Value-added Conversion of Waste Cooking Oil, Post-consumer PET Bottles and Soybean Meal into Biodiesel and Polyurethane Products

THESIS

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Abstract

Biodiesel is an environmentally friendly alternative to petroleum diesel. It is biodegradable, nontoxic and has lower greenhouse gas emission profiles compared to petroleum diesel. Polyurethane (PU) products such as PU foams and PU coatings are widely used in many aspects of our life. Traditionally, the PU industry is heavily petroleum dependent because both the feedstocks - isocyanates and polyols - are petrochemical products. Bio-based PU products became a very promising research field due to concerns about the environment and the depletion of petroleum resources.

Waste cooking oil (WCO), which is abundantly available and about 2 or 3 times cheaper than virgin vegetable oil, is considered a good source for production of biodiesel. Also, post-consumer PET bottles contribute a large volume fraction in the solid waste stream and their non-biodegradability has caused concern. In this study, a sustainable process of value-added utilization of wastes, specifically WCO and post-consumer PET bottles for the production of biodiesel and PU foams, respectively, was developed. WCO collected from campus cafeteria was firstly converted into biodiesel, which can be used as vehicle fuel. Then crude glycerol (CG), a byproduct of the above biodiesel process, was incorporated into the glycolysis process of post-consumer PET bottles collected from campus to produce polyols. Thirdly, PU foams were synthesized through the reaction of the above produced polyols with isocyanate in the presence of catalysts and other additives. The characterization of the produced biodiesel demonstrated that its properties
meet the specification of the biodiesel standard. The effect of CG loading on the properties of polyols and PU foams were investigated. With the increase of CG loading from 0% -15%, the hydroxyl value increased from 478 mg KOH/g to 592 mg KOH/g. This is most likely due to the high hydroxyl value of glycerol (1829 mg KOH/g). The PU foams produced showed density of 46.03-47.66 kg/m³ and compressive strength of 235.9 to 299.9 kPa, which are comparable to some petroleum-based analogs. A mass balance and a cost analysis for the conversion of WCO and waste PET into biodiesel and PU foams indicate potential economic viability of the developed process.

Soybean meal (SM) is the soy protein residue after the extraction of oil from soybeans. With its high protein content, SM has the potential to become one of the feedstocks for PU production. In this study, a novel way was developed to produce UV-curable PU acrylate coatings from SM. High oleic SM was hydrolyzed by dilute acid to amino acid oligomers, then a hydroxyl-terminated PU oligomer was synthesized through a non-isocyanate pathway: i) amination of the amino acid oligomers with ethylene diamine to produce amino-terminated compound; ii) amidation of the amino-terminated compound was reacted with ethylene carbonate. Functionalization of hydroxyl-terminated PU oligomers was achieved by esterification and acrylation reactions to produce PU acrylate oligomers. PU acrylate oligomers were then formulated with multifunctional monomer and photo initiator to form a PU coating under UV light. The PU oligomer after esterification showed a hydroxyl value of 223 mg KOH/g and viscosity around 6.1 Pa·s at 10.9 1/s shear rate. The UV-cured coating showed higher tensile strength (approximately 18.2 MPa) and modulus (approximately 450.1 MPa), and
lower elongation at break (approximately 4.5%) compared to other PU acrylate coatings reported in literature, which might due to hydrogen bonding between amino acid and urethane bond and enhanced cross-linking density with the incorporation of oleic acid in esterification reaction.

In summary, the value-added conversion of WCO, post-consumer PET bottles and SM into Biodiesel and PU products (i.e. PU foams and coatings) have been successfully developed in this study. All the parameters of biodiesel produced from WCO meet the requirements in the ASTM D6751 standard. The PU foams showed good compressive strength and insulation properties and have potential application as construction materials. The PU coatings also showed promising mechanical properties and good thermal stability.
This document is dedicated to my family.
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Chapter 1: Introduction

1.1 Background

Biodiesel is a promising alternative to fossil fuels. The production of biodiesel involves a transesterification reaction of renewable feedstocks, such as vegetable oils and animal fat, with alcohol. It is biodegradable and nontoxic, and has lower greenhouse gas emissions than petroleum diesel, so is environmentally beneficial (Ma and Hanna, 1999). The limitations to extensive commercialization of biodiesel are high manufacturing cost and competition for vegetable oil with food consumption. Waste cooking oil (WCO), which is abundantly available and about 2.5-3.0 times cheaper than virgin vegetable oils (Demirbas, 2009), can considerably reduce biodiesel production cost. It is estimated that an average of 10 kilograms of total waste grease per person are produced annually in the U.S. (Wiltsee, 1998).

Crude glycerol (CG) is a major byproduct generated during biodiesel production. Basically, the production of every 10 kg of biodiesel yields approximately 1 kg of CG (Kongjao et al., 2010). Depending on the feedstock, the process and the post-treatment methods used, CG contains various impurities such as free fatty acids (FFAs), alcohols, water, salts, and soap and has a low value (approximately $0.11/kg) (Johnson and Taconi, 2007). The refining of CG to pure glycerol is an important value-added processing step because glycerol is a versatile platform chemical in the industries of foods and beverages,
pharmaceuticals, cosmetics, textiles, etc. However, refining processes are costly (approximately $0.44/kg (Werpy et al., 2004)), especially for small- and medium-sized biodiesel plants (Pachauri and He, 2006). CG has become a potential financial and environmental liability for biodiesel producers (Johnson and Taconi, 2007). Many studies have been conducted to develop both chemical and biological processes for value-added conversion of CG (Johnson and Taconi, 2007; Pachauri and He, 2006; Pagliaro et al., 2007; Yang et al., 2012). Examples of products derived from CG include: 1,3-propanediol (Mu et al., 2006; Oh et al., 2008), citric acid (Rywińska and Rymowicz, 2010), hydrogen (Sabourin-Provost and Hallenbeck, 2009), poly(hydroxyalkanoates) (Mothes et al., 2007), succinic acid (Scholten et al., 2009), polyols, and polyurethane (PU) foams (Hu et al., 2012; Luo et al., 2013). Poly (ethylene terephthalate) (PET) is a semi-crystalline thermoplastic material widely used in the manufacture of fibers, films and food packaging materials-mainly bottles. Although waste PET materials do not create a direct hazard to the environment, its substantial fraction by volume in the waste stream and its high resistance to atmospheric and biological agents has led to concerns over its environmental pollution (Paszun and Spychaj, 1997; Sinha et al., 2010). Recycling and reprocessing PET can serve as a way to reduce solid waste and also contribute to the conservation of raw petrochemical products and energy. Chemical recycling is one of the most attractive techniques of recycling PET waste as it can depolymerize PET to generate feedstocks for the production of highly valuable polymers (Sinha et al., 2010). Chemical recycling of PET can be divided by the type of chemical agents used: hydrolysis of PET is carried out in alkaline solution or
concentrated acid (Paszun and Spychaj, 1997); glycolysis of PET is carried out in glycols, most frequently ethylene glycol (Baliga and Wong, 1989), diethylene glycol (Pardal and Tersac, 2006), propylene glycol (Vaidya and Nadkarni, 1987) or dipropylene glycol (Vaidya and Nadkarni, 1988); methanolysis of PET is carried out in methanol (Kishimoto et al., 1999; Yang et al., 2002).

Soybeans are widely grown as an industrial crop cultivated for oil and protein. Soybeans account for 55% global oilseed production and 90% U.S. oilseed production (Cromwell, 2011). In the U.S., about 70% of soybean oil goes to human consumption; about 22% goes to the production of biodiesel, and the remainder to other uses, including the production of coatings, inks, lubricants, soy polyols and other industrial products.

Soybean meal (SM) is the soy protein residue after oil extraction, for each ton of crude soybean oil, about 4.5 tons of SM is produced (Watchararuji et al., 2008). SM has long been considered an excellent supplemental protein source in diets for livestock and poultry because of its high content (44% to 49%) of digestible protein. Recently, soy-based plastics, adhesives, films and coatings are being considered in agricultural equipment, marine infrastructure, automobiles and civil engineering (Kumar et al., 2002). However, the low mechanical properties and weak water resistance of soy protein has hindered expansion of its industrial use. Nowadays, most SM is used as animal feed (96.49%), and only a small portion (3.29%) is refined to flour, concentrates or isolates suitable for human consumption, and an even smaller amount (0.22%) of SM is used in industrial applications, such as fibers, adhesives, and paper coatings (United Soybean Board, 2015).
PUs are versatile polymeric materials and can be used in many aspects of modern life. Due to the large variety of their isocyanate and polyol feedstocks, PUs can be easily tailored for wide applications, such as foams, coatings, adhesives, constructional materials, fibers, paddings, paints, elastomers and synthetic skins. Traditionally, the PU industry is heavily petroleum dependent because isocyanates and polyols are both petrochemical products. With the growing awareness of the need to find alternatives to petroleum resources, the demand for green or bio-based PUs is increasing. Different renewable feedstocks have been studied for the production of bio-based polyols and PU, including vegetable oils and their derivatives, lignocellulosic biomass, and protein based feedstocks (Li et al., 2015).

In this study, we developed a sustainable process for value-added conversion of WCO and post-consumer PET bottles into biodiesel and PU foams, and a process for the production of UV-cured PU acrylate coatings from SM, respectively. The properties of the produced biodiesel, polyols, PU foams and PU acrylate coatings were evaluated. The effects of CG loading on properties of polyols and the resulting PU foam also were investigated. A mass balance and a cost analysis for the conversion of WCO and waste PET to biodiesel and PU foams are discussed.

