

## Biodegradability of crude glycerol-based polyurethane foams during composting, anaerobic digestion and soil incubation



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### ABSTRACT

In this study, the biodegradability of polyurethane (PU) foams made from crude glycerol- and petroleum-based polyols was compared during composting, anaerobic digestion (AD), and soil incubation. Chemical changes in the PU foams before and after composting were further analyzed using Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), Evolved Gas Analysis–Mass Spectrometry (EGA–MS), and Fourier Transform Infrared Spectroscopy (FT-IR). The results showed that during composting, AD, and soil incubation conditions, none of the PU foams were mineralized more than 10%. PU foams made from 100% crude glycerol-based polyols were mineralized during 320 days of soil incubation at rates faster than those observed for the petroleum-based analogs. However, no significant differences in soil mineralization rates were observed between PU foams made from blend polyols, which contained 50% crude glycerol-based polyols and 100% petroleum-based polyols. SEM analysis showed that some surface deterioration occurred in the PU samples made from bio-based and blend polyols during composting. Minor differences were observed in the TGA curves of the PU foams made from petroleum-based polyols before and after composting and pronounced differences occurred in PU foams made from both crude glycerol-based and blend polyols in the thermal regions of urethane and ester segments. In terms of EGA–MS analyses, the major degradation of PU foams made from crude glycerol-based and blend polyols was attributed to the decomposition of FAMES and fatty acid chains in the polyol side of the polymer. FT-IR analysis showed that little degradation of urethane and ester segments of the polymer occurred during composting of petroleum-based PU foam. FT-IR analysis of PU foams made from 100% crude glycerol-based polyols revealed that the ester segments (–COO–) of the material were the preferred sites of microbial attack. The PU foams made from blend polyols showed some structural changes in urethane linkages (–NHCOO–) but degradation was more noticeable in the ester segments (–COO–) of the polymer, similar to that observed for 100% bio-based polyols.

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### 1. Introduction

It is estimated that the polyurethane industry in the U.S. contributes approximately \$59.9 billion to the national economy. Three major sectors where polyurethanes are used are building and construction, transportation, and furniture and bedding [1]. Polyurethane (PU) foams, such as rigid and flexible foams, are one type of widely used PU products that include insulation panels, seating cushions, adhesives, coatings, sealants, etc.

PUs are generally produced by the reaction of two chemical feedstocks; polyols and isocyanates. Nearly all of these feedstocks

are made from petroleum [2]. Global concerns about the availability and rising price of petrochemical-derived products have led to investigations into substitutes that are produced from renewable sources and can meet cost and performance requirements of the market [3]. This represents both challenges and opportunities for renewable-based chemicals to supply this billion dollar industry.

Due to the limited choice of isocyanates, a majority of the research on renewable substitutes used for the production of PUs has focused on the polyol component. Polyols are alcohols containing two or more hydroxyl functional groups. Currently, most bio-based polyols (biopolyols) are produced from lignocellulosic biomass or vegetable oils [4]. Lignocellulosic feedstocks such as cornstalks, wheat straw, and dried distillers grains have been studied for bio-based polyols [5,6]. Vegetable oils including castor oil, soybean oil, and palm oil have also been studied as sources of bio-based polyols [7,8]. Recently, increasing interest has been

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focused on the value-added uses of crude glycerol, a byproduct of biodiesel production and a potential renewable substitute for petroleum-based feedstocks. Several studies have reported the production of crude glycerol-based biopolyols with properties suitable for PU applications [9–11].

While significant achievements in the production of PUs from bio-based polyols have been made [12], there are still numerous uncertainties about the interaction of these polymers with the environment. Understanding the biodegradability of PUs is particularly important since substantial amounts end up in waste management facilities and in natural environments [13]. From an engineering standpoint, biodegradability is desirable for single-use and short lifespan applications, such as packaging materials, but are undesirable for long lifespan applications, such as automotive and construction uses [14]. From an environmental standpoint, the potential biodegradability of products and their interaction with the environment need to be understood in addition to the material's life cycle [15].

Biodegradation is the transformation of materials as a result of the action of naturally-occurring microorganisms such as bacteria and fungi [16]. The biodegradation of PUs is limited by many factors including chemical properties of the polymer such as chemical structure, cross-linking density, crystallinity, and the fact that most plastics are xenobiotic [17]. Microbially-induced deterioration of the urethane bonds in PUs has been reported to be influenced by the polyol type, i.e. polyether or polyester polyols [18]. PUs made from polyether polyols have been found to be relatively resistant to microbial degradation, whereas the polyester analogs are reported to be more vulnerable to biodegradation processes [19]. Differences in biodegradation rates have been attributed to the degradation mechanism in which endo- and exo-type enzymatic depolymerization pathways are undergone for polyester and polyether PUs, respectively [18]. In polyesters, microbial degradation has been postulated to occur mainly due to the hydrolysis of the ester bonds by membrane-bound and extra-cellular polyurethanases [20].

