POLYESTERS DERIVED FROM BIOBASED 1,5-PENTANEDIOL FOR COATINGS, ADHESIVES, AND BIODEGRADABLE PLASTICS

Lei Zheng

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POLYESTERS DERIVED FROM BIOBASED 1,5-PENTANEDIOL FOR
COATINGS, ADHESIVES, AND BIODEGRADABLE PLASTICS

A Dissertation Presented

by

LEI ZHENG

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
of the requirements for the degree of

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Department of Chemical Engineering
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ABSTRACT

POLYESTERS DERIVED FROM BIOBASED 1,5-PENTANEDIOL FOR COATINGS, ADHESIVES, AND BIODEGRADABLE PLASTICS

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Directed by: Professor John Klier

Biomass-derived polymers are drawing increased attention from researchers due to unique performance attributes, potential for biodegradability, new low-cost feedstocks, and improved sustainability. Biobased feedstocks are employed in both major applications of polymers thermosets and thermoplastics. For thermoset coatings and adhesives, biobased resins such as biobased alkyds, epoxy resins, benzoxyazine resins, starch derivatives, and proteins from plants and animals, are promising candidates to replace petroleum-derived counterparts. Thermoplastics such as polyethylene are mainly produced from fossil resources, generally have poor degradability and are difficult to effectively recycle. Currently, in the United States, less than 10% plastics are recycled, and more than 70% are landfilled. The plastics escaping from the waste management system will ultimately find their ways to oceans. Therefore, there is an urgent demand to
develop degradable, recyclable, and biobased alternatives to replace conventional plastics. Although biobased materials continue to grow, petroleum-derived polymers still account for the majority of markets. To compete with the conventional thermosets and thermoplastics, biobased alternatives are required to overcome technical challenges, to provide equivalent or better performance, to become more environmentally friendly, and to offer equivalent or lower price.

In this thesis, we applied 1,5-pentanediol (PDO), which is an emerging biobased and low-cost monomer, to thermoset coatings, adhesives, and biodegradable plastics. Polyesters based on PDO were designed, synthesized, and investigated. We developed a reactor for melt polymerization and understood the effects of reaction conditions to synthesize target polyesters with molecular weights ranging from 1KDa to over 100KDa.

First, various low molecular weight polyester polyols were characterized for end group compositions, monomer incorporation and thermal transitions. Bio-PDO-based coatings exhibited performance, including hardness, flexibility, adhesion strength, and solvent resistance, similar to the coatings based on petroleum-derived 1,6-hexanediol (HDO). Bio-PDO-based adhesives exhibited lower green strength (initial adhesion strength) and longer open time (workable time to bond substrates) than HDO-based adhesives. The effects of common biobased impurities, such as lactones (delta-valerolactone as an example of impurities), on polyester polyols were studied. We found hydroxyl functionalities of polyols were mainly controlled by the excess diols in monomer feeds instead of ring-opening polymerization of delta-valerolactone.
Second, high molecular weight aliphatic-aromatic polyesters, poly (pentylene adipate-co-terephthalate)s (PPAT), were successfully synthesized via thin-film polymerization and chain extension. The effects of reaction temperature and catalyst on molecular weight were investigated. The final PPAT co-polyesters were characterized for microstructure, mechanical properties, and biodegradability. We have achieved PPAT compression films with 1.5 times tensile modulus than petroleum-based poly (butylene adipate-co-terephthalate) (PBAT), and comparable mechanical properties with low density polyethylene. Meanwhile, our preliminary results show PPAT films exhibited biodegradability similar with PBAT in soil.
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CHAPTER 1

INTRODUCTION

Industrial and academic researchers are increasingly investigating, and commercializing polymers based on biobased feedstocks. Biobased feedstocks provide several important advantages over their conventional petroleum-based counterparts. Bio routes provide unique and economically attractive feedstock molecules not available economically via petrochemical routes. These novel molecules may provide polymers with unique, valuable, and differentiated properties or lower cost (which is critical to adoption of new polymer technologies) versus petrochemical feedstocks. In addition, biobased feedstocks may reduce the reliance on fossil sources.

In this work, we will describe two types of novel biobased polymers

(a) The first part center around polyols for thermosetting coatings and adhesives where the bio-sourced feedstocks provide a lower cost alternative to petrochemical feedstocks while preserving performance of high-cost petrochemical alternatives.