1.2 Research hypothesis

The central hypothesis of this study is that CG, post-consumer PET materials and SM can be effectively utilized for the production of polyols and PU products with commercially-acceptable properties and production costs.

1.3 Research objectives
1) Produce biodiesel and PU foams from WCO and post-consumer PET bottles, investigate the effect of CG loading on the properties of polyols and PU foams, conduct mass balance and cost analysis of the whole process. (Chapter 3)

2) Prepare UV-cured PU acrylate coatings from SM and evaluate their mechanical properties and thermal properties. (Chapter 4)
Chapter 2: Literature review

2.1 Introduction

Polyol generally refers to compounds that contain two or more reactive hydroxyl groups in one molecule. Polyols used in polyurethane (PU) manufacture are divided into two groups based on their structure. The first group is monomeric polyols with low molecular weight ($M_w$), such as: propylene glycol, ethylene glycol, dipropylene glycol, diethylene glycol, 1, 4 butanediol, triethanolamine, glycerol, and others. These polyols are often used as chain extenders and crosslinkers in PU production. The second group is polymeric polyols, i.e. polyols that are low $M_w$ polymers with terminal hydroxyl groups. Most common polymeric polyols used in the PU industry are polyether and polyester polyols (Ionescu, 2005). By controlling the functionality of the initiator and the degree of polymerization, a wide range of polyols are commercially available for various types of PU applications. Generally, polyols with high functionality (3.0-8.0), low molecular weight (150-1000 g/mol), and high hydroxyl value (250-1000 mg KOH/g) are used for the production of rigid foams and high performance coatings, while polyols with low functionality (2.0-3.0), higher molecular weight (1000-6500 g/mol), and low hydroxyl value are used for the production of flexible foams and elastomers (Fink, 2005; Szycher, 1999).
Currently, the PU industry is heavily depended on petroleum derivatives, because most commercial polyols and isocyanates are petrochemical products. Recently, concern over the depletion of petroleum has led to the development of bio-based polyols and PUs from renewable sources. Three major sources for producing bio-based polyols include: vegetable oils and their derivatives, lignocellulosic biomass and protein-based feedstocks (Li et al., 2015).

Vegetable oils, such as palm oil, soybean oil, rapeseed oil, and sunflower seed oil, and their derivatives have been widely used for the production of polyols and PUs. The pathways for the production of polyols from vegetable oils are: (1) epoxidation and oxirane ring-opening, (2) hydroformylation and hydrogenation, (3) ozonolysis, (4) thiol-ene coupling, and (5) transesterification/amidation (Li et al., 2015). The polyols and PUs prepared from vegetable oils have comparable properties to petroleum-based analogs. However, polyols and PUs made from vegetable oils and their derivatives still face challenges including technical barriers and high cost. It is also worth noting that the production of polyols and PUs from vegetable oils will compete with food supplies and biodiesel production.

Value-added conversion of biodiesel industry byproducts such as crude glycerol (CG) and soybean meal (SM) into biobased polyols and PU products has the potential to improve the economics of biodiesel production as well as the sustainability of the polyol and PU industry.

2.2 Polyols and PUs from CG

2.2.1 Polyols and PUs from direct conversion of CG
Direct utilization of CG to produce bio-based polyols and PU foams has been reported. Hoong et al. (Hoong et al., 2011) produced polyglycerol from CG. The preferred CG composition from biodiesel industry was: 60 to 90% glycerol, 10 to 25% methanol and 10 to 15% soap. The process steps included (a) thermal dehydration reaction of CG to polyglycerol at 270°C for 3 to 5 hours, soap in CG could act as a catalyst in this step, (b) acidification of the crude product with phosphoric acid at 50-90°C, (c) centrifugation to separate the fatty acid and salt from the product. However, the properties of the polyglycerol produced through this process, such as hydroxyl values, were not tested, and the feasibility of using polyglycerol for the production of PU materials was not investigated. Thermochemical conversion of CG for polyols was also reported (Hu et al., 2015; Li et al., 2014; Luo et al., 2013). The reactions involved in the thermochemical conversion are mainly (1) acidification of soap using sulfuric acid, (2) esterification of glycerol and fatty acids, (3) transesterification of glycerol and fatty acid methyl esters (FAME) (Figure 1) (Li et al., 2015). The reaction parameters, such as sulfuric acid loading, reaction temperature and reaction time, were investigated by Luo et al. (Luo et al., 2013). It was discovered that the preferred reaction conditions for the CG used in the study (composition: 22.9% glycerol, 10.9% methanol, 18.2% water, 26.2% soap, 21.3% FAMEs, 1.0% FFAs, and 1.2% glycerides) were 200°C, 90 min and 3% sulfuric acid loading. Hu et al. (Hu et al., 2015) also investigated the effect of soap content in CG on polyol production. Their study showed that at higher soap levels, FAMEs were converted more rapidly than at low levels due to the intensified emulsifying and/or catalytic effects of soap. However, it is worth noting that high residual soap
content in the polyols is unfavorable for PU production. Therefore, after balancing these two contradictory effects of soap, they concluded that the preferred soap content was 6.6%, and the polyol produced at 190°C and 120 min had low FFA (< 1%) and FAME (ca. 2.5%) contents.

Figure 1 Reactions involved in the thermochemical conversion of CG for the production of polyols (Li et al., 2015)

Polyols produced from CG have been used to make PU foams and waterborne PU coatings. PU foams using polyol produced from CG (acid value 5.02 ± 0.03 mg KOH/g, hydroxyl value 481 ± 10 mg KOH/g) and polymeric methylene-4,4’-diphenyl
diisocyanate (pMDI) (Luo et al., 2013) had a compressive strength of 184.5 kPa and a density of 43.0 kg/m³, both of which are comparable to petroleum based and vegetable oil based analogs (Li et al., 2015; Luo et al., 2013). Waterborne PU coatings derived from CG-based polyols had higher glass transition temperatures ($T_g$) (66-81 ºC) than coatings from soybean oil-based polyl due to higher functionality ($f_n$: 4.7) and higher hydroxyl number (378 mg KOH/g) of the CG-based polyols. The waterborne PU coatings from CG-based polyl also had similar thermal degradation properties as vegetable-oil based PU coatings, excellent adhesion properties and low flexibility (Hu et al., 2015).

2.2.2 Polyols and PUs from CG based liquefaction of lignocellulosic biomass

Lignocellulosic biomass refers to the dry matter in plants, and is the world’s most abundant renewable biomass feedstock. The main structural units in lignocellulosic biomass are carbohydrate polymers (30-35% cellulose, 15-35% hemicellulose), and aromatic polymers (20-35% lignin), all of which are highly functionalized materials rich in hydroxyl groups, making them promising candidate for bio-based polyl production. Currently, polyols from lignocellulosic biomass are mainly produced by two technologies: (1) oxypropylation and (2) liquefaction. The oxypropylation of lignocellulosic biomass is a polymerization process that grafts oligo (propylene oxide) or propylene oxide onto macromolecular structures of lignocellulosic biomass. The reaction often requires KOH as catalyst and is often carried out under high pressure (650-1820 kPa) and high temperature (100-200 ºC) (Evthiougunia et al., 2000; Li et al., 2015). The polyols produced from oxypropylation process is a mixture containing oxypropylated
biomass, polypropylene oxide, and some unreacted or partially oxypropylated biomass, and usually can be directly used in the production of PU materials (Aniceto et al., 2012).

Liquefaction of lignocellulosic biomass is the degradation and decomposition processes of biomass into smaller molecules by polyhydric alcohols via solvolytic reactions. The liquefaction process is often conducted at elevated temperatures (150-250 °C) under atmospheric pressure, and can be either acid- or base-catalyzed. Polyols produced via liquefaction of lignocellulosic biomass are a mixture of different compounds rich in hydroxyl groups and can be used directly in the preparation of PU foams (Yan et al., 2008), adhesives (Juhaaida et al., 2010; Lee and Lin, 2008) and films (Kurimoto et al., 2001).

A variety of lignocellulosic biomasses such as wood, wheat straw, corn bran and cornstalks have been studied for production of polyols by either oxypropylation or liquefaction.

