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Polyurethane foams produced from components received in microwave assisted recycling of PUR waste and starch liquefaction

Summary — Starch-based polyurethane foams were synthesized in a reaction of polyol blend derived from microwave assisted liquefied corn starch product and chemically recycled polyol from cold cured polyurethane foam waste, in blending with virgin one polyol with MDI as an isocyanate portion. The effect of microwave irradiation program was investigated in the starch liquefaction and recycling of polyurethane foam waste processes in order to achieving optimum conditions. Reactivity factors, densities and thermal properties of synthesized starch/recycled polyol based foams were investigated and results revealed the performances in thermal resistivity of prepared foam with containing 45 % of recycled polyol in comparison with foam obtained from virgin polyol alone and without starch/recycled polyol.

Keywords: starch, polyurethane foam waste, microwave assisted reactions, starch liquefaction.

PIANKI POLIURETANOWE (PUF) Z UDZIAŁEM KOMPONENTÓW OTRZYMANYCH W MIKROFALOWO WSPOMAGANYCH PROCESACH RECYKLINGU ODPADÓW POLIURETANOWYCH I UPŁYNNIANIA SKROBI

Streszczenie — Syntezowano pianki poliuretanowe z mieszaniny polioliu, diizocyjanianu metylu (MDI), glikolu dietylenowego (DEG) i gliceryny. Do polioliu pierwotnego dodawano polioli otrzymane w procesie, wspomaganego promieniowaniem mikrofalowym, recyklingu chemicznego odpadowych pianek poliuretanowych oraz upłynnioną, również za pomocą mikrofal, skrobię kukurydzianą. Stosując różne programy napromieniania poddano ocenie wpływ mikrofal na przebieg ww. procesów i na tej podstawie dobrano optymalne warunki ich prowadzenia. Badano szybkość syntezy, gęstość oraz właściwości termiczne (TGA) otrzymywanych pianek stwierdzając, że najlepsze wyniki uzyskuje się wówczas, gdy zawartość recyklowanego polioliu w mieszaninie reakcyjnej wynosi 45 % mas.

Słowa kluczowe: skrobia, piankowe odpady poliuretanowe, reakcje wspomagane promieniowaniem mikrofalowym, upłynnianie skrobi.

Polyurethane foams (PUFs) are frequently used as polymeric materials in the world and due to their versatile characteristics production of vast volume of waste is inevitable [1]. Besides polyurethanes are non biodegradable materials and formation of high volume waste during production as well as aged and used materials led to environmental damages. Therefore many efforts have been taken to recover valuable materials and reuse recycled materials for production of new products. One of important methods to overcome environmental drawbacks is the recycling and it is recommended for recovery and regeneration of valuable materials from the waste. Among the recycling methods, the chemical method is mentioned as a versatile and economical method with its

own merits and drawbacks [1–19]. Unfortunately, due to thermosetting characteristics of the PUFs, employment of recycling methods is limited and the synthesis of biodegradable PUFs is recommended as a possible alternative solution to reduce the amount of waste [20]. Literature survey shows reports on liquefaction of cellulose based materials and the using of liquefied polyhydric compounds as a portion of polyol for biodegradable PUFs preparation. For instance, MW assisted wood liquefaction has been reported by Feng and his coworkers using a domestic MW instrument in the presence of inorganic acids as the catalyst and oxypropylation of the liquefied wood what was suitable in synthesizing of wood based polyols. In their study the MW power has been set at

500 W and the liquefaction reaction completed in 15 min [21]. Fei and his coworkers reported dried distillers grains (DDG) liquefaction and preparation of PUFs in combination with virgin fissile based materials [22]. Kim and *et al.* investigated the formation of rigid PUFs and found the formation of structural cells using starch content as 30–50 wt. % in blend with virgin polyol [23]. Another artwork had been reported on structure-property relationship of castor oil based chain extended polyurethane/starch biocomposites [24]. In addition, other reports have been published in application of starch and/or other cellulosic materials in preparing of polyurethane biopolymers using virgin and commercially available starting materials [25–27].