(b) In the second part, we will describe the use of biobased feedstocks to provide biodegradable and chemically recyclable polyester plastics for applications in single-use films (such as found in food packaging), where the biobased feedstock enables superior polymer properties, allowing the new polyesters to compete with petrochemically derived non-degradable polymers.
In both sections, we will synthesize and investigate the polymers based on (bio) 1,5-pentanediol. This molecule was recently described [1], [2] and has potential as a low-cost alternative to high volume petrochemically derived 1,6-hexanediol in thermosetting resins as well as a performance enhancing alternative to 1,4-butandiol in biodegradable thermoplastics.

1.1 Biobased resins for thermoset coatings and adhesives

An increasing number of coatings and adhesives manufactures are managing to improve the sustainability of their products by replacing petroleum-based materials with biobased alternatives. One of the oldest biobased resins is alkyd, which is ordinarily polyester based on fatty acids, diacids, and polyols, while polyesters are usually preserved for the polymers without fatty acids or vegetable oils. All of these components can be extracted from renewable resources with the final biobased content up to 100%. Alkyd resins alone may be not able to meet both environmental challenges (e.g. low VOC) and property requirements. Hybrid alkyds have been developed by modifying or blending alkyds with various chemistries or resins to form acrylic-alkyd, urethane-alkyd, epoxy-alkyd, silicone-alkyd and amide-alkyd [3]. However, alkyds provide limited performance and do not meet performance requirements of many industrial coatings. Industrial coatings often require thermoset resins of structurally well controlled polymers such as linear or branched polyesters, and multifunctional acrylics. Epoxy resin is another type of popular resins, however, 90% of which is produced from petroleum-based bisphenol A. Biobased epoxy resins can be produced from the epoxidation of vegetable oil, renewable phenols (e.g. cardanol), lignin, biomass-derived platform monomers (e.g.
glycerol, sorbitol, terpenoids, furan, isosorbide), etc [4], [5], [6]. So far, biobased epoxies have not shown attractive cost/performance profiles. Biobased benzoxazine resins are relatively new thermoset resins, which are produced from phenols, primary amines and aldehydes via Mannich condensation reactions. Benzoxazine precursors come from various biobased compounds including lignin derivatives, cardanol, urushiol, etc [4]. Although biobased coatings continue to play an important role in the coating businesses, they only account for 1% in volume of total coating market in 2020 [7]. Similarly, various biopolymers or biobased resins with desired functional groups are applied in adhesive applications, including starch derivatives, proteins from plants and animals, plant oils and derived polyols, and lignin phenols [8].

Petroleum-based polyester polyols are important resins used in thermoset coatings and adhesives including solvent-borne coatings, water-based coatings, UV-cure coatings, powder coatings, and hot melt adhesives. Polyester resins are synthesized from co-monomers including dicarboxylic acids, diols, and multifunctional co-monomers. Thanks to the variability of polymer compositions, polyesters properties and structures can be readily tuned for target applications and performance, such as thermal properties, flexibility, hardness, adhesion strength, chemical resistance, abrasion resistance, impact resistance, etc. Coupling with different crosslinking chemistries (epoxy, melamine, urethane, silane, UV-cure), coatings and adhesives can be formulated for numerous applications. By introducing biobased monomers to polyester backbones, biomass content of final formulations may be significantly increased. Moreover, the oxygenated monomers (e.g. diols, diacids) may be more cost-effective to be produced from biomass sources than fossil resources because of inherent oxygen content in biomass.
1.2 Biobased, biodegradable, and recyclable thermoplastics

Polyolefins (e.g. low-density, high-density polyethylene, polypropylene) are the most widely used thermoplastics in variety of applications. However, most polyolefins are not successfully recycled and reused. Polyolefin single use plastic packaging film – such as found in food packaging - is particularly challenging to recycle. These packaging films are often made from low or linear low-density polyethylene in multilayer structures with other polymers, contain various polymer additives and require precise molecular structures for processability. Mechanical (isolation and re-extrusion) recycling of these materials results in unacceptable levels of cross contamination and property degradation, precluding their successful and cost-effective reuse. In fact, the industry only manages to recycle 9% of plastics, and realistically only high-density polyethylene and polyesters (e.g. PET bottles) are recycled [9]. These plastics are mostly used in simple, single component structures where cross contamination with other polymers, additives and other ingredients is limited and where the parts can be easily isolated.