Currently, almost all liquefaction solvents are expensive petroleum-derived polyhydric alcohols, such as polyethylene glycol, ethylene glycol, glycerol and ethylene carbonate. Typically, 5-6.25 g solvent/g biomass is needed to obtain high-quality polyols. Because of its potential to reduce the high cost of solvent and increase the sustainability of the biomass liquefaction process, CG from the biodiesel industry has also been studied as an alternative biomass liquefaction solvent for polyol production. The effects of reaction temperature, reaction time, sulfuric acid loading and biomass loading on the liquefaction process of soybean straw have been evaluated (Hu et al., 2012). With an increase in reaction temperature from 120 to 240 °C, the biomass conversion rate
increased from 15% to 50%, the viscosity of the polyol increased from 36 to higher than 100 Pa·s, the polyol hydroxyl and acid value decreased from approximately 635 to 533 mg KOH/g and from 23 to 2.7 mg KOH/g, respectively. Increasing reaction time from 45 to 360 min increased the biomass conversion ratio from 46% to 75%. The optimal loading of sulfuric acid as catalyst was between 3% and 5%, and optimal biomass loading was between 10% and 15%. This study showed that liquefaction temperature, reaction time, and acid loading had significant effects on the density of the PU foams ($p < 0.05$), while liquefaction temperature, reaction time and biomass loading had significant effects on the compressive strength of the PU foams ($p < 0.05$). Despite the slightly lower biomass liquefaction efficiency, the polyols and PU foams produced exhibited properties comparable to those prepared from conventional petroleum solvent based liquefaction processes (Hu et al., 2012). A two-step sequential CG-based liquefaction of lignocellulosic biomass (corn stover) also was developed (Hu and Li, 2014). The first step, acid-catalyzed liquefaction, was highly effective in liquefying biomass, which helped enhance biomass conversion rate; the second step, base-catalyzed liquefaction, featured extensive condensation reactions, increased the molecular weight of the produced polyol and decreased its acid number. The PU foams produced using polyol from the two-step liquefaction process showed higher compressive strength than those of PU foams produced from only acid- or base-catalyzed biomass liquefaction process, and are excellent thermal insulation materials due to their low thermal conductivity (Hu and Li, 2014).

**2.3 Polyols and PUs from glycolyzation of PET**
PET is semi-crystalline thermoplastic polyester that has been widely used in the manufacture of apparel fibers, disposable soft-drink bottles, and photographic films (Mir et al., 2012). This has caused environmental concerns due to large number of post-consumer PET products, especially bottles and containers. Although PET products are non-toxic and do not create a direct hazard to the environment, they have high resistance to atmospheric and biological agents, and have a high volume fraction in solid waste streams. Chemical recycling of PET materials have many advantages over land filling of such non-biodegradable material: (1) consumption of waste materials by converting them into new useful materials, (2) conversion of a non-biodegradable polymer into a biodegradable one (Mir et al., 2012). Among many PET chemolysis processes, such as hydrolysis (Paszun and Spychaj, 1997), alcoholysis (Kishimoto et al., 1999; Yang et al., 2002), glycolysis (Baliga and Wong, 1989; Pardal and Tersac, 2006; Vaidya and Nadkarni, 1987), aminolysis (Shukla and Harad, 2006), and ammonolysis (Blackmon et al., 1990), glycolysis using various glycols is most popular. During the glycolysis reaction, PET polymer is depolymerized by glycols, which break the ester linkages and replace them with hydroxyl groups in the presence of trans-esterification catalysts (mainly metal acetates). The effects of reaction conditions, such as type of glycol used, glycolysis time, glycolysis temperature, catalyst concentration, and glycol concentration on the glycolysis process of PET, have been studied (Chen et al., 2001; Pardal and Tersac, 2006). Glycolysis of PET by diethylene glycol (DEG), dipropylene glycol (DPG) and glycerol (Gly) was studied at 220 °C without catalyst and at 190 °C with titanium (IV) n-butoxide by Pardal and Tersac (Pardal and Tersac, 2006). It was found that the
order of reactivity for uncatalyzed glycolysis at 220 °C is: DEG ≫ Gly ≫ DPG, while the order of reactivity for catalyzed reactions is DEG > DPG ≫ Gly. DEG showed the best reactivity in both reaction conditions and allows low molecular mass oligomers to be obtained quickly. A 2³ factorial experiment studied the main, two-factor interaction and three-factor interaction effect of glycolysis temperature, glycolysis time, and the amount of catalyst (cobalt acetate) on the glycolysis of recycled postconsumer soft-drink PET bottles. The sequence of main effects on the glycolysis conversion of PET was found to be: catalysis concentration > glycolysis temperature > glycolysis time (Chen et al., 2001).

Luo and Li (Luo and Li, 2014) reported for the first time the utilization of CG in the recycling process of waste PET to produce polyols. In their study, post-consumer PET was first glycolyzed by DEG, the obtained PET oligomer was then further reacted with pretreated CG at different weight ratios. They concluded that increasing weight ratio of CG to PET and DEG, lead to polyols with decreased molecular weights and viscosities, and increased hydroxyl numbers. Polyols prepared using CG as the sole glycolysis agent showed slightly higher acid values than those of polyols prepared from DEG and CG (Luo and Li, 2014). Chaudhary et al (Chaudhary et al., 2013) reported micro-wave assisted glycolysis of PET for preparation of polyester polyols, and they discovered that the reaction time required for glycolysis using microwave (about 30 min) is significantly shorter than conventional thermal glycolytic processes (8-9 h for the same level of depolymerization).

The polyols produced from recycled PET have been used to produce PU foams and coatings. Vitkauskiene et al. (Vitkauskiene et al., 2011) synthesized polyurethane-
polyisocyanurate (PU-PIR) foams from a series of aromatic polyester polyols from glycolysis of PET waste using DEG. In their study, glycerol, adipic acid, polypropylene glycol and hexanediol also were tested as functional additives in the glycolysis process. PU-PIR foams based on PET-waste-derived polyols had high isocyanurate yield (67%-90%), high closed cell content (more than 94%), and excellent mechanical properties exceeding those of typical PU-PIR foams. They also discovered that the incorporation of glycerol as a functional additive decreased isocyanurate yield, core density, and tensile strength but increased elongation at break, while the incorporation of adipic acid acted vice versa (Vitkauskiene et al., 2011). Kathalewar et al. (Kathalewar et al., 2013) glycolyzed post-consumer PET using neopentyl glycol and prepared PU coatings from the glycolyzed oligomers. The coatings showed excellent gloss and chemical resistance, good hardness and thermal stability, but poor impact resistance due to the brittle nature of the films (Kathalewar et al., 2013).

2.4 polyols and PUs from protein based feedstocks

2.4.1 Introduction of different types of protein feedstocks

Proteins are large macromolecules (polypeptides) formed by linking many α-amino acids via amide bonds (peptide bonds). The presence of many functional groups, such as amino (-NH₂) groups, carboxyl (-COOH) groups, hydroxyl (-OH) groups and disulfide (-S-S-) groups (Schulz and Schirmer, 1979), makes protein a promising material for the production of bio-based polymeric materials. Feedstocks that contain high protein content are also abundant in nature, including soybean protein products, such as soy flour, defatted SM, soy protein concentrates, and soy protein isolates (Kumar et al.,
2002a). Each of the soybean protein products have different protein content and are used to produce different protein products in the food industry. Soy flour has a protein content ranging from 40-60% (Kumar et al., 2002a) and is used as a source material for soymilk, tofu and other specialty foods (Singh et al., 2008). SM has a protein content ranging from 10-90%, and is often used as animal feed (United Soybean Board, 2015). Soy protein concentrates contain about 60-70% protein (Kumar et al., 2002a), and are used in bakery products, baby foods, cereals and milk replaces (Singh et al., 2008). Soy protein isolates have the highest protein content (80-90%) (Kumar et al., 2002a) and are often used as poultry and meat protein replacements (Singh et al., 2008). Corn is another high volume protein source, with products such as corn gluten meal, corn gluten feed, distillers dried grains (DDG), and distillers dried grains with solubles (DDGS). Corn gluten meal has the highest protein content (65%), corn gluten feed has about 23% protein content, and DDGS has about 27% protein content. Zein, a functional prolamine protein, can be produced from corn gluten meal and has been used in the production of plastics, coatings, inks, chewing gum, adhesive and fibers (Anderson and Lamsa, 2011). A third source, wheat gluten, generally contains about 75-85% protein and has been successfully utilized for the production of bio-based plastics (Domenek et al., 2004). Fourthly, algal biomass, which can be classified into macroalgal and microalgal biomass, following the extraction of oil for the production of biodiesel, has a protein content of about 48%. In order to improve the economics of algae oil based biodiesel, value-added conversion of algal biomass residue including the production of methane through anaerobic digestion has been developed (Chisti, 2007).
2.4.2. Polyols from protein feedstocks

Two methods are mainly used for the production of polyols from protein feedstocks: (1) modification of proteins into polyols, (2) liquefaction of proteins. The modification of proteins have been achieved via the addition reaction with polyethylene glycol (PEG)-aldehyde, or the substitution reaction with cyanuric chloride-modified PEG (Figure 2) (Li et al., 2015). Oxypropylation of hydrolysate of SM mixed with sucrose based polyol has been reported to produce polyols (Narayan et al., 2014). The derived polyol obtained from oxypropylation had a hydroxyl value of 442 mg KOH/g, an amine value of 102 mg KOH/g and a water content lower that 0.2% (Narayan et al., 2014). Algal protein-based polyols have been produced through reactions of algal hydrolysate with ethylene diamine and ethylene carbonate (Figure 3) (Kumar et al., 2014a). The polyols obtained showed a hydroxyl value of 422 mg KOH/g, an acid value of 3 mg KOH/g, and an amine value of 26 mg KOH/g (Kumar et al., 2014a).
Figure 2 Modification of protein with PEG and cyanuric chloride for the production of polyol (Li et al., 2015)
Liquefaction also has been shown to be effective in generating protein-based feedstocks for polyol production. Liquefaction of DDG under atmospheric pressure in ethylene carbonate with sulfuric acid as catalyst was most successful using a liquefaction solvent/DDG ratio of 4, liquefaction temperature of 160 °C, liquefaction time of 2 h, and sulfuric acid loading of 3 wt% (Yu et al., 2008).