The introduction of potato starch nanocrystals into waterborne polyurethane (WPUR) had been investigated by Chen and coworkers. In this study they found improvements in mechanical properties of WPUR by incorporation of nanocrystalline starch [28]. Another report investigated the effects of starch nanocrystals as a reinforcing material to improve WPUR properties [29].

Recently Spsychaj and coworkers investigated the effects of polyurethane foam powders in combination with montmorillonite on the physical and mechanical properties of thermoplastic starch polymers. They found that by application of a 25 weight per parts of the powdered polyurethane foam/100 parts per weight of starch ratio in the thermoplastic starch (formamide and urea)/MMT/PUR powder mixture, Young's modulus increased and elongation at break decreased in comparison to those obtained from the thermoplastic starch (formamide and urea) system [30]. In another report the effects of some commercially available fillers namely, aluminum hydroxide, melamine, starch, talc, chalk or borax had been studied in production of rigid PUFs and results showed improving of combustion properties in filled foams [31]. Both chemical recycling method and synthesis of biodegradable PUFs can be used as versatile methods to reduce waste and nowadays designing a combined method can open a new window in reducing of PUFs waste and other polymeric waste. By applying the microwave technique as an energy source in performing of chemical reactions, significant decrease is observed in reaction times and nowadays this performance of MW method makes it a versatile and economic process [1].

In this communication and in the continuations of our previous works on polyurethane chemical recycling, cellulose based materials liquefaction and based on our experience in microwave assisted reactions, we decided for the first time to study the performance of this technique in the liquefaction of starch as well as recovering of the polyol from PUR waste and the using of liquefied starch and recycled polyol in the formation of the new biobased PUFs [1, 4–9, 11–13]. In addition, in this study, the reactivity factors, densities and thermal degradations of the prepared foams were studied in detail.

EXPERIMENTAL

Materials

PUFs for chemical recycling were obtained using flexible foam grade polyol of trade name Daltoflex[®] EC 20240 (Table 1) and diphenylmethanediisocyanate (MDI) Suprasec[®] 5005 (Table 2), both purchased from Huntsman. Formation and mold conditions were as follows: Daltoflex[®] EC 20240 – 100 parts by weight, Suprasec[®] 5005 – 65 parts, recommended mold temperature 40–45 °C, demold time 5 min (molding density 42–47 kg/m³).

Table 1. Specification of virgin polyol for cold cure PUFs formulation (Daltoflex[®] EC 20240)

M_w	1900
Appearance	viscous colorless liquid
Viscosity (cps at 20 °C)	1250
Specific gravity (g/cm ³)	1.035
Functionality	2.0
Hydroxyl number (mg KOH/g)	59

Table 2. Specification of MDI (Suprasec[®] 5005) used for preparation of PUFs

Appearance	dark brown liquid
Viscosity (cps at 25 °C)	220
Specific gravity (g/cm ³ at 25 °C)	1.23
NCO value (% by weight of NCO groups)	30.9
Average functionality	2.7
Flash point, °C	233
Fire point, °C	245

Virgin polyol for preparation of rigid polyurethane foams was Daltofoam[®] TA 14066 and the specification of this polyol is shown in Table 3.

Table 3. Specification of virgin polyol for rigid PUFs formulation (Daltofoam[®] TA 14066)

Appearance	viscous yellow liquid
Viscosity (cps at 25 °C)	5263
Specific gravity (g/cm ³)	1.06
Water content (%)	2.3
pH	9.45
Functionality	>2.0
Hydroxyl number (mg KOH/g)	430 ± 20

Starch was purchased from Iranian corn starch producing company and used without any further treatment. Other chemicals were purchased from Merck and

used as received. Recycling of PUFs and polyol recovering were done using our previously reported methods and the recovered polyol was characterized using spectroscopy methods and data were compared with basic sample data [1].

Microwave assisted reactions

Microwave assisted reactions were performed in a Milestone MicroSYNTH „NP” Ethos 1600 microwave oven under atmospheric pressure (Table 4).