Chemical recycling (hydrolysis, glycolysis, and methanolysis) where the polymer is broken down to the monomers and repolymerized, dissolution-based recycling, thermal decomposition (pyrolysis), liquefaction, and gasification are attracting much attention because these routes hold the potential of breaking the polymers down to monomers which can be purified and subsequently repolymerized to high quality polymers, avoiding the cross contamination issues found with mechanical recycling [9].
As a result of the difficulties with recycling conventional plastics, 16% of plastics are incinerated and 76% are landfilled. Plastics that escape from the waste management system often ultimately enter the aquatic ecosystem, including rivers and oceans. To reduce plastic pollution, governmental interventions may include mandates to reduce and substitute plastics (e.g. with paper, and compostable materials), and recycle used plastics. However, even if these interventions are implemented in a timely manner, the mass of plastic pollution between 2016 and 2040 will still reach to 250 million metric tons in aquatics and 460 million metric tons in terrestrial systems, among which flexible plastics account for a large fraction of total plastic pollutions [10].

Furthermore, single-use LDPE products easily escape into natural environments because these materials are immediately disposed after use. These LDPE polymers consist of continuous C-C bond backbone and therefore are resistant to degradation in natural environments. The estimated half-lives of LDPE 100 μm films (the conversion of 50% of polymer mass and specific degradation rates were estimated from previously reported results) in landfill are about 4.6 years and in marine environments are 1.4 - >2500 years (>2500 years indicating no measurable degradation) [11]. Further evidence shows LDPE with 60 μm thickness only partially degraded on the surface over 32-year bury in natural soil [12]. Under UV exposure by accelerated weathering, semi crystalline polyethylene can be degraded via surface fragmentation to generate nano particles and then agglomerate to form polar micro plastics in aquatic environments during an equivalent 1.5 years of outdoor weathering [13]. Therefore, it is critical to develop plastics with the ability to be degraded in landfills, controlled composting environments, or aquatic environments. Biodegradable plastics including PLA, polyhydroxybutyrate
(PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polycarbonate (PCL) or starch-based polymers are estimated to be degraded much faster (half-lives in landfill: 0.035-2.5 years, in marine: 1.7-6.7 years) than conventional LDPE in landfill and aquatic environments [11].

Poly (butylene adipate-co-terephthalate) (PBAT) is a synthetic biodegradable polyester recently introduced as an alternative to polyethylene. When degraded in aquatic environments with UV pre-treatments, PBAT mechanical properties were reduced more significantly than LDPE; PBAT suffered 70% reduction in tensile strength and 60% reduction in extensibility, while LDPE suffered 40% and 30% reduction respectively. This is because UV exposure caused the photooxidation to generate carbonyl groups and these oxidative components migrated into water from films, whereas LDPE underwent this process much slower than PBAT [14]. Without UV treatments, PBAT and LDPE may degrade much slower, for example, PBAT powders with high specific surfaces only degraded <2% in anaerobic and aerobic aquatics within 150 and 55 days respectively [15]. In industrial composting environment, bioplastics such as PBS, PBAT, PCL, PLA, and PHB, can be degraded up to 90% within 45-200 days, much faster than conventional LDPE [16].

However, biodegradable plastics only comprise less than 1% of total plastics in 2020 due to their relatively poor properties and/or high cost. Therefore, there are still demands to further improve physical properties, degradability, increase renewable content, and reduce cost. On the other hand, the replacement of conventional polyolefins with polyesters opens the possibility to chemically recycle plastics because polyesters
have the cleavable carbon-oxygen bonds. The depolymerization of single polyesters or mixed polymers (e.g. PET, PLA, PBS, PBAT, PCL, and polycarbonates) allow plastic wastes to be converted into original monomers or value-added chemicals [17]. The chemical recycling may solve the challenges associated with collecting polymers for mechanical recycling, otherwise these hard-collected plastics are destined for disposal. Therefore, polyesters are promising alternatives to polyolefins from the perspectives of biodegradable, recyclable, and biobased.

This thesis will focus on the polyesters derived from (biobased) 1,5-pentanediol with applications in thermoset coatings, adhesives, and biodegradable plastics.