2.4.3 PUs of protein feedstocks

PU foams, coatings/films, and composites/plastics have been successfully prepared based on protein feedstocks. Both algae polyol and SM polyol were used in
combination with other polyols to prepare PU foams. The most noticeable property of foams formulated with algae-based polyol and SM based polyol was the self-catalytic property due to the presence of tertiary amine groups in their protein structures. This was confirmed by shorter cream time, gel time, rise time, and tack-free time compared to reference foam samples from commercial polyols. Both algae- and SM-based foams showed similar physical properties to reference foams (Kumar et al., 2014b; Narayan et al., 2014).

Soy protein has significant potential for the production of coatings and films due to its good biocompatibility, biodegradability, and processability (Song et al., 2011). However, poor water resistance and brittleness of soy protein-based films has limited their use in industrial applications. Various modification methods have been studied including denaturation and cleavage of proteins, crosslinking, enzyme modification, plasticization, and blending with other polymers (Kumar et al., 2002b; Tong et al., 2015). Among these methods, blending is the most popular and useful one (Li et al., 2015). Liu et al. (Liu et al., 2008) have successfully prepared blended films from hydrophobic castor oil-based PU and p-phenylene diamine soy protein (PDSP), and the blended films combined good mechanical properties with optical transmittance. It was discovered that PDSP exhibited good miscibility with PU with its content varying from 10 to 80 wt%, and PDSP and PU had strong hydrogen bond and chemical cross-linking interactions. With the increase of PU content, the blend films showed increased elongation at break, thermal stability, and water resistance and decreased tensile strength and Young’s modulus (Liu et al., 2008). Waterborne PU (WPU) was used to modify soy protein isolate
(SPI) to improve the flexibility and water resistance of the soy protein films (Tian et al., 2010). The blended films exhibited good compatibility due to strong hydrogen bonding interactions between the SPI and WPU. Not only did the blended film have improved flexibility and water resistance, the incorporation of WPU also enhanced the mechanical properties of the blend films in water, leading to the applications suited to wet conditions (Tian et al., 2010).

PU composites/plastics are the materials that combine PU and other constituent materials with different physical or chemical properties. PU composites/plastics containing protein feedstocks have been reported in which a series of protein composites from 30 to 50 wt% PU prepolymer (PUP) with soy dreg (SD), soy whole flour (SWF), and soy protein isolate (SPI) were compression-molded at 120 °C(Chen et al., 2003). The results in this study indicated that the protein component in the soy products plays an important role in the enhancement of adhesivity, processability and biodegradability of the composites. It is also possible to obtain different materials, from plastic to elastomer, by changing the type of soy protein product and the content of PUP (Chen et al., 2003). Zein-based PUs were synthesized by chemical modification of zein protein with isocyanates (phenyl isocyanate (PI) and n-hexyl isocyanate (HI)) and diisocyanates (isophorone diisocyanate (IPDI) and methylenediphenyl 4,4’-diisocyanate (MDI)) (Sessa et al., 2013). Moisture uptake decreased with isocyanate and diisocyanate modifications, indicating improved waster resistance of zein-based PU polymers compared to pure zein polymers. The authors suggested potential applications of zein-based PUs in bioplastics, floor coating, and printing ink (Sessa et al., 2013).
Chapter 3 Value-Added Conversion of Waste Cooking Oil and Post-consumer PET Bottles into Biodiesel and Polyurethane Foams

Value-added utilization of waste cooking oil (WCO) and post-consumer PET bottles for the production of biodiesel and polyurethane (PU) foams was developed. WCO collected from campus cafeteria was firstly converted into biodiesel, and then crude glycerol (CG), a byproduct of the above biodiesel process, was incorporated into the glycolysis process of post-consumer PET bottles to produce polyols. PU foams were synthesized from the above produced polyols. The characterization of the produced biodiesel demonstrated that its properties meet the specification of biodiesel standard. The effect of CG loading on the properties of polyols and PU foams were investigated. All the polyols showed satisfactory properties for the production of rigid PU foams which had performance comparable to those of some petroleum-based analogs. A mass balance and a cost analysis for the conversion of WCO and post-consumer PET into biodiesel and PU foams were also discussed. This study demonstrated the potential of WCO and PET waste for the production of value-added products.

3.1 Introduction

Biodiesel (fatty acid ester) produced by transesterification of renewable feedstocks such as vegetable oils and animal fats with alcohol, has been widely
considered as an alternative to petroleum diesel. However, the commercialization of biodiesel is mainly limited by its high manufacturing cost (Camobreco et al., 1998; Meher et al., 2006). WCO, as a cheaper alternative than virgin vegetable oil, can largely reduce the biodiesel production cost. The production of biodiesel from WCO is mainly performed under the catalysis of alkalis, acids, or enzymes, with alkaline catalysts such as NaOH, KOH, and NaOCH₃ being most commonly used due to their higher reaction rate than acid and enzymatic catalysts. CG is a byproduct of the biodiesel production process. It has the potential to be converted into value-added products through biological or chemical reactions. Chemical recycling of PET can depolymerize PET to generate feedstocks for the production of highly valuable polymers (Sinha et al., 2010). In this chapter, value-added conversion of WCO and post-consumer PET bottles into biodiesel and PU foams was successfully developed (Figure 4). The biodiesel production from WCO and the glycolyzation of post-consumer PET were integrated by CG. The properties of the produced value-added products, i.e. biodiesel, polyols, and PU foams, were characterized to examine the feasibility of designed process. The effects of CG loading polyols and PU foams were investigated. Mass balance and a preliminary cost analysis for this process were discussed.
Figure 4 The process diagram for value-added conversion of WCO and post-consumer PET bottles into biodiesel and PU foams

Figure 5 Mass balance analysis for the production of biodiesel and PU foams from WCO and post-consumer PET bottles

3.2 Experimental

3.2.1 Materials

WCO and post-consumer PET water bottles were collected from the cafeteria in Ohio State Agricultural Technical Institute (Wooster, OH) and from the recycle center at the Ohio Agricultural Research and Development Center (Wooster, OH). After the
removal of polyethylene caps and polypropylene labels, the collected PET bottles were washed, dried, and cut into small pieces (5 × 30 mm) using a HSM Shredstar BS10CS shredder (Downingtown, PA). DEG, glycerol, and 0.1 mol/L and 10.0 mol/L NaOH solution were purchased from Fisher Scientific (Pittsburgh, PA). Ethanol and Tetrahydrofuran (THF) as high performance liquid chromatography (HPLC) grade were purchased from Pharmco-AAPER (Shelbyville, KY). Titanium isopropoxide, HYDRANAL-Composite 5, HYDRANAL-Water Standard 10.0 and HYDRANAL-Methanol Rapid for Karl Fischer titration; glycerin, monoolein, diolein, triolein, butanetriol, tricaprin and N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) for the quantitative analysis of total monoglycerides and free/total glycerol in biodiesel, were purchased from Sigma-Aldrich (St. Louis, MO). Standard polystyrene samples were purchased from Agilent Technologies (Santa Clara, CA). Polycat 5, polycat 8, and Dabco DC5357 used in foaming process were obtained from Air Products & Chemicals, Inc. (Allentown, PA). Polymeric methylene-4,4´-diphenyl diisocyanate (pMDI) was obtained from Bayer Material Science (Pittsburgh, PA). Chemicals were reagent grade, except those specifically mentioned.

3.2.2 Characterization of WCO

To determine whether any pretreatment was needed, the water and FFA contents of WCO were determined prior to transesterification for biodiesel production. The water content was measured by Mettler Toledo volumetric Karl Fisher compact titrator V20 (Mettler Toledo, Columbus, OH) was 0.1%. The FFA content was 0.53%, measured in accordance with AOCS Ca 5a-40.
3.2.3 Production of biodiesel from WCO

Due to the low water and FFA contents, the transesterification of WCO was carried out in a one-step alkali-catalyzed process for the production of biodiesel. 1,500 g WCO, 300 mL methanol, and 9.15 g KOH (7.5 g for catalyst and 1.65 g for neutralizing the FFA) were charged into a 2.5-L glass reactor equipped with a magnetic stirring bar (Banani et al., 2014). The mixture was stirred for 2h at 37 °C, and then settled overnight. The crude biodiesel located in the upper layer was washed three times with deionized water to remove residues of catalysts and glycerol, and dried by rotary evaporation to yield biodiesel. The CG in the bottom layer also was collected for subsequent applications to produce polyols from PET waste. The residual methanol in the glycerol was removed by evaporation. Other common impurities of CG such as water, soap an salts (Yang et al., 2012) might still exist.

3.2.4 Characterization of biodiesel and CG from biodiesel production

The density of biodiesel samples were determined by measuring their masses in fixed volume. Dynamic viscosity was measured by a Brookfield DV-II+Pro Viscometer (Brookfield, Middleboro, MA) at 40°C and converted to kinematic viscosity by dividing the dynamic viscosity by the fluid mass density. Water contents of biodiesel and CG were determined using a volumetric Karl Fisher compact titrator V20 (Mettler Toledo, Columbus, OH). The glycerol and methanol contents in CG were determined using a Shimazu LC-20 AB HPLC system (Shimadzu, Columbia, MD) equipped with a RID-10A refractive index detector and a Phenomenex RFQ- Fast Fruit H⁺ (8%) column. The mobile phase was 0.005 N H₂SO₄ aqueous solution, which ran at 60°C with a flow rate of
0.6 mL/min. The monoglyceride and free/total glycerol contents in the biodiesel were measured according to ASTM D6584-13 by gas chromatography (GC) using a Shimadzu GC-2010 plus GC system (Shimadzu, Columbia, MD) equipped with a flame ionization detector (FID). The results were compared to requirements for biodiesel listed in ASTM D6751-15a.