Table 4. Controllable microwave program for liquefaction process

Fixed temperature, °C	Step	Irradiation time <i>t</i> , min	Ramp and hold temperatures, °C	Maximum MW power Watt
120	1	3	120	up to 500
	2	2	120	up to 300

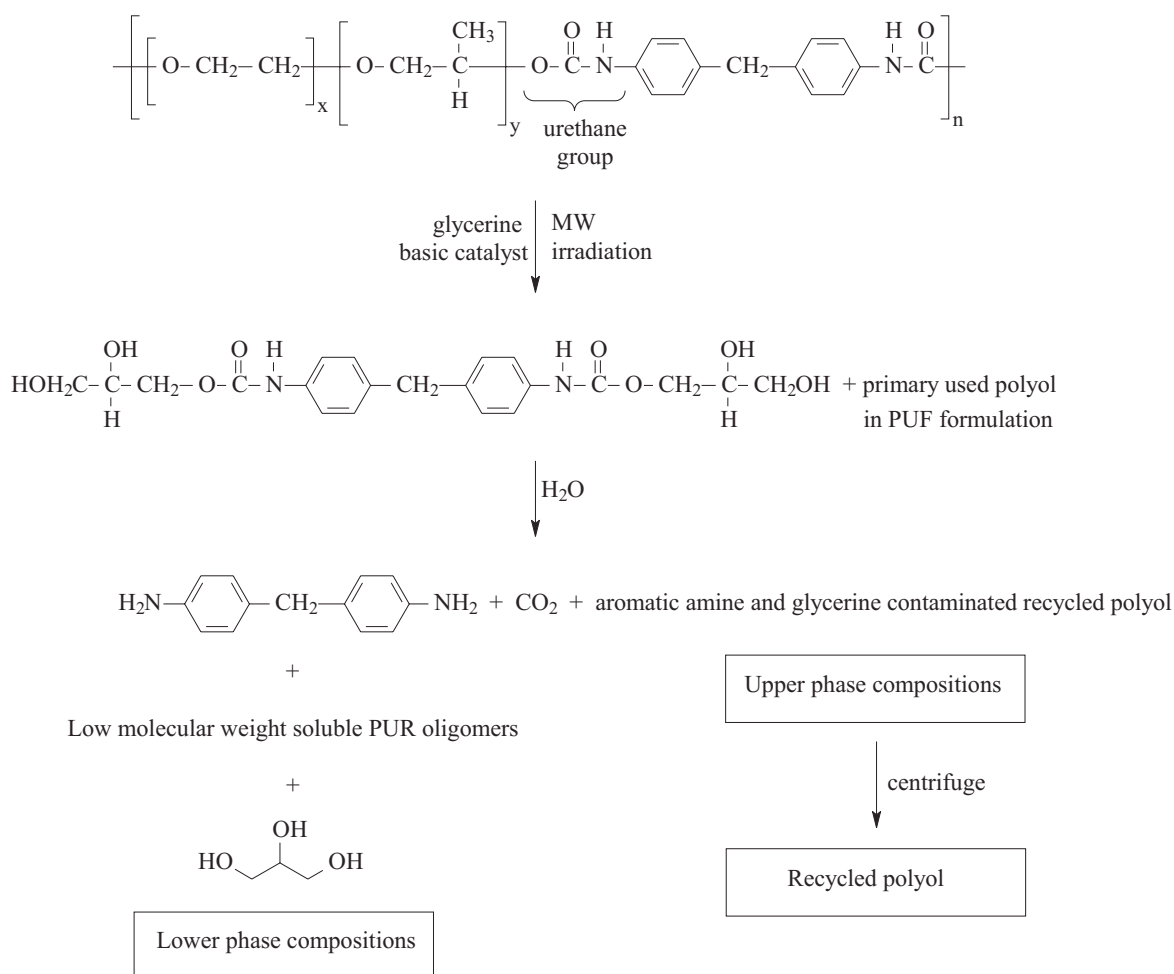
General procedure for MW assisted PUF recycling

For recycling process, the scraps of flexible PUR foam (5 g) (cut into small pieces), NaOH (1 % w/w) in the pre-

sence of solvent mixtures composed of glycerol 95 %, sorbitol 3.5 % and water 1.5 % and poured into a two necked flask. The total amounts of the destroying solvent fixed in 5 g according to our report [1]. The mixture put into the microwave oven at atmospheric pressure and irradiated at 180 °C and 800 W. After the foam digestion was completed, the mixture was removed from microwave oven and left to separate into two distinguishable phases. The upper phase (recycled polyol) was decanted carefully and centrifuged for 20 min and then characterized by spectroscopy methods and data were compared with basic sample data [1].

