converted into biopolyol in the presence of binary solvent and acid catalyst. A total of 18 polymerization reactions were carried out under three different acid catalyst, two different reaction times and three different catalyst concentration conditions. Synthesized biopolyols were characterized by reaction completion temperature, reaction rate, acid-hydroxyl number, density, viscosity and surface tension parameters. The polyol, which was suitable in terms of all parameters, was used in the second polymerization reaction to synthesize PU thermal insulation material. The synthesized PU material was analyzed according to its physical, mechanical, crystallographic and chemical internal bonding and then compared with commercial petroleum-product PU thermal insulation material.

In the liquefaction reaction of biomass with starch main composition and cellulose side composition, sulfuric acid showed the best catalyst activity. With increasing concentration of all three catalysts, the amount of reacted biomass increased and partial recondensation was observed. Partially low catalytic activity observed during the polymerization reaction of hydrochloric acid and phosphoric acid; were attributed to the water content of the HCl consumable, the difficult proton release of phosphoric acid, and the excess water formed in the environment during both reactions. With increasing reaction rate, density, viscosity and surface tension increased, whereas the acid-hydroxyl number decreased or increased slightly depending on the equilibrium moment. In all synthesized biopolyols, the hydroxyl number at which polymerization can occur was obtained. All biopolyol synthesis reactions took place exothermically. The microwave heating method achieved efficient heat transfer.

According to X-ray diffractometer analysis, the amorphous structure expected from PU thermal insulation material was formed. The amorphous structure gives partial elasticity to PU foam. Compared to commercial petroleum-based PU thermal insulation material; It positively improved its compressive strength, elastic modulus, and permanent deformation. Low density starch, cellulose and neutralization salt peaks were observed. PU polymer with high amorphous character and trace crystallinity was synthesized. All its properties are more advanced than those of the commercial benchmark material.

The density of the synthesized biomass-based PU foam which is at 0.0544 g.cm^{-3}, is slightly higher than the comparison PU foam with a density value of 0.0456 g.cm^{-3}. However, it is within the range of thermal insulation material standards.

ATR-FTIR analysis shows that the biomass is corporeal into biopolyol and PU polymer. Starch and cellulose bands of the biomass were detected, and it was understood from the decreasing peak intensity that it was incorporated into the PU polymer. Urethane hydrogen, urethane chain, aromatic starch-cellulose and ester-internal ester bonds were determined, proving that biomass PU polymer was formed. Excess unreacted isocyanate (NCO) was found.

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The addition of biomass to the PU structure significantly increased its biological degradation. It is inevitable that it will have a positive impact on environmental health, environmental cleanliness and global cooling.

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Conflict of Interest

I declare that there is no a conflict of interest with any person, institute, company etc.

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