3.2.5 Synthesis of polyols

Polyols were prepared by PET glycolysis in the presence of DEG and CG as a trifunctional additive. Glycolysis was carried out at 230°C for 4 h in a 500 mL three-neck round bottom flask equipped with a magnetic stirring bar, condenser, thermometer, and nitrogen inlet. Titanium isopropoxide (0.5 wt.% of PET) was added as a catalyst (Luo and Li, 2014). The molar ratio of PET to DEG was kept constant at 1:2 to investigate the effect of CG loading on the properties of polyols. The CG loading varied from 0% to 5%, 9% and 15% based on the total weight of PET, DEG or CG.

3.2.6 Characterization of polyols

Both hydroxyl and acid numbers of polyols were determined following ASTM D4272-05D and ASTM D4662-08. The viscosities of polyols were determined in accordance with ASTM D4878-08 using a Brookfield DV-II+Pro Viscometer (Brookfield, Middleboro, MA) at 25°C. The average molecular weights and molecular weight distributions of polyols were determined by gel permeation chromatography (GPC) analysis in THF at 35°C with an elution rate of 1.0 mL/min using a Shimadzu LC-20 AB GPC system (Shimadzu, Columbia, MD) equipped with a RID-10A refractive index detector, a SPD-M20A prominence photodiode array detector, and a Waters
styrigel HR1 column (7.8 × 300 mm). Polystyrene standard samples were used to calibrate the GPC column.

3.2.7 Synthesis of PU foams

PU foams from the above obtained polyols were prepared according to our previous study (Hu et al., 2012). Polyols, catalysts, a surfactant, and a blowing reagent (water) were mixed by rapid stirring using a hand mixer for 10-15 s in a 250 mL plastic cup to achieve homogeneous mixing. Pre-weighed pMDI with an isocyanate index of 110 was then quickly added and vigorously mixed for 5 s. The mixture was poured into a square wood box (11cm × 11cm × 11cm) with aluminum foil lining and left to rise at room temperature. The cream time, rising time, and tack free time were recorded according to ASTM D7487-13. PU foams were allowed to cure at room temperature for 24 h before the thermal conductivity test, and for 1 week before density and compressive strength tests. The formula used for the PU foam preparation is shown in Table 1.

Table 1 PU foam production formula

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET-based polyols</td>
<td>100</td>
</tr>
<tr>
<td>Catalyst-Polycat 5</td>
<td>1.26</td>
</tr>
<tr>
<td>Catalyst-Polycat 8</td>
<td>0.84</td>
</tr>
<tr>
<td>Surfactant-DABCO DC5357</td>
<td>2.5</td>
</tr>
<tr>
<td>Blowing agent-Water</td>
<td>3</td>
</tr>
<tr>
<td>pMDI</td>
<td>Equivalent weight for isocyanate index of 110</td>
</tr>
</tbody>
</table>

3.2.8 Characterization of PU foams
The thermal conductivity of PU foams was measured by a Lasercomp FOX 314 heat flow meter (Lasercomp, Saugus, MA) according to ASTM C518. The compressive strength parallels to the foam rise direction were measured following ASTM D1621-10 using Instron 3366 (Instron, Norwood, MA). The PU foam density was measured following ASTM D1622M-14. Fourier transform infrared (FT-IR) spectroscopy for PET, CG, DEG, polyols and PU foams were obtained from PerkinElmer Spectrum 2 IR spectrometers (Perkin Elmer, Waltham, MA).

3.3 Results and Discussion

3.3.1 Properties of biodiesel and CG from WCO

As shown in Table 2, all measured parameters, including viscosity, water content, monoglyceride, and free and total glycerol of biodiesel produced from WCO, meet the requirements in ASTM D6751 standard. Compared to parameters reported for biodiesel produced from different sources of feedstock, such as beef tallow (free glycerol: 0.01%, total glycerol 0.33%, and monoglycerides: 0.13%) (da Cunha et al., 2009) and WCO with high content of FFA (free glycerol: 0.08% and total glycerol: 0.21%) (Meng et al., 2008), the biodiesel produced in this study had lower contents of free/total glycerol and monoglycerides. This indicates that complete transesterification between WCO and methanol occurred in the study. The post-treatment of crude biodiesel (separation and water washing) produced high-quality biodiesel.
Table 2 Properties of biodiesel sample compared to ASTM D6751 standard

<table>
<thead>
<tr>
<th></th>
<th>Kinematic Viscosity (mm²/s, 40°C)</th>
<th>Water content (% in volume)</th>
<th>Monoglycerides (wt %)</th>
<th>Free glycerol (wt %)</th>
<th>Total glycerol (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ASTM D6751</strong></td>
<td>1.9-6.0</td>
<td>&lt;0.050</td>
<td>&lt;0.40</td>
<td>&lt;0.02</td>
<td>&lt;0.240</td>
</tr>
<tr>
<td><strong>Biodiesel</strong></td>
<td>5.5</td>
<td>0.049</td>
<td>0.06</td>
<td>BDL&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.206</td>
</tr>
</tbody>
</table>

Note: <sup>a</sup> Below detection level (0.0001%)

The produced CG after evaporation of methanol contains 84.46% glycerol, 2.64% water, and 4.03% residual methanol. Compared to the CG collected from a WCO biodiesel plant (glycerol content 27.31-30.25%, water content 5.10-8.20%) (Kongjao et al., 2010), CG collected in this study had a much higher glycerol content and lower water content. This difference could be attributed to the different feedstocks and the processes used for biodiesel production. Moreover, the CG has significantly different composition from the one previously used for the production of PET-based polyols (Luo and Li, 2014) and may produce polyols and PU foams with different properties.

### 3.3.2 Properties of polyols

Polyols were synthesized by the glycolysis of PET with DEG in the presence of different loadings of CG (0%, 5%, 9%, and 15%). The acid values of all polyols were below 0.6 mg KOH/g (Table 3), which fell within the maximum acidity (around 2 mg KOH/g) acceptable for polyester polyols (Ionescu, 2005). With CG content increasing from 0 to 15%, the hydroxyl number of the derived polyols increased by 23.8%. This is most likely due to the high hydroxyl number of glycerol (1829 mg KOH/g). Similar results have also been observed for the PET-based polyols produced previously (Luo and Li, 2014). In that study, as CG contains 22.9% of glycerol, the actual glycerol contents in the reaction mixture were 6.87% and 11.45% at CG loadings of 30% and 50%,

30
respectively. Compared to polyols produced in the previous study with similar glycerol content, the polyols in this study had higher hydroxyl numbers (Table 3), and were more favorable for the production of rigid PU foams. The difference in hydroxyl number between the polyols obtained in the previous study and this study was mainly caused by the impurities in CG. The high contents of impurities such as fatty acid esters, soap and fatty acids in CG used for the production of PET-based polyols in the previous study participated in reactions and consumed hydroxyl groups, resulting in low hydroxyl numbers (Luo and Li, 2014). It was also observed that the dynamic viscosity and the molecular weight of polyols increased from 819.4 to 1511.5 cP and from 738 to 806 ($M_n$), respectively, as the CG loading increased from 0 to 15% (Table 3). This is possibly caused by the participation of glycerol in glycolysis of PET. Glycerol has been widely used as a crosslinker in polymeric material production, and could compete with DEG in the depolymerization of PET for the formation of cross-linking structures, resulting in increased molecular weights of the glycolyzed PET polyols. Furthermore, the glycolyzed PET with increased cross-linking structures can cause more entanglement, resulting in increased viscosity. Due to the high purity of CG, polyols yields above than 92% were obtained under all conditions. Polyols in this study showed lower viscosity, higher molecular weight and yield, and increased hydroxyl number compared to polyol produced previously (Luo and Li, 2014). It concluded that the composition of CG has a significant impact on polyol properties, which could affect PU foam performance.
3.3.3 Performance of PU foams

PU foams (PUF-x) were produced by the polymerization of the above prepared PET-based polyols (Pol-x) and polymeric methylene-4,4'-diphenyl diisocyanate (pMDI) using polycat 5 and polycat 8 as catalysts, Dabco DC5357 as a surfactant, and water as a blowing agent. As shown in Table 4, the cream time, rise time and tack free time of PU foams increased as CG loading increased in the preparation of PET-based polyols. In general, the cream time and rise time are related to the expansion rate, while the tack free time is used for the characterization of gelation rate (Hu et al., 2002). As a result, the PU foams showed slower expansion rate and gelation rate with the increase of CG loading. This was most likely related to the increase of secondary hydroxyl groups from glycerol and the increased viscosity of the polyols. Water content in CG might also affect the foaming characteristics of PU foams. According to Chen et al. (Chen et al., n.d.), the cream time, rise time and tack free time of the PU foam increase with the increase of...
water used in the formulation. As the CG loading increasing from 0 to 15%, the water content in CG as an impurity also increased, thus resulting in increased water in polyols even the formulation remained the same for four foams with different CG loadings. Moreover, with an increase of hydroxyl number of polyols, the required amount of pMDI increased under the same isocyanate index, and thus slightly longer time might be needed for well-mixing.