In all recycling procedures studied here, „split-phases” were formed and the upper phase has been used as a portion of polyol in the PUFs formulation. The polyol chemical structure has been explained in our previously published paper and it was determined as poly(ethylene-propylene) oxide copolymer [4]. Scheme A shows the recycling process and formation of lower and upper phases.

As the aim of this work is the evaluation of the recycled polyol efficiency in obtaining of the new starch based polyurethanes, then in order to achieve the adequate results the upper phase has been used directly in combination with other components and used as the



Scheme A. MW assisted PUFs recycling process and formation of two phases

Table 5. Components ratios and reactivity factors of prepared polyurethane foams

Component	Sample					
	SPUF1	SPUF2	SPUF3	SPUF4	SPUF5	SPUF6
Virgin polyol, g	75	70	60	50	40	30
Starch solution, g	25	25	25	25	25	25
Recycled polyol, g	0	5	15	25	35	45
MDI, g	100	100	100	100	100	100
Cream time, s	2.9	3.0	3.4	3.7	4.0	4.8
String time, s	42	43	48	54	70	72
End of rise, s	65	64	73	72	84	113
Tack free time, s	65	64	73	72	86	115

polyol component to obtain rigid PUFs as shown in the Table 5. The recycled polyol was first identified structurally with spectroscopy methods namely, ^1H NMR, ^{13}C NMR and FT-IR and data compared to a basic sample and our previous results and we found that the data fully match the report [1]. The results from hydroxyl number determination of the recycled polyol showed it higher than virgin polyol OH value (59 mg KOH/g). This phenomenon occurs due to partial solubility of glycerine and/or sorbitol in the upper phase what is important in increasing of OH content in the recycled polyol. The hydroxyl values for the recycled polyols were determined as 73 and 64 before and after centrifuging, respectively.

Another important property, directly affecting the final foam properties, is water content in the recycled polyol, which was determined as 1.80 ± 0.1 %. Determined water level in the recycled polyol was less than water content in virgin polyol, what applied to preparation of final rigid foams (see Table 3).

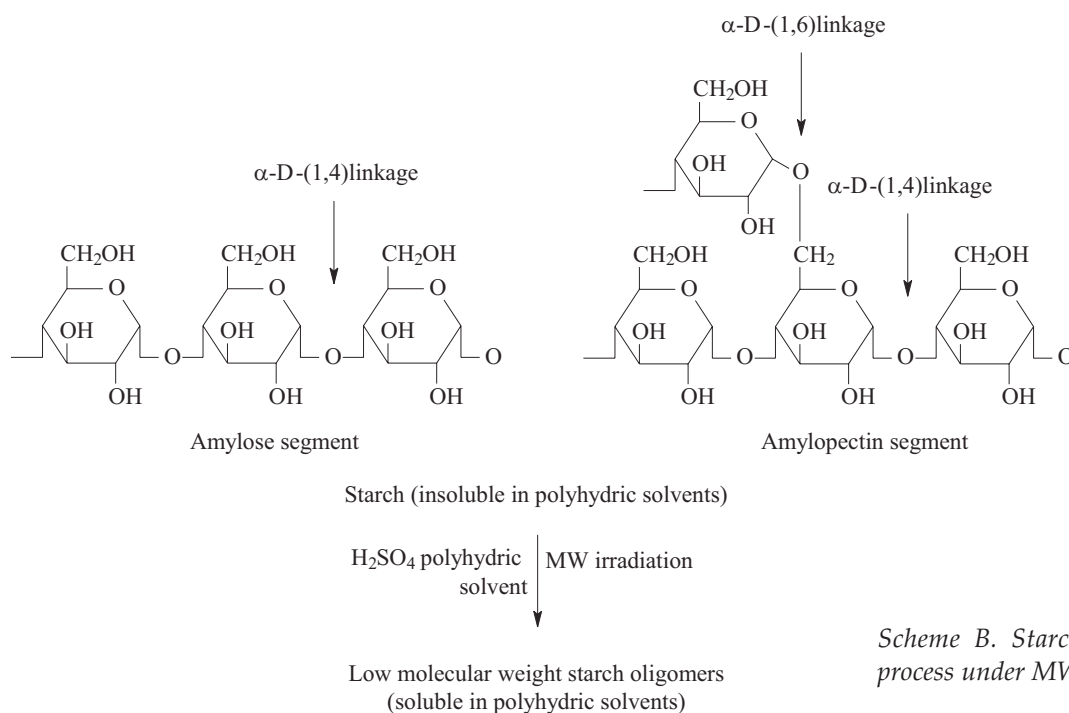
General procedure for MW assisted starch liquefaction

