Research paper

Synthesis of bio-based polyurethane foams with liquefied wheat straw: Process optimization

Hongwei Li[a,b], Chunbao (Charles) Xu[b,*], Zhongshun Yuan[b], Qin Wei[a,**]

[a] *College of Forestry, Northwest A&F University, Yangling, Shaanxi, 712100, China*
[b] *Institute for Chemicals and Fuels from Alternative Resources (ICFAR), Western University, London, Ontario, N6A 5B9, Canada*

ARTICLE INFO

ABSTRACT

Bio-based polyurethane (BPU) foams were successfully prepared using hydrothermally liquefied wheat straw (WS) to substitute a mass fraction of up to 50% of polyols. Response surface methodology (RSM) based on central composite design (CCD) was employed to optimize four process parameters: NCO/OH molar ratio, loading of crosslinking agent (glycerol), loading of catalyst (a mixture of triethylene diamine, stannous octoate, and triethanolamine), and loading of blowing agent (water) for the maximum compression strength of the rigid BPU foams. With the quadratic orthogonal regression model, verified by experimentation, the maximum compression strength of approximately 180 kPa was obtained at the following optimal conditions: NCO/OH molar ratio of 1.24:1, glycerol addition of 12.11%, catalyst loading of 0.76%, and blowing agent addition of 1.31% in relation to the total mass of polyols. The BPU foam prepared at the optimal conditions exhibits good thermal conductivity $(0.045 \, Wm^{-1}K^{-1})$ and thermal stability, comparable to those of a reference foam prepared with 100% PPG400.

1. Introduction

Polyurethane (PU) foams are widely used as bedding, packaging, cushion, flotation, automotive parts and insulation materials [1–3]. However, the PU industry is heavily dependent on petroleum chemicals because PU synthesis involves two major component materials (i.e., polyols and isocyanates) currently both derived from non-renewable petroleum resources. The growing bioeconomy has intensified the interest of the PU industry in developing bio-based PU (BPU) foams using bio-polyols derived from renewable agricultural and forestry resources. BPU foams preparation with renewable resources such as liquefied soybean straw [4], cornstalk [5,6], wheat straw [7,8], waste paper [9], bark and starch [1,10], avocado seeds [11], bagasse [12] and lignin [13,14] have been reported. These studies mainly focused on the properties of the prepared BPU foams, feasibility of making BPU foams, and reaction mechanism of BPU foaming.

In our earlier studies, wheat straw was liquefied in an ethanol-water mixed solvent with a base catalyst. The liquefied wheat straw was subsequently used as bio-polyols for the preparation of BPU foams [7]. However, the process parameters including NCO/OH molar ratio, addition amounts of blowing agents, catalysts (a mixture of triethylene diamine, stannous octoate, and triethanolamine), and crosslinking agents, have not been optimized to achieve the best mechanical/

thermal properties, and network structure of the BPU foams and to minimize the foams production costs. To the best of the authors' knowledge, optimization of process parameters for preparation of BPU foams using liquefied wheat straw as a bio-polyol has not been reported.

Response surface methodology (RSM), is a widely used and effective statistical technique to optimize complicated processes [15], such as bio-oils production from various biomasses [16–18], extraction of specific compounds [19–21], and synthesis of bio-polymers [22,23]. In this work, a central composite design (CCD) of RSM was employed to optimize the process parameters for BPU foams preparation to maximize the compression strength of the foam samples. The key BPU foaming parameters selected for process optimization in this study are: NCO/OH molar ratio, and addition amounts of crosslinking agent (glycerol), foaming and blowing agent (water).

2. Materials and methods

2.1. Materials

Wheat straw (WS) was harvested and baled in 2016 on a local farm in London, Ontario. After storing for six months at ambient conditions on the farm, the WS was milled into particles (20 mesh) in our lab and

Table 1
Physical properties of all chemicals used in the PU foams preparation.

Ingredients	Functionality	Equivalent weight (g/mol)	Hydroxyl number (mgKOH/g)	Comments
PMDI	2.7	135.0	–	NCO content of 31.2%
PPG400	2.0	200.0	280.5	Petroleum polyol
Glycerol	3.0	30.7	1829.4	Crosslinking agent
Poly(Siloxane ether)	–	–	–	Silicon surfactant
Triethanolamine	3.0	49.73	1128.1	Co-catalyst
Triethylene diamine	–	–	–	Foaming catalyst
Stannous octoate	–	–	–	Gelling catalyst
Water	2.0	9.0	6233.3	Chemical blowing agent

oven-dried at 105 °C for 24 h before using for the liquefaction processes. The WS used contains cellulose, hemicellulose, lignin and ash at a mass fraction of 41.3%, 30.7%, 20.7% and 7.3%, respectively, determined by the Ververis' method [24]. Other chemicals including alcohols (methanol and ethanol), sodium hydroxide, acetone, polypropylene glycol PPG400, polymeric diphenylmethane diisocyanate (PMDI, with weight-average molecular weight, M_w, of 364.5 g/mol), catatysts (triethanolamine, triethylene diamine, and stannous octoate), surfactant, are all CAS reagent grade chemicals, purchased from Sigma-Aldrich. Physical properties of the all chemicals used for the preparation of PU foams are presented in Table 1.