<table>
<thead>
<tr>
<th>PU foams</th>
<th>Cream time (s)</th>
<th>Rise time (s)</th>
<th>Tack free time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUF-0</td>
<td>8-10</td>
<td>14-16</td>
<td>13-15</td>
</tr>
<tr>
<td>PUF-5</td>
<td>10-12</td>
<td>19-21</td>
<td>18-20</td>
</tr>
<tr>
<td>PUF-9</td>
<td>16-18</td>
<td>23-25</td>
<td>20-22</td>
</tr>
<tr>
<td>PUF-15</td>
<td>16-18</td>
<td>24-25</td>
<td>24-25</td>
</tr>
</tbody>
</table>
The compressive strength, density and thermal conductivity of the PU foams made from PET-based polyols are shown in Figure 6. CG loading had little impact on the density of the foams but significantly influenced their compressive strength and thermal conductivity.

All the foams produced showed similar densities ranging from 46.03 to 47.66 kg/m³. With increasing CG loading from 0 to 15%, the compressive strength increased from 235.9 to 299.9 kPa. This could be explained by the increased cross-linking structures of polyols and the resulting PU foams due to the trifunctional characteristics of glycerol. Compared to PU foams made from polyols from PET and other CG sample (Luo and Li, 2014), PU foams in this study showed much higher compressive strengths.
due to the higher hydroxyl number of polyols. Moreover, the presence of very low content fatty acid chains from impurities of CG also contributed to the improvement of compressive strength perhaps because the dangling fatty acid chains in PU structures could generate plasticizing effect. It further indicated that the composition of CG influences properties of PU foams. In addition, the compressive strength of PU foams were superior over that (compressive strength of 220 kPa) of a commercial analog for construction applications (Demharter, 1998). Thermal conductivity of PU foams decreased from 38.7 to 33.3 mW·m⁻¹·k⁻¹ with the increase of CG loading from 0 to 9%, after which it increased to 40.8 mW·m⁻¹·k⁻¹ at CG loading of 15% (Figure 6). Most of the PU foams showed thermal conductivities comparable to those of conventional rigid PU foams (38 mW·m⁻¹·k⁻¹) (Kacperski and Spychaj, 1999) and commercial EPS foams (37 mW·m⁻¹·k⁻¹) (Zarr and Pintar, 2012). PU foams with 9% of CG loading had the best insulation properties.

3.3.4 Structural characterization

The FT-IR spectra of PET, DEG, CG, a representative polyol (pol-9), and the resulting foam are presented in Figure 7. In the spectra of DEG and CG, characteristic hydroxyl stretching at 3200-3400 cm⁻¹ was observed, along with absorption bands related to C–H of alkyl groups at 2850-3000 cm⁻¹. Small peaks at 1570 cm⁻¹ and 1740 cm⁻¹ in the spectrum of CG indicate the presence of some amount of impurities: the small band at around 1570 cm⁻¹ represents the COO- of soap, while the small band at 1740 cm⁻¹ is evidence of C=O of fatty acids and their esters (Kongjao et al., 2010). An absorption band at 1714 cm⁻¹ due to ester stretching is present in the spectrum of polyol as a result of
glycolysis of PET (Chaudhary et al., 2013). This peak is also present in the spectrum of PET. The absorption bands of polyol at 3200-3400 cm⁻¹ and 2850-3000 cm⁻¹ are similar to the absorption band in the spectra of DEG and CG, representing hydroxyl groups and C–H of alkyl groups in the polyol. The spectrum of the PU foam showed the presence of several characteristic urethane bands: –N–H stretching at 3304 cm⁻¹, C=O stretching at 1707 cm⁻¹, C–O stretching at 1217 cm⁻¹, and C-N stretching of carbamate group at 1595 cm⁻¹, and N-H bending at 1511 cm⁻¹ (Čuk et al., 2015; Mishra et al., 2009).

3.3.5 Mass balance and cost analyses of the process from WCO and waste PET to biodiesel and PU foams
Table 5 Breakdown of biodiesel production costs in dollars per liter

<table>
<thead>
<tr>
<th></th>
<th>Costs for 50 L of Biodiesel ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WCO</td>
<td>9.38</td>
</tr>
<tr>
<td>Methanol</td>
<td>2.16</td>
</tr>
<tr>
<td>Potassium hydroxide</td>
<td>0.28</td>
</tr>
<tr>
<td>Electricity</td>
<td>0.17</td>
</tr>
<tr>
<td>Water</td>
<td>0.02</td>
</tr>
<tr>
<td>Total</td>
<td>12.00</td>
</tr>
<tr>
<td>Unit cost ($/L)</td>
<td>0.24</td>
</tr>
</tbody>
</table>

*WCO price: approximately $200/ton (Zhang et al., 2003)

Table 6 Breakdown of PU foam production costs in dollars per kilogram

<table>
<thead>
<tr>
<th></th>
<th>Costs for 50kg of PU foams ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recycled PET flakes*</td>
<td>2.92</td>
</tr>
<tr>
<td>CG (from biodiesel process)</td>
<td>0.28</td>
</tr>
<tr>
<td>DEG</td>
<td>4.80</td>
</tr>
<tr>
<td>TPP</td>
<td>0.14</td>
</tr>
<tr>
<td>Electricity</td>
<td>10.65</td>
</tr>
<tr>
<td>Nitrogen gas</td>
<td>0.74</td>
</tr>
<tr>
<td>Water</td>
<td>0.01</td>
</tr>
<tr>
<td>pMDI</td>
<td>49.49</td>
</tr>
<tr>
<td>Polycat 5</td>
<td>1.11</td>
</tr>
<tr>
<td>Polycat 8</td>
<td>0.43</td>
</tr>
<tr>
<td>DABCO DC 5357</td>
<td>2.72</td>
</tr>
<tr>
<td>Total</td>
<td>73.29</td>
</tr>
<tr>
<td>Polyol unit cost ($/kg)</td>
<td>1.17</td>
</tr>
<tr>
<td>Foam Unit cost($/kg)</td>
<td>1.47</td>
</tr>
</tbody>
</table>

*Recycled PET flakes market price: approximately $0.40/kg


During biodiesel production, the cost of raw materials, especially vegetable oil, is the biggest contributing factor for the overall operating cost. Hass et al. (Haas et al., 2006) designed a model to calculate the annual operating costs for a $3.87 \times 10^7$ L/year biodiesel production facility. In their analysis, biodiesel production cost is around $567/ton, in which soybean oil itself constitutes 90.2%. WCO is usually sold at $200/ton (Zhang et al., 2003), which is much cheaper than the price of virgin canola oil ($500/ton)
(Zhang et al., 2003) and virgin soybean oil ($520/ton) (Haas et al., 2006). Together with other fats such as beef tallow, waste greases have the potential of producing 3.5 billion liters of biodiesel per year (Nelson et al., 1994). Based on the mass balance analysis shown in Figure 5, the estimated cost for biodiesel produced from WCO is around $0.24/L (Table 5), which is about half the price of biodiesel produced under similar process using virgin vegetable oil as a feedstock [30].

The market price for PU foam production is about $2.2-4.4/kg, which is significantly dependent on the cost of polyol. Table 6 shows the estimated cost for the production of polyols and PU foams from PET and CG with a loading of 15%. The production cost of polyol is $1.17/kg, less than half of the average price of petrochemical-based polyol ($2.69/kg) (Nikje and Garmarudi, 2010). Besides the cost for pMDI, the main contributing factors for the overall production cost of PU foam are the cost of DEG and electricity, and the production cost of PU foam can be as low as $1.48/kg. During the cost analysis, 50L biodiesel and 50kg PU foams were chosen to represent the scale of typical lab size production. The mass balance and preliminary cost analyses for biodiesel and PU foams production indicate a very competitive production cost advantage of the presented process in the comparison with biodiesel from virgin vegetable oil and polyols and PU foams from petroleum. Incorporating biodiesel byproduct into PET recycling for PU foams production appears a promising application. Furthermore, the comprehensive utilization of waste into value-added products can improve the sustainability of the PU foams industry and help enhance competitiveness of biodiesel as a sustainable energy source against petroleum diesel.
3.4 Conclusion

A sustainable process for value-added conversion of WCO and post-consumer PET bottles into biodiesel and PU foams was developed successfully. CG, a byproduct of the biodiesel production from WCO, can be effectively used as a functional additive during the glycolysis of post-consumer PET bottles with DEG for the production of polyols with properties suitable for rigid PU foam applications. CG composition affects the properties of polyols and PU foams. With the increase of CG loading from 0 to 15%, polyols showed increased hydroxyl numbers, viscosities, and molecular weights, and the resulting PU foams presented increased compressive strength while at similar densities. Best insulation properties were obtained from PET-based polyol prepared with 9% CG. The PU foams also showed physical performance comparable to those of some of petroleum-based analogs. A preliminarily mass balance and cost analyses indicated the potential of economic viability of this process. Overall, this sustainable process effectively combined biodiesel production from WCO with recycling of post-consumer PET bottles for PU foam production, and is promising for converting them into value-added products for industrial uses.
Chapter 4 Value-added Conversion of soybean meal into UV-curable polyurethane acrylate coatings

In this study, a novel way has been developed to produce UV-curable polyurethane (PU) acrylate coatings from soybean meal (SM). High oleic SM was hydrolyzed by dilute acid to amino acid oligomers, then a hydroxyl-terminated PU oligomer was synthesized through a non-isocyanate method: i) amination of the amino acid oligomers with ethylene diamine to produce amino-terminated compound; ii) amidation of the amino-terminated compound was achieved with ethylene carbonate. Functionalization of hydroxyl-terminated PU oligomers was achieved by esterification and acrylation reactions to produce PU acrylate oligomers. PU acrylate oligomers were then formulated with multifunctional monomer and photo initiator to form a PU coating under UV light. Pure glutamic acid (Glu) was used as a model compound to verify the feasibility of the process. The hydroxyl number, acid number and chemical structures of both PU acrylate oligomers derived from Glu and SM were determined. The thermal and mechanical properties, such as tensile strength, modulus, glass transition temperature and degradation temperature, of UV-cured PU acrylate coatings from SM were characterized. The diagram for this process is shown in Figure 8.
Figure 8 Process diagram for the conversion of SM into UV-cured PU acrylate coating

4.1 Introduction

SM is the soy protein residue after oil extraction, and has long been considered a promising feedstock for the production of bio-based polymer materials due to its high protein content.