Green solvents namely DEG (diethylene glycol) and glycerin and/or blends thereof, catalyst and powdered starch mixtures in various ratios were irradiated in MW oven under controlled conditions as shown in the Table 6. In addition, Scheme B shows the chemical formula of starch as well as the liquefaction process under MW irradiation. As shown in the scheme, starch containing two main components namely, amylose and amylopectin liquefied under acidic condition by their main chain scissions. After completion of the liquefaction reaction, the hydroxyl number of liquefied starch was determined as 430 ± 20 and the water content as 0.55 %, respectively.

Thermogravimetric analysis (TGA) was performed with Perkin-Elmer Pyris Diamond TG/DTA, at heating rate of $20\text{ }^\circ\text{C}/\text{min}$ under N_2 atmosphere. Foam samples were prepared in paper cup by hand mixing.

Table 6. Collected data on starch liquefaction under MW irradiation

Entry	DEG, g	Glycerin, g	Starch powder, g	Sulfuric acid 20 %, g	Results
1	70	0	30	0	after 150 s of irradiation, a clear solution formed but after cooling the starch agglomerations observed: unsuccessful liquefaction
2	70	0	30	0.7	after 120 s of irradiation, very low viscous and slightly yellowish and clear solution formed which was stable after cooling: successful liquefaction
3	70	0	30	2.1	after 100 s of irradiation, a high viscous and dark green solution formed: liquefaction combined with degradation
4	0	70	30	0	after 160 s of irradiation, the starch agglomerations was observed even in hot solution: unsuccessful liquefaction
5	0	70	30	0.7	after 130 s of irradiation, very low viscous and clear yellow solution observed which was stable in cold form: successful liquefaction
6	0	70	30	2.1	after 130 s of irradiation, a dark green solution formed: liquefaction combined with degradation
7	56	14	30	1	after 120 s of irradiation, a yellowish stable clear solution appeared. The viscosity is similar to viscosity of virgin polyol: successful liquefaction
8	56	14	30	1.5	after 120 s of irradiation, a dark green high viscous solution formed: liquefaction combined with degradation



RESULTS AND DISCUSSIONS

Microwave irradiation program for starch liquefaction

DEG and glycerin and mixtures thereof were used as liquefaction solvents and the reactions were studied under acid catalyzed and uncatalyzed conditions. In addition and in order to investigate solvents roles in the liquefaction of starch, all experiments were done under controlled MW conditions and data were collected in Table 4.

As shown in the table, in the first step, all samples were irradiated under scanned MW power up to 500 W for 3 minutes and the bulk temperature was held at 120 °C. Liquefaction process continued at MW power decreased to 300 W in the second step and at the bulk temperature 120 °C. Liquefaction process was monitored visually and formation of clear solution was the criterion for the process completion. Detailed data are collected in Table 5.

Results in the table show the unsuccessful liquefactions in uncatalyzed reactions. In addition, the data show the performance of acidic media in breaking down of starch molecules and the conversion of high molecular weight starch polymers to corresponding oligomers (Scheme B). In the meantime, in the uncatalyzed reactions, dispersing of starch molecules takes place in solvent media and starch particles precipitated during cooling (entries 1 and 4).

