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WATER ABSORPTION AND BIODEGRADATION PROPERTIES OF POTATO WASTE-BASED POLYURETHANE FOAMS

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Abstract: *Potato-based polyurethane foams(PUFs) were prepared from the liquefied potato waste-based polyols. Potato wastes liquefied in the presence of polyethylene glycol/glycerin-dominant liquefaction reagent by using sulphuric acid as catalyst in a microwave oven system under stirring. 350 watt/min as micro-wave energy, 300 rpm/min as mixing speed and mass ratio as Biomass/PEG400/Glycerol 5/12/3 w/w/w had been constanted. The liquefied potato waste-based polyols were characterized for the preparation of polyurethane foams. The potato-based polyol which was obtained from 9% sulfuric acid catalyst within 30 min liquefaction reaction period was chosen for the preparation of PU foams. Biodegradation and water absorption properties of PU foams were measured and contrasted with syntetic petroleum-based commercial foams. Biodegrability of PU foam-based on liquefied potato wastes-contained foams was determined according to service biodegradation test for three months. The mean amount of water absorption of potato wastes-based PU foams was measured within 1, 2, 4, 8, 12, 24 and 48 hour. The weight losses of the liquefied potato wastes-based foams along with commercial synthetic PU-type rigid foams had been found 17.84% and 0,107% respectively. The mean amount water intake at potato wastes-based PU foams were higher within seven different time period than synthetic foams. Biodegradation and water absorption properties were found to be higher than those of petroleum-based PU foams dependently biomass content.*

Key words: Potato waste, liquefaction, polyurethane foam, biodegradation, water-absorption

1. Introduction

Polyurethane (PU) is one of the most useful three-dimensional polymers, since it can exist in various forms of sheets, adhesives and paints. Polyurethanes can be produced through the interaction between polyols and polyisocyanate in polyaddition-type polymerization reaction (Alma et. al, 2003).

Polyols (polyether and polyester) and isocyanate are the two main raw materials for PU foam (PUF) production and currently are obtained from the fossil resources (Pan et. al,2011). The major drawback of petroleum-based products is that they are non-renewable and not-biodegradable (Pan et. al, 2011).

The preparation of low-cost polyols from abundant and renewable biomass resources has long been an interesting subject in the polyurethane industry (Yao et. al,1996). Liquefying biomass to produce the industrial chemicals is a novel method to utilize biomass resource. Earlier researches on this area were started from the liquefaction of wood mill (Besteu et. al,1985; Maldas and Shiraishi,1997;Vuori and Niemela,1988;Yamada and Ono,1999). However, most of the reaction are rigor and consume lots of energy. Researches improved the reaction conditions and the liquefaction product was able to be used to produce the resin or foam (Wang and Chen, 2007; Alma et.al, 2003;Lin et. al,1994;Yao et. al,1993). The methods and principles of liquefying the wood mill gave some idea on the utilization of the agricultural straw which had the similar composition as the wood mill (Wang, 2013). In addition, some scientific studies were reported on the liquefaction of the agricultural wastes (Cineli et. al, 2013; Wang and Chen, 2007;Alma et. al,2003;Lin et. al, 1994;Yao et. al,1993;Wang,2013;Hakim et. al,2011).

According to the Turkish Statistical Institute report, 4,750 million tone potato in Turkey and 376,45 million tone in the world were cultured in 2016 (agricultural wastes based on potato (potato crust and potato vines)) almost are burned or (potato crust) were carried out in soil for decaying. This condition pollutes the environment and wastes the biomass resource.

Granola strain potato contain mainly 84,62% water and 15,37% solid substances. Solid substance components are 11,80% starch, 0,78% invert sugar, 0,77% saccharose, 0,80% cellulose and other parts about protein and phenolic matters (Didin et. al, 2000).

The research is based on the production of rigid PU foam derived from starch-contained potato waste, which is environmentally-friendly pathway and has good water-absorptive and biodegrability property to reduce the demand for non-renewable fossil fuels and to restrain production of carbon dioxide “greenhouse gas” to lower global warning.