1.3 Biomass derived diols (1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol) and polyesters

![Diagram of biomass derived diols and polyesters]

Figure 1.1. 1,5-pentanediol feedstock chemicals from petroleum and biomass
Polyesters are synthesized from various monomers including dicarboxylic acids, diols, and multifunctional co-monomers. Although a wide variety of commodity chemicals are produced from petroleum, some highly oxygenated chemicals (e.g. 1,3-propanediol, 2,5-furandicarboxylic acid) have been synthesized from bio-based feedstocks (Figure 1.1). In addition to polyesters, polymer materials such as polycarbonates and polyurethanes, made from bio-based monomers also draw increasing attention from researchers. In this section, I will briefly introduce three diols, and polyesters derived therefrom. Based on economics and performance enhancements, our work will principally focus on 1,5-pentanediol based polymers.

1.3.1 1,4-Butanediol (BDO)

BDO can be produced via numerous methods by using petroleum-based chemicals such as acetylene, propylene oxide, butadiene, and butane, via traditional Reppe process, Lyondell process, Mitsubishi-Kasei process, Huntsman process and Davy process. [18]. Biobased BDO has been produced from sugar via engineered E. coli [19], produced from hydrolysis of erythritol that is fermented from glucose [20], synthesized via hydrogenation of fumaric acid from furfural [21], or synthesized from tetrahydrofuran from furfural [22]. Moreover, biobased BDO has been commercialized by Genomatica, and more companies are entering this market such as Cargill and HELM. The applications of BDO include the manufacturing of engineering plastics, i.e. polybutylene terephthalate (PBT), polyurethane in the leather industry, and hot melt adhesives. The fast crystallization rate of PBT allows the resins to be processed by injection molding to
produce durable goods at high yields with applications including electronic and communications equipment, kitchen and household appliances, industrial equipment, etc. Another less common BDO-based plastic is polybutylene succinate (PBS), a type of biodegradable aliphatic polyesters, and its applications include mulching films, compostable bags, nonwoven sheets, and garments, catering goods, and foams. Another BDO-based biodegradable polyester is poly (butylene adipate-co-terephthalate) (PBAT), which have been applied in packaging industries to partially replace low-density polyethylene products. However, BDO-based polymers suffer insufficient properties such as the brittleness of pure PBS and low tensile modulus of PBAT. To boost its properties for different purposes, PBS are usually modified and treated by various methods including copolymerization with other polymers, surface alteration, addition of additives or fillers, etc [23]. PBAT is blended with starch or rigid polymers to extend its applications. According to the techno-economic analysis based on Genomatica’s route, the minimum selling price of biobased BDO is $1,820/ton, lower than petroleum-based BDO $2,500/ton [24].

1.3.2 1,6-Hexanediol (HDO)

HDO is commercially produced from benzene through numerous reaction steps with low conversion (~60%), high separation and recycle costs, which use flammable solvents and release N₂O as a byproduct [25]. The HDO market is expected to grow up to $1.4 billion by 2025 at a compound annual growth rate (CAGR) of 8% [26]. Biobased HDO has been synthesized from cellulose by academic and industrial researchers [27].
However, biobased HDO has not been commercialized due to its high cost. HDO is commonly used to synthesize polyester polyols with applications in adhesives, elastomers and coatings including hot melt adhesives, powder coatings, solvent-borne coatings, water-based coatings, and UV-cure coatings [28], [29]. Polyesters containing HDO impart cured coatings with desired flexibility and formability [30] [31] [28], behave as flow modifiers in powder coatings to improve surface levelling [32], and are formulated into adhesives to generate adhesion strength. However, 1,6-hexanediol market price is about $2,500 - $4,500/ton.

1.3.3 1,5-Pentanediol (PDO)

PDO is currently produced by glutaric acid hydrogenation [33]. The 5-carbon glutaric acid is only made in limited quantities as a byproduct during cyclohexanol and cyclohexanone (KA oil) oxidation to adipic acid. No current process exists to produce PDO on purpose. Recently, researchers have reported a new low-cost process to produce bio-based PDO (Bio-PDO) from furfural [34], [2]. Due to the high cost of existing PDO, only a limited number of studies have employed PDO as a component of polyols, most of which were for polycarbonate-derived polyurethanes. Polycarbonate polyols containing PDO or mixture of PDO with 1,6-hexanediol (HDO) have been commercialized by Ube Industries, Ltd, and Caffaro Industrie S.p.A. because of their superior performance in high-value products. For example, PDO was used as a building block in polycarbonate polyols and a chain extender in polyurethane elastomers with high transparency, flexibility, water resistance, chemical resistance, and excellent mechanical properties.
PDO based polycarbonate polyols were also formulated into high-performance polyurethane coatings with excellent abrasion resistance and aging resistance [39]. The very recent availability of low cost biobased PDO is motivating our studies to explore its utility in a wide range of applications. The minimum selling price of Bio-PDO is $1,973/ton, which is lower than the market price of petroleum-based PDO ($5,000/ton) and HDO, and competitive with BDO price [2]. Due to the emerging cost-effective Bio-PDO, the demand of this monomer may increase after exploratory research.