UV radiation curing has been widely used in the production of PU coatings. The main advantages of using UV radiation are: very high polymerization rates, low energy input compared with traditional thermal cured coatings, and no or low volatile organic compounds (VOCs) (Decker and Decker, 2002; Decker, 1998, 1996). A UV-curable PU coating formulation is mainly composed of a PU oligomer, a multifunctional monomer that acts as a reactive diluent to adjust formulation viscosity, and a photoinitiator.

4.2 Materials and methods

4.2.1 Materials

High oleic SM was provided by Cargill Inc. (Sidney, OH). After receiving the SM, its protein content was determined to be 51.06% by the Kjeldahl method. Glutamic acid, sodium hydroxide solution, oleic acid, hydroxyethyl acrylate (HEA), isophorone diisocyanate (IPDI), phenolphthalein, imidazole and methyl ethyl ketone were obtained.
from Fisher Scientific (Pittsburgh, PA). Ethylene diamine, ethylene carbonate, hexanediol diacrylate (HDDA), 1-hydroxy-cyclohexyl-phenylketone (Irgacure 184), bromophenol blue, and phthalic anhydride were obtained from Sigma-Aldrich (St. Louis, MO). Pyridine, ethanol and hydrochloric acid were obtained from Pharmco-AAPER (Shelbyville, KY). Dibutyltin dilaurate (DBTDL) was obtained from Pfaltz & Bauer, Inc., (Waterbury, CT).

4.2.2 Measurements

Fourier transformed infrared spectroscopy (FT-IR) analyses were performed on a PerkinElmer spectrum Two IR spectrometer (PerkinElmer, MA), and all samples were scanned from 4000 to 400 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). Thermal properties of UV-cured PU acrylate coatings were investigated by differential scanning calorimetry (DSC) (TA Instruments Q20, TA Instruments, New Castle, DE). Each measurement was performed in three cycles at a rate of 10 °C/min under nitrogen atmosphere. The samples were first heated from 40 to 200 °C to eliminate the thermal history, then cooled to −50 °C and held for 3 min, and heated again to 200 °C. The glass transition temperature (T\(g\)) was determined based on the third cycle. Thermal degradation behaviors of UV-cured PU acrylate coatings were evaluated by thermogravimetric analysis (TGA), which was performed under nitrogen atmosphere at a heating rate of 20 °C/min from 50 to 700 °C using a TA Instruments Q50 thermogravimetric analyzer. Both DSC and TGA data analyses were conducted using a TA Universal Analysis 2000. Pencil hardness of the coatings cured on iron plates was determined in accordance with ASTM D3363-05.
Tensile strength, modulus and elongation at break of the films were measured using an Instron 3366 tensiometer (Instron, Norwood, MA) at room temperature.

4.2.3 Synthesis of glutamic acid based hydroxyl terminated PU oligomer

Glutamic acid (Glu) was chosen as a model amino acid because it commonly has the highest abundance among amino acids in soybean (Berk, 1992). The synthesis from Glu to amino terminated compound and hydroxyl terminated compound is illustrated in Figure 9. Glu (14.71g, 0.1mol), excess ED (36.06g, 0.6mol) and DBTDL (0.51g, 1wt%) were added to a 250-ml round bottom flask equipped with a magnetic stirrer, a three-way adapter, a condenser, a vacuum adapter, a receiving flask and a thermometer. The system was raised to 105°C and reacted for 6 hours to yield amino-terminated compound (Glu-ED). Unreacted ED was distilled out at the end of the reaction for reuse.

Glu-ED obtained from the previous step was first dissolved in ethanol. Since unreacted Glu is insoluble in ethanol, it was simple to separate Glu-ED with unreacted Glu by centrifugation followed with filtration. The Glu-ED thus obtained (24.52g, amine value equals to 465.5 mg KOH/g) was reacted with EC (17.91g, 0.203mol) with ethanol as solvent in a 250-ml three-neck flask equipped with a magnetic stirrer, a condenser and a thermometer. The ratio of the total amine value equivalents to the total carbonate equivalents was kept close to 1. The reaction was carried out at 70°C for 2 hours to produce hydroxyl-terminated PU oligomer (Glu-ED-EC).

4.2.4 Synthesis of SM based polyol

100g SM (51.06% protein) and 300 ml 60% (v/v) aqueous ethanol solution was added to a round bottom flask equipped with a magnetic stirrer. After constant stirring for
1 hour under room temperature, the slurry was filtered under vacuum and the wet SM was dried in 40ºC oven overnight. 80.32g SM without soluble carbohydrates was obtained.

The hydrolysis of SM was carried out in a 500-ml three neck flask, equipped with a magnetic stirrer, a condenser, a thermometer and a N₂ inlet, under atmosphere pressure with constant stirring. About 50g ethanol extracted SM and 200 ml 2N HCl was added to the flask and heated to 100ºC in an oil bath with constant stirring. The temperature was held constant for 24 hours of reaction time. After reaction, the solution was cooled to room temperature and centrifuged at 1000 rpm for 10 min. The supernatant was decanted and neutralized using 10M NaOH to a pH 6 and then the solvent was evaporated using a rotary evaporator at 50-70ºC.

SM-ED, SM-ED-EC were synthesized using the same procedure as the syntheses of Glu-ED and Glu-ED-EC. SM-ED-EC (10 g, hydroxyl value=478.6 mg KOH/g, contains 0.085mol hydroxyl groups) and oleic acid (11.99g, 0.043mol) (the molar ratio of hydroxyl groups to carboxyl groups is 2:1) were added to a three-necked flask equipped with a magnetic stirrer, condenser and thermometer. The temperature was held constant at 130ºC under vacuum for 20 hours of reaction time (Figure 10).

In order to react with 10g SM-PUOFA (hydroxyl number = 222.5mg KOH/g, contains 0.04mol hydroxyl groups), IPDI-HEA derivative was first synthesized. 8.30 IPDI (0.04mol) and 0.22 ml DBTDL were placed in a three-necked flask equipped with magnetic stirrer, a dropping funnel with a drying tube, a thermometer and a nitrogen inlet. The flask was placed to a previously heated oil bath. The reaction mixture was
stirred at 35°C while 4.17 ml 2-HEA (0.04mol) was dripped into the flask. After the dripping was finished, the reaction mixture was stirred until the absorption peak of OH group (3500 cm⁻¹) in FT-IR had disappeared. After that, 10g SM-PUOFA was dissolved in 20ml methyl ethyl ketone (MEK) and added to the flask. The reaction mixture was stirred at 75°C until the absorption peak of NCO groups (2267cm⁻¹) in FT-IR had disappeared. The solvent was then evaporated (Figure 10).
Figure 9 Synthesis route of hydroxyl-terminated PU oligomer
Hydroxyl-terminated polyurethane oligomer

Polyurethane oligomer-grafted fatty acid

IPDI derivative

Polyurethane acrylate oligomer

Figure 10 Synthesis route of PUOFA and PUAO
4.2.5 Preparation of UV cured PU coating

PUAO was first mixed with 20% hexanediol diacrylate (HDDA) and 4% I gracure 184, and then the mixture was coated on an iron plate by an applicator with a 6 mils (152.4 μm) gap, and cured under UV light for 10 passes on a 5m/min conveyor.

4.3 Results and discussion

4.3.1 Model compound glutamic acid based polyol

![Figure 11 FT-IR spectra of (A) Glu-ED-EC, (B) Glu-ED, and (C) Glu](image)

Figure 11 shows the FT-IR spectra of Glu-ED-EC, Glu-ED, and Glu. The main changes between Glu and Glu-ED were the appearance of new peaks at 1647cm⁻¹ and 1255cm⁻¹, corresponding to C=O deformation and C-O deformation of the amide groups; the peak corresponding to N-H of the primary amine at 1501cm⁻¹ was shifted to 1548cm⁻¹ and is attributed to the transformation of amine into amide. The acid value of Glu-ED

48
(Table 7) indicates that most of the carboxylic groups were protected and converted to amides. However, when comparing the experimental amine value to the theoretical value (731.7 mg KOH/g), there is a 36.4% difference, which is 17% larger than data from similar experiments (Kumar et al., 2014a). This might due to the chemical structure of Glu. With carboxylic groups on both ends of the glutamic acid, when one side of carboxylic group has reacted with ED, the steric hindrance for the carboxylic group on the other side of Glu becomes larger; thus it becomes more difficult to ensure that both carboxylic groups on Glu have reacted with ED.