2. Methods

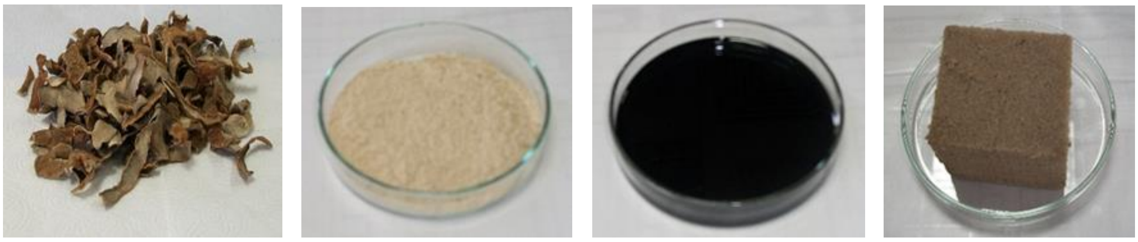
Potato waste were cut and dried under atmospheric pressure. Potato meal (0-80 mesh) was dried in an oven at 103 ± 2°C for 24 hours before re-use. The liquefaction reagent was a mixture of PEG#400 and glycerin. Sulfuric acid was used as catalyst. Liquefaction reaction of biomass was realized by microwave-assistant heating method. The normal heating program was used, which was at 350 watt/min with 300 rpm/min mixing speed. An equivalent amount of sodium hydroxide aqueous solution (40% w/w) was added to neutralize the acid catalyst, thus the liquefied potato waste-based polyols were obtained. The specific gravity, apparent viscosity and surface tension of the liquefied potato-based polyols were measured according to ASTM 4669, ASTM D 4878 and Pendant Drop Method respectively. Measurements were conducted at 25 ± 2 ºC. The acid and hydroxide number of the biomass-based polyol were also determined by the titration method according to ASTM D 4662-08 and ASTM D 4274-05 individually.

Preparation of the Rigid Foams

The pH of the potato crust-based polyol obtained above was adjusted by adding 40 wt % sodium hydroxide aqueous solution as blowing agent. Thus, the definite amounts of liquefied potato crust-based polyol, catalyst, surfactant (polymer editor) and water premixed thoroughly in a plastic cup in first step polymerization. Then, the prescript amount of MDI (at an isocyanate index of 90) was added and mixed quickly at a high stirring speed of 8.000 rpm for 15-20 seconds in second step polymerization. It was allowed to rise freely at room conditions. Foams were allowed to cure at room temperature for two days and then were removed from the plastic cup before cutting into test samples.

Table 1. Foam Formulations for the Liquefied Potato Wastes-Based Polyols.

	Ingredients	Parts by Weight
1. Liquid	Potato-based polyol	100
	Catalyst	3
	Surfactant	2.5
	Blowing agent (water, including water from neutralization with NaOH solution)	6.25
	PEG 400 (Polyethylene Glycol 400)	20
2. Liquid	MDI (Diphenylmenthanediisocyanate)	130



Potato   Potato miles   Liquefied potato   Potato-based foam

Fig. 1. Photographs of potato waste, potato miles, potato-based polyol and polyurethane foam derived from potato.

Biodegradation of Potato-based PU Foams

Biodegrability of potato waste-based PU foams and synthetic foams were evaluated according to service test. Oven-dried foam blocks (1cm x 1cm x 1cm) were buried in culture soil. ($CaCO_3$:20.35%, Salinity: 0.52 mhos/cm, pH: 7.96, organic matter: 49%, Total nitrogen: 0.13%, Phosphorous: 30.4 ppm, Exchangable K^+ ions: 1,56 m.e/100 g soil and Exchangable Mg^{+2} ions: 6.96 m.e/100 g) then incubated at 25^{o}C for 3 months. Water contents of soil was maintained at 60% by occasional addition of water. At the end of the incubation period, impurities on the samples were completely removed and oven dried. Eventually, the percent weight loss was calculated by the conventional method (Alma et al.2003).

Water Intake Test of PU Foam Based on Liquefied Potato

Prepared PU foam was cut into small pieces of equal volume (10 mm x 10 mm x 10 mm) before water intake test. The mean amount of water absorption of potato waste-based PU foams and petroleum-based foams were measured within 1, 2, 4, 8, 12, 24 and 48 hour according to following equation :

$$Water\ \ absorption = \frac{W_S - W_0}{W_0}\ X\ 100$$

where W_0 is the original weight of the PUF (g) and W_s is the weight of the PU foam after water-absorption.

3. Results and Findings

Table 2. Effects of the reaction conditions on liquefaction reaction

Biomass	Catalyst	acid catalyst concentration %	Reaction time (min)	*PIP (%)	Reaction Completion Temparature (^{o}C)
Potato	H_2SO_4	9	15	4.88	80.3
Potato	H_2SO_4	4	15	6.04	78.2
Potato	H_2SO_4	3	15	9.25	76.6
Potato	H_2SO_4	9	30	0.60	97.0
Potato	H_2SO_4	4	30	4.70	90.4
Potato	H_2SO_4	3	30	5.74	84.2

Conditions: Potato waste/PEG400/Glycerin = 5/12/3, 350 watt/min microwave-heating energy, 300 rpm/min mixing speed

*PIP: Percent Insoluble Part

As can be seen from Table 2, by incremental acid catalyst concentrations, the PIP and reaction completion temperature had been decreased. In addition, the flash result was obtained from liquefaction reactions is as to liquefaction reactions of starch-main componently potato waste were not a balanced reaction and re-polymerizations were not occurred all the time.

Table 3. Properties of the Liquefied Potato-Based Polyols

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	1.317	586	218.7	38.92	412.00
H_2SO_4	4	15	1.337	589	223.7	40.03	388.03
H_2SO_4	9	15	1.348	744	347.6	43.75	385.82
H_2SO_4	3	30	1.158	877	193.9	33.41	407.90

H_2SO_4	4	30	1.212	880	199.5	43.68	381.75
H_2SO_4	9	30	1.257	893	334.2	50.31	372.49

[a] Polyols don't contain residue.

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

Generally, the viscosity of the liquefied mixtures obtained by microwave assistant liquefaction was slightly higher than the fossil-based polyol due to biomass components remaining in the liquefied mixture. These values listed in the Table 3 were somewhat larger but were still suitable for the preparation of polyurethane foam.

From the Table 3, the most significant change is the hydroxyl value (about three quarter of the mixture of PEG400 and glycerin). Table 3 showed that the hydroxyl value of the liquefied mixture had decreased and acidic substances had been produced with increasing liquefaction time (Pu and Shiraishi, 1994). These results suggested that dehydration and/or oxidation reactions occurred during the liquefaction of potato crust (Yao et al., 1996).

Biodegradation of Potato-based PU Foams

The weight losses (resulted from a 3-month service biodegradation test) of the liquefied potato-based foams along with commercial synthetic PU-type rigid foams are 17.84% and 0,107%, respectively. This can be explained by the fact that potato waste-based foams contain much more natural components as starch and cellulose (Alma et al., 2002;Ge and Sakai, 1993;Chen and Lu, 2009).

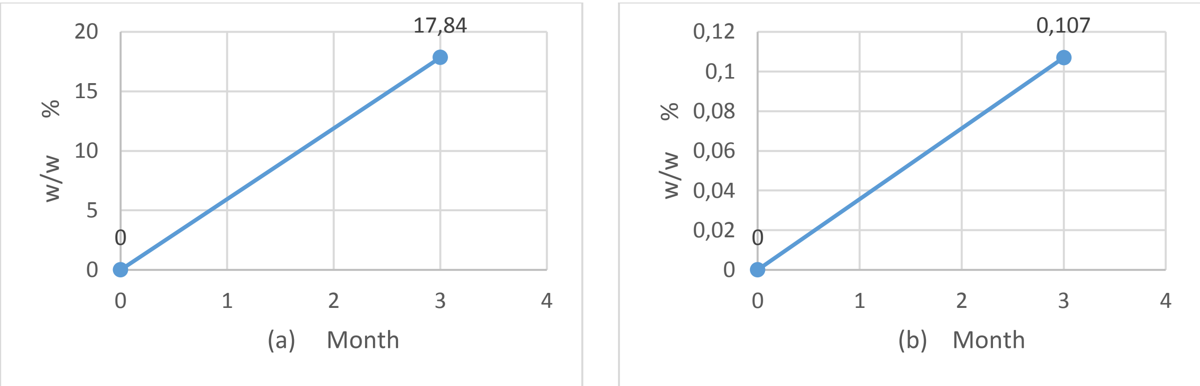


Fig.2 Biodegradation Test Results of (a)Potato PU foam and (b)Synthetic PU foam

Water Intake Test For Potato-based Foams

The mean amount water intake at potato waste-based PU foams were 137%, 156%, 226%, 249%, 393%, 608%, 1,030% within 1, 2, 4, 8, 12, 24, and 48 hour respectively. The mean amount of water intake at petroleum-based foams were as to 35%, 42%, 52%, 65%, 76%, 84%, and 89% within 1, 2, 4, 8, 12, 24, 48 hour. This situation can be explained by the excellent hydrophilic characteristic properties of potato structure. Hydrophilic or water-absorbing foams are useful in manufacturing absorbent products or in agricultural or horticultural purposes (Alfani et. al, 1998; Perkins, 1992;Hostettler, 1980).

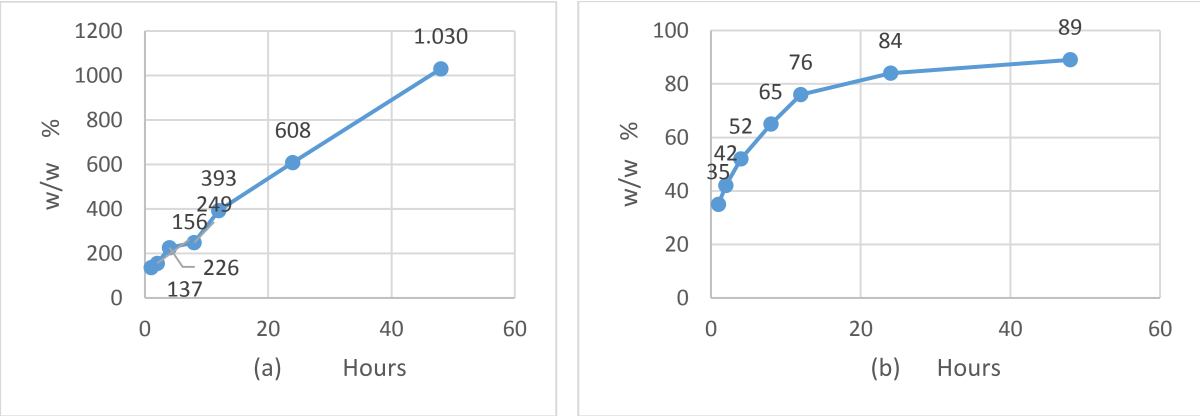


Fig.3 Water Intake Results of (a)Potato PU foam and (b)Synthetic PU foam

4. Conclusion

In this study, potato meal was liquefied with PEG#400 main solvent and glycerin excipient solvent about 99.4% in mild conditions. This phenomenon was related to the high functionality of starches. During the liquefaction, starch and miserable cellulose degraded. Catalyst concentration, liquefaction time affected the liquefaction of potato meal-based polyols and their characteristics. Characteristic properties of biomass-based polyol were similar and slightly much over those of petroleum polyols.

1. Polyols showed to be good candidates for being used in PU foam synthesis.

2. Potato meal-based PU foams have greater biological degradability than synthetic fossils-based PU foams.

3. Water absorption of PU foams were found to be higher than synthetic foams.

Due to the concerns over the depletion of petroleum resources, there must been extensive interests to develop bio-based polyols and PUs (Luo et al., 2013; Gu et al., 2013; Zhang et al., 2014)

Recommendations

As a novel technology, liquefaction of potato components has still many issues and further efforts are required for practical applications.

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