Research has been conducted to evaluate the biodegradability of PUs made from vegetable oil-based and liquefied biomass-based polyols. Wang et al. [21] studied the biodegradability of PU foams made from castor oil-derived polyols by measuring weight loss during soil incubation and reported reductions ranging between 10 and 40% in a 4-month period. In addition, microbial deterioration of PUs made from castor oil has been reported to occur in the ester bonds of the polymer [8]. Shogren et al. [22] reported that PUs made from different vegetable oil-based polyols with hydrolyzable bonds such as esters were biodegradable to an appreciable extent. In studies conducted by Zhang et al. [23], 16% mass loss in a 12-month period during soil burial experiments was reported and the hydrolysis of the ester and urethane bonds due to microbial activity in PUs made from liquefied wood-based polyols was observed. Weight losses ranging between 6 and 14% after 6 months of soil incubation were reported for PUs produced from liquefied waste paper [24] and wheat straw [25] and were attributed to the degradation of the biomass portion of the polymers.

Studies on the biodegradation of PUs produced from crude glycerol-based polyols have not been reported. More research needs to be conducted to understand the extent to which PUs made from crude glycerol-based polyols will biodegrade in different waste management scenarios, such as composting, anaerobic digestion (AD) or natural settings. The objective of this study was to compare the relative biodegradability of PU foams produced from petroleum- and crude glycerol-based polyols under composting, AD, and soil conditions. The hypothesis of this research is that PU foams made from polyols with higher bio-based content are chemically different and will biodegrade to a greater extent than their petroleum-based analogs.

## 2. Materials and methods

### 2.1. Materials

Petroleum-based (Stepanpol®) and bio-based (crude glycerol-derived) polyester polyols were provided by Bio100 Technologies, LLC. (Mansfield, OH, U.S.). Bio-based polyol is produced via a thermochemical conversion of crude glycerol. It is commonly composed of glycerol, monoglycerides, diglycerides, and unreacted fatty acid methyl esters [11]. Chemical properties of the polyols are shown in Table 1. Polycat 5, Polycat 8, and DABCO DC5357 used in PU foaming were obtained from Air Products & Chemicals, Inc. (Allentown, PA, U.S.). Polymeric methylene-4,4'-diphenyl diisocyanate (pMDI) was obtained from Bayer Material Science (Pittsburgh, PA, U.S.). Three types of PU foams were prepared from petroleum-based, bio-based, and their blend polyols (50/50, w/w) via their polyaddition reaction with pMDI (Scheme 1) following a commonly used formula [26] and ASTM D7487-08.

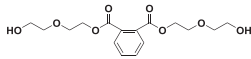
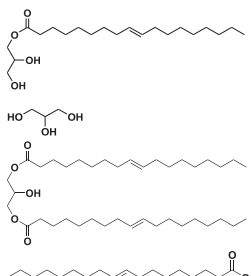
PU foams were cut in 10 × 10 mm squares with an average thickness of 2.1 ± 0.4 mm for composting, AD, and soil incubation tests. Physical and chemical properties of the foams are shown in Table 2. Cellulose paper (Fisher Scientific, PA, U.S.) was used as the positive control for all experiments.

### 2.2. Biodegradation of polyurethane foams

Laboratory-scale experiments were conducted to measure the relative biodegradability of PU foams during soil incubation, composting, and AD.

Experiments to determine the biodegradability of PU foams in soil were conducted using an assay based on a standard protocol (ASTM D5988-03). A more complete description of the methodology to study the mineralization of polymeric materials in soil can be found elsewhere [27]. The soil media used for the experiments was a mixture of 43% certified organic top soil, 43% no-till farm soil, and 14% sand. The chemical properties of the soil mixture are shown in Table 3. The soil media was amended with ammonium phosphate

**Table 1**  
Properties of the petroleum- and bio-based polyols used to produce the PU foams samples.

Polyol	Major components	Acid number <sup>b</sup> (mg KOH/g <sub>sample</sub> )	Hydroxyl number <sup>b</sup> (mg KOH/ g <sub>sample</sub> )
Petroleum-based		2.5 ± 1	315 ± 4
Bio-based		5.0 ± 1	524 ± 7

<sup>a</sup> Oleic acid is used as a representative fatty acid in crude glycerol.

<sup>b</sup> The acid and hydroxyl numbers were determined in accordance with ASTM D4662-08 and ASTM D4274-05D, respectively. Values are means ± standard deviation of three determinations.

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