1.4 Synthesis of polyesters

![Diagram of polyester synthesis](image)

**Figure 1.2.** Synthesis of low molecular weight and high molecular weight polyesters

In this thesis, polyesters are synthesized by esterification and transesterification reaction at melt state. Figure 1.2 describes a general synthesis route for polyesters by melt polymerization. The equilibrium constant, K, of esterification is typically 1-10 and K value of transesterification is about 0.1-1 [40], indicating the polymerization (molecular weight) is limited by the reaction equilibrium. Therefore, polyesters are usually
synthesized in open systems to continuously remove by-product, such as water or diols, by high temperature, reduced pressure or nitrogen purging to move the reaction forward.

1.4.1 Key factors in synthesis

1.4.1.1 Monomer feed ratio

To synthesize low molecular weight polyester polyols with applications in thermoset coatings and adhesives, excess diols to diacids is initially charged into reactor to ensure majority of polyester chains ending with two hydroxyl groups. These hydroxyl groups are reactive functional groups that are able to react with isocyanates, melamine resins, and epoxy resins typically used in thermoset applications. Excess diols also decrease the intramolecular cyclization of polyester chain as shown in Figure 1.3. In addition, as Figure 1.4 shows, the ratio of diols to diacids also influences reaction rate of esterification, measured by carboxyl groups conversion rate \( X \) at \( \frac{n_{\text{hexanediol}}}{n_{\text{adipic acid}}} = 1.2 \) is obviously greater than \( \frac{n_{\text{hexanediol}}}{n_{\text{adipic acid}}} = 1.1 \) [41].

Figure 1.3. (a) Extra diols to diacids generate OH ends, (b) Equivalent moles of diols and diacids causing intramolecular cyclization
Figure 1.4. Conversion of carboxyl group (X) as a function of time at $n_{\text{hexanediol}}/n_{\text{adipic acid}}=1.1, 1.2$ and 1.5 (Figure derived from ref. [42])

1.4.1.2 Reaction temperature

Reaction temperature has large effects on reaction kinetics, polyester stability, and final product quality. High temperature is required to melt all components to form a homogeneous low-viscosity phase, which facilitates the diffusion and removal of by-product (e.g. water, diols). On the other hand, based on Arrhenius equation, $\ln k = -\frac{E_a}{RT} + \ln k_0$, reaction rate constant, $k$, increases with temperature. [43], [42] However, appropriate temperature is necessary to minimize side reactions such as dehydration of diols, β-scission of polyester and thermooxidative degradation which causes discoloration of polymers. For example, poly (ethylene terephthalate) exposed at 280°C discolored due to the formation of cyclic oligomers by elimination of diethylene glycol, terephthalic acid or water and hydroxylation of terephthalic ring. [44]
1.5 Overcome reaction kinetic limitation

When targeting high molecular weight (MW) for thermoplastic applications, the melt viscosity of polymers increases continuously with MW, which causes the residual diols that terminate the polymers (note premature termination leads to low molecular weight) ends more and more difficult to be removed. Removing these diols during the polymerization is critical to achieving high MW. To overcome the mass transfer limitation from high melt viscosity, multiple methods have been applied to boost MW. These methods may originate from two mechanisms, utilizing highly reactive chemistries to couple short polymer chains into higher MW chains and decreasing the diffusion path of by-products (e.g. diols) in order to reduce premature chain termination and allow the polymer chains to achieve high MW.