2.2. WS liquefaction

Dried WS particles, was mixed in a solvent of ethanol-water or methanol-water (with a volume ratio of 50 cm^3–50 cm^3) and 15% sodium hydroxide (in relation to WS mass) in a 100 cm^3 autoclave reactor. The reactor was then sealed, and heated to the specific temperature at approx. 283 K/min after being vacuum-purged with N_2 for 3 times. The mixture was soaked at the temperature for desired residence time under stirring. Finally, the reactor was quenched in an ice-water bath. The reactor contents were washed using acetone into a beaker after venting the gasses inside the reactor in a fume hood (the formation of gaseous products mainly CO_2 was negligible). The liquefied products in acetone were filtered to separate solid residue, and the filtrate was evaporated in a rotary evaporator at reduced pressure to completely remove the organic solvents (alcohol and acetone) and water. The resultant viscous liquid products were designated as bio-polyols (BP), and yield was approx. 70%–75% determined gravimetrically, as reported previously [7].

The hydroxyl number of the BP was measured in accordance with the ASTM D 4274-99 standard, and the viscosity with Brookfield CAP 2000 + Viscometer at 323 K. The weight-average molecular weight (M_w) of the BP was determined with a Waters Breeze gel permeation chromatograph (GPC) (1525 binary pump; UV detector at 270 nm; Waters Styrylgel HR1 column (300 mm × 7.8 mm × 5 μm) at 313 K) with tetrahydrofuran (THF) as the eluent at a flow rate of 1 cm^3/min. The GPC instrument was calibrated using five polystyrene standards with the weight-average molecular weight (M_w) of 1000 g/mol, 2500 g/mol, 5000 g/mol, 11000 g/mol and 17000 g/mol, respectively. The concentration of the standards was 20 mg/cm^3 with the injection volume of 15 mm^3.

2.3. Preparation and characterization of BPU foams

The BP was used to substitute a mass fraction of 50% of petroleum-based polyol (PPG400) in the preparation of bio-based PU (BPU) foams. The isocyanate index (NCO/OH) was calculated using the following equation:

$$NCO/OH = \frac{P_{NCO} \times 1000 \times W_{NCO}}{42 \times \left(\sum \frac{M_{OH} \times W_{OH}}{56.1} + \sum \frac{M_{Ad} \times W_{Ad}}{56.1} + \frac{M_{H2O} \times W_{H2O}}{56.1} \right)} \quad (1)$$

Where, P_{NCO} is the mass fraction (in %) of NCO in the isocyanate, 1000

is the unit conversion factor, 42 is the molecular mass of NCO, M_{OH} is the hydroxyl number of polyols (the BP or PPG400), M_{Ad} is the hydroxyl number of the additives (the co-catalyst and crosslinking agent), M_{H2O} is the hydroxyl number of water, 56.1 is the molecular weight of KOH, W_{NCO}, W_{OH}, W_{Ad} and W_{H2O} is the mass (g) of isocyanate, polyol, additives and water, respectively.

BPU foam was prepared in a plastic cup (455 cm^3) using the one-shot method. In addition to polyols, the foaming formulation also includes glycerol as a cross-linking agent at a mass fraction from 7.5% to 17.5%, catalysts (including triethylenediamine, stannous octoate, and triethanolamine) at a mass fraction from 0.25% to 1.25%, silicon oil as a surfactant at a mass fraction of 2%, and water as a blowing agent at a mass fraction from 0.75% to 1.75%, all in relation to the total mass of polyols. PMDI was added at an NCO/OH ratio of 1.15–1.35.

The foaming procedure included the following steps (1) weighing specific amounts of the ingredients (i.e., polyols, catalysts, surfactant and blowing agent): into a plastic cup, followed by 9.2 Hz mechanical stirring for 12–15 s to achieve a homogeneous mixture, (2) adding desired amount of PMDI into the mixture and stirring vigorously for 10–12 s at ambient temperature (296 K ± 2 K), and (3) placing the mixture in a fume hood, where the foaming started owing to the exothermic reaction between the blowing agent (H_2O) and isocyanate. All foams were left in the fume hood for 24 h–48 h for further curing prior to analysis. The foam appearance (i.e., shrinkage, and cell structural uniformity), foaming (cream and free rise) times, and stability were observed. Prior to further characterization, all foam samples were conditioned at ambiin the fume hood for at least 7 days, depending on the sample testing requirements.

2.4. Experimental design

The parameters that affect compression strength of rigid BPU foams were studied using a standard RSM design based on central composite design (CCD) for one response, i.e., the compression strength of the prepared foam sample. Four key process parameters, i.e., the addition amounts (mass fraction in relation to the total mass of polyols) of glycerol, catalysts, blowing agent (water), and NCO/OH molar ratio, were chosen in this RSM study, each at five levels (shown in Table 2): two star levels, two factorial levels, and one center lever. The value ranges for the four parameters were chosen based on our previous studies: 7.5%-17.5% glycerol addition, 0.25%-1.25% catalyst loading, and

Table 2
Independent variables and levels used for the CCD.

Variable	Symbol	Coded factor levels				
		−2 (α)	−1	0	1	2 (α)
Glycerol addition (%)[a]	A	7.5	10	12.5	15	17.5
Catalyst loading (%)[a]	B	0.25	0.5	0.75	1.0	1.25
Water amount (%)[a]	C	0.75	1.0	1.25	1.5	1.75
NCO/OH molar ratio (−)	D	1.15	1.2	1.25	1.3	1.35

[a] Mass fraction in relation to the total mass of polyols.