The formation of urethane groups in Glu-ED-EC was confirmed by the appearance of a peak corresponding to carbonyl stretching of the urethane groups at 1679 cm⁻¹. On the spectrum of Glu-ED-EC two small peaks at 1773 and 1805 cm⁻¹ corresponding to C=O stretching in EC can be observed, which indicate a small amount of unreacted EC in Glu-ED-EC (Nyquist and Setyineri, 1991). The amine, acid and hydroxyl values of Glu-ED-EC are shown in table 7. From the amine value we calculated that the conversion rate of amines to hydroxyl terminated urethanes is around 83%, which is 10% smaller than previously reported (Kumar et al., 2014b). This difference can also be explained by larger steric hindrance of the amine groups in the middle of Glu-ED chain.
Table 7 Amine, acid and hydroxyl value of Glu and SM derived oligomers

<table>
<thead>
<tr>
<th></th>
<th>Amine value (mg KOH/g)</th>
<th>Acid value (mg KOH/g)</th>
<th>Hydroxyl value (mg KOH/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glu-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glu-ED</td>
<td>465.5±19.3</td>
<td>59.8±3.2</td>
<td>-</td>
</tr>
<tr>
<td>Glu-ED-EC</td>
<td>79.4±0.29</td>
<td>37.3±1.5</td>
<td>402.6±15.2</td>
</tr>
<tr>
<td>SM-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SM-ED</td>
<td>533.4±9.4</td>
<td>24.8±0.4</td>
<td>-</td>
</tr>
<tr>
<td>SM-ED-EC</td>
<td>98.2±1.2</td>
<td>22.6±1.6</td>
<td>478.6±9.6</td>
</tr>
<tr>
<td>SM-PUOFA</td>
<td>-</td>
<td>1.5±0.5</td>
<td>222.5±10.9</td>
</tr>
</tbody>
</table>

4.3.2 SM-based polyol

The amine value, acid value and hydroxyl value of SM-ED, SM-ED-EC and SM-PUOFA are summarized in Table 7. The SM-based polyol and its intermediate showed similar values to the model Glu compound, which indicates that the amino acids from hydrolyzed SM went through the same chemical reaction as the model compound.
As shown in Figure 12, after the esterification of SM-ED-EC with oleic acid, the resultant SM-PUOFA showed decreased viscosity (at shear rate 10.9 1/s) from 41.2 Pa·s to 6.1 Pa·s at 25°C. The decrease in viscosity is evidence that oleic acid has successfully reacted with SM-ED-EC and that the incorporation of oleic acid with long aliphatic chain gave the SM-ED-EC oligomer chain more flexibility. Furthermore, the decrease in viscosity will also be beneficial to the control of acrylation reaction following the preparation of UV-curable PU coating. Both oligomers showed decreased viscosity with increasing shear rate, demonstrating the shear thinning effect of non-Newtonian fluids.

4.3.3 Properties of the coating film

4.3.3.1 Mechanical properties
Mechanical properties of the SM-based PU acrylate coating are reported in Table 8. Compared to PU acrylate coatings reported by Gite et al. and Kim et al. (Gite et al., 2010; Kim et al., 1996), the coating prepared in this study showed higher tensile strength and modulus and lower elongation at break. Pencil hardness test also shows that the coating film has the highest level of hardness. The results indicated that the coating prepared in this study exhibited rigid and brittle mechanical properties. This may due to possible hydrogen bonds between the N-H of the amide group and the C=O of another amide, urethane carbonyl or the ether oxygen (Lu and Larock, 2008) and enhanced cross-linking density due to the additional double bonds in oleic acid.

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
<th>Modulus (MPa)</th>
<th>Elongation at break (%)</th>
<th>Pencil hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM-based PU acrylate coating</td>
<td>18.2±3.6</td>
<td>450.1±17.3</td>
<td>4.5±0.7</td>
<td>9H</td>
</tr>
<tr>
<td>PUA-1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.12</td>
<td>1.60</td>
<td>81</td>
<td>-</td>
</tr>
<tr>
<td>PUA-2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.00</td>
<td>1.65</td>
<td>82</td>
<td>-</td>
</tr>
<tr>
<td>PUA-3&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>43.4</td>
<td>70</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: <sup>a</sup> PU acrylate coatings prepared by Gite et al. (Gite et al., 2010)

<sup>b</sup> PU acrylate coating prepared by Kim et al. (Kim et al., 1996)

4.3.3.2 Thermal properties
Figure 13 shows the TGA and DTA curves of PU acrylate coating, it can be seen that the coating showed a two-stage decomposition process. The first stage of weight loss happened between 200-310 °C is related to the decomposition of urethane groups existed in PUAO from the reaction between SM-ED and ethylene carbonate and the reaction between hydroxyl group in PUAO with isocyanate group in IPDI (Duquesne et al., 2001; Tamami et al., 2004). The second stage of weight loss between 310-500 °C reflects the decomposition of urethane-acrylate terminal groups (Dzunuzovic et al., 2005; Gao et al.,

<table>
<thead>
<tr>
<th>TGA</th>
<th>DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>T5 (°C)</td>
<td>Tg (°C)</td>
</tr>
<tr>
<td>SM-based PU acrylate coating</td>
<td>203.2</td>
</tr>
</tbody>
</table>

Table 9 Thermal properties of SM-based PU acrylate coating

Figure 13 TGA and DTA curves of UV-cured PU acrylate coating
2011) and also the scission of oleic acid chains in the PU acrylate coating (Li et al., 2014; Lu and Larock, 2008).

The decomposition temperatures at 5% and 50% weight loss and the glass transition temperature ($T_g$) based on DSC measurements are summarized in Table 3. The initial weight loss before 5% was mainly caused by the removal of uncured components with low molecular weight. The glass transition temperature is higher than many PU acrylate coatings reported (Xu and Shi, 2005; Xu et al., 2012), the $T_g$ agrees well with the coating’s rigid and brittle mechanical properties discussed previously.

### 4.4 Conclusions

UV-curable PU acrylate coatings derived from SM were successfully prepared through a series of reactions, including amination, amidation, esterification and acrylation. The feasibility of the process and the chemical structure of the oligomers was studied using glutamic acid as the model compound. The oligomers prepared from SM showed similar amine, acid and hydroxyl values as the oligomers prepared from model compound. Compared with other PU acrylate coatings reported in literature, the UV-cured PU acrylate coating prepared in this study showed higher $T_g$, tensile strength and modulus, and lower elongation at break.

The high protein content in SM makes it a potential feedstock for amino acid based polymers. The value-added conversion of soybean oil byproduct has the potential to lower the price of biodiesel produced from soybean oil, and also lower the cost for producing PU coatings. The developing of polymer from bio-based feedstocks also helps reduce reliance on petrochemical feedstocks.
Chapter 5 Conclusions and Suggestions for Future Research

5.1 Conclusions

In the studies, value-added conversion of waste cooking oil (WCO), post-consumer PET bottles into biodiesel and polyurethane (PU) foams and value-added conversion of soybean meal (SM) into PU coatings have been successfully developed and evaluated.

The first study demonstrated that WCO is suitable feedstock for the production of biodiesel and that crude glycerol (CG) can be effectively used as a functional additive during the glycolysis of post-consumer PET bottles with DEG for the production of polyols suited to rigid PU foam applications. Increasing CG loading from 0 to 15%, increased polyol hydroxyl numbers, viscosities, and molecular weights, and the resulting PU foams had increased compressive strength while having similar densities. Best insulation was obtained from PET-based polyol prepared with 9% CG. A preliminarily mass balance and cost analyses indicated the probable economic viability of this process.

The second study demonstrated that SM can be converted into polyol for the production of UV-cured PU acrylate coatings. The feasibility of the process and the chemical structure of the oligomers was studied using glutamic acid as the model compound. The oligomers prepared from SM showed similar amine, acid and hydroxyl values to the oligomers prepared from the Glu model compound. The UV-cured PU acrylate coating
prepared in this study showed good mechanical properties and thermal stability, with higher $T_g$, tensile strength and modulus, and lower elongation at break than PU acrylate coatings reported in literature.

5.2 Suggestions for Future Research

The preliminary cost analysis in chapter 3 included the market cost of transportation and collection of WCO and recycled PET. However, the labor cost, facility cost, and transportation cost for making biodiesel and PU foams are not included. A more comprehensive techno-economic analysis or life cycle analysis is needed to better analyze the feasibility of this process. What’s more, the varying composition of crude glycerol could be a major barrier to the commercialization of this process. Future research should focus on how to standardize or control the compositions of crude glycerol to produce PU foams with stable qualities.

The produced PU acrylate coatings exhibit brittle, plastic-like properties, and future research should focus on further modification of the product process to produce PU coatings with improved elongation at break. Research should also be conducted on the adhesion and water resistance properties of the coating, and to explore other SM-based PU products such as PU elastomers or plastics.

Lastly, we should investigate other processes for value-added conversion waste materials into useful PU products. The value-added conversion of waste polymer materials and biodiesel byproducts can enhance the cost-effectiveness of the biodiesel and polymer industry, and also reduce the environmental impact of polymer materials.
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