The first method is chain extension. Prepolymers with low or medium MW and terminated with various reactive functional groups, e.g. hydroxyl groups and carboxyl groups are synthesized first. By bridging these reactive end groups of different macromolecular fragments, the MW can be increased rapidly. The chain extenders typically have highly reactive functionalities including isocyanate functionality or anhydride functionality that primarily reacts with hydroxyl groups, epoxy functionality that reacts with both hydroxyl and carboxyl groups, or oxazoline functionality for the reaction with carboxyl groups. For example, high MW PBAT has been synthesized by extending PBAT prepolymers with hexamethylene diisocyanate at melt state and the resulting polymer achieved MWs of 125KDa to 232KDa, even if the polydispersity became broader (PDI=4) [45].
Secondly, solid-state (and more recently thin film) polymerization has been extensively exploited in industry to facilitate removal of chain-terminating species and increase MW. Polymer prepolymer with low or medium MW are synthesized by melt polymerization, and then powders, chips or pellets of these prepolymer are prepared and transferred to a solid-state polymerization reactor. Solid-state polymerization is usually conducted under relatively mild conditions, e.g. at a temperature between polymer glass transition temperature and melting point and in the presence of inert gas flow or under vacuum, which attributes to fewer side reactions and less thermal degradation [46], [47]. Due to the high surface area of polymer powders, chips or pellets, the diffusion path of by-product is largely reduced so that the ultra-high MW can be achieved. By using solid-state polymerization, PET with intrinsic viscosity of 5 dL/g (number average MW of 400KDa) has been successfully produced at 240°C under fast flow of nitrogen [47]. Other methods include thin-film polymerization, swollen state polymerization and solution polymerization. By utilizing thin-film polymerization, thin layer (1mm, 2mm, and 4mm) of PET prepolymer melts were heated under high vacuum for polycondensation reaction and the higher MW was achieved at thinner layers and higher vacuum. As a continuous version of the thin-film polymerization, high molecular weight PET resins were continuously synthesized in a rotating disk polymerization reactor where a thin layer was continuously generated by the rotating equipment [48]. For solvent-assisted post-polymerization (e.g. swollen-state and solution polymerization), low or medium MW polyesters are either swollen by solvents or completely dissolved in high boiling point solvents and transesterification reaction was conducted at high temperature along with by-products being continuously steamed out by nitrogen [49]. The added
solvents enhance the end group mobility, improve the by-product diffusion and therefore increasing MW.

1.6 Odd-even effects

Although the odd diol, 1,5-pentanediol (PDO), has only one carbon difference with even diols, 1,4-butanediol and 1,6-hexanediol, it can cause large difference in macro properties of final polyesters. Therefore, it is critical to understand the odd-even effects, which are the influence of odd and even co-monomers (diols, diacids) on polyester properties including thermal transitions, crystalline structures, crystalline behaviors, and mechanical properties.

![Graph showing Glass transition temperatures (Tg) and melting temperatures (Tm) of polyesters synthesized from 1,6-adipic acid with C2-C6 diols (Data from ref. [50])]
Figure 1.6. Peak melt temperature ($T_m$) and crystallization temperature ($T_c$) of polyesters synthesized from 1,12-dodecanedioic acid with C2-C10 diols (Figure derived from ref. [51])

Figure 1.7. Melt temperature ($T_m$) and crystallinity ($X_c$) of polyesters synthesized from 1,5-pentanediol with C4-C12 diacids (Data from ref. [52])
Figure 1.8. Melt temperature ($T_m$) of polycarbonates containing 6 to 12 methylene units ($n_{CH_2}$). (Figure derived from ref. [53])

Figure 1.9. Wide-angle X-ray scattering patterns (2θ) of polyesters synthesized from 1,12-dodecanedioic acid with C4-C10 diols (Figure derived from ref. [51] Red and black points represent {200} and {110} planes respectively).

As Figure 1.5 shows, melting temperatures of adipate polyesters synthesized from ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol and 1,6-hexanediol show a zig-zag fluctuation [50]. Moreover, adipate polyesters based on C3 diol exhibit slower a crystallization rate than C2 and C4 diols as measured by half-crystallization time.
Similar zig-zag trend is also observed in 1,12-dodecanedioic acid-based polyesters synthesized from C2-C10 diols, while overall Tm increases with diol chain length as Figure 1.6 shows [51]. However, the odd-even effect on Tm cannot be generalized to all co-polymer compositions. As Figure 1.7 shows, the crystallinity and Tm linearly increase with the carbon number of diacids except for poly (pentylene glutarate) (glutarate is a 5 carbon dicarboxylate), which exhibits a lower Tm versus the trend [52]. Similarly, as Figure 1.8 shows, Tm of polycarbonates with 6 to 9 methylene units exhibit a zig-zag fluctuation, however, Tm linearly increases with methylene unit number from 10 to 12 [53]. The zig-zag fluctuation is because polyesters synthesized from even-carbon monomers can be aligned more regularly than synthesized from odd-carbon monomers. According to molar melt