The performances of an acid catalyst and MW irradiations have significant effect on liquefaction as well as chain breaking of the starch. As it was shown in the table, under intensive conditions, chain breaking reactions combined by the over oxidation reactions (entries 3, 6, 8). In other words, in entries 2, 5 and 7 the liquefaction process was performed without an over oxidation reaction and denoted as successful liquefaction process. Among the successful

liquefaction reactions, entry 7 is considered as the convenient condition in this study due to formation of a stable media and reaching the viscosity of the virgin polyol and further studies have been performed on this solution.

Starch based polyurethane foam preparation and reactivity factors determinations

All samples were prepared by hand mixing at weight ratios presented in Table 6 and well known Cup test were performed to determine the reactivity factors. Sample SPUF1 (Smeans starch) was mentioned as the blank sample and data were compared to other samples data. As the reactivity factors have significant effects on foam producing technology and affect the operational and reaction injection molding (RIM) conditions as well as the final foam properties, we focused our studies on determining the factors. As shown in Table 6, the starch solution ratios were considered constant in all formulations and the recycled polyol portion varied slightly in order to studying reactivity factors. By increasing the amount of recycled polyol, reaction times are increased due to decreased concentrations of the additives in the formulated virgin polyol. All samples have stable dimension after 24 h foam formation, they have no holes or any apparent shrinkages. In the meantime, during foam formation, exothermic destructive reactions were not observed which reveals the performance of starch based polyol in the new foam formulation.

Density determination

Density tests were performed for all sample foams by cutting the samples from inside and data are collected in Table 7.

Table 7. Densities of starch based PUFs

Sample	Density (kg/m ³)
SPUF1	40.3
SPUF2	41.4
SPUF3	42.8
SPUF4	50.5
SPUF5	63.6
SPUF6	63.8

As shown in Table 7, densities are increased in samples SPUF4 to SPUF6 due to increase of recycled polyol content in the foam formulations. Due to slight solubility of destroying agents in the upper phase, higher hydroxyl number is expected in comparison with virgin polyol. The formulated foams were denser when the recycled polyol content was increased in the formulation (comparison of SPUF1–6 samples) and the formulated foams are denser in comparison with prepared foams with liquefied starch/virgin polyol blended with small recycled polyols portions.

Thermogravimetric analysis (TGA)

Thermal behaviors of prepared foams were studied in order to find the effects of starch and recycled polyol on thermal resistivity of the foams. In this study, a blank sample PUF obtained exclusively from commercially available polyol and isocyanate was considered and other foams data were compared with blank sample data. $T_{d,10\%}$ and $T_{d,80\%}$ were found as the target 10 % and 80 % weight loss temperatures, respectively, and results are shown in Table 8. As can be seen in the table, the highest thermal resistance has the sample containing 45 % of recycled polyol (SPUF6). Increase in the content of the recycled polyol over 45 % results in collapse of the foam and an the foaming process fails to complete. This phenomenon is expected due to insufficient content of foaming agent in the sample which decreases in concentration by increasing of recycled polyol ratios. As our goal was the studying of the performance of liquefied starch and recycled polyol without any additions of additives, this point is achieved as a boundary condition in recycled polyol content.

Table 8. TGA weight losses data for starch based PUFs

Sample	$T_{d,10\%}$	$T_{d,80\%}$
Blank	225	483
SPUF1	200	478
SPUF2	233	490
SPUF3	225	455
SPUF4	233	600
SPUF6	252	640

CONCLUSIONS

MW irradiation has a significantly decreases of starch liquefaction as well as polyurethane foam chemical recycling reaction times. Liquefied starch/recycled polyol and virgin polyol compositions were stable without any phase separations. Foams prepared from liquefied starch and recycled polyols showed superior properties concerning thermal resistivity in comparison with prepared foam from commercially available raw materials. The presence of an inorganic acid is necessary in starch chain session and high acid concentration affects the liquefaction time in combination with undesired over oxidation reactions.

The methodology can be regarded as a novel way to produce toward biobased polyurethane foams which has merits such as short liquefaction time; using green solvent namely glycerin and applying MW technique as a clean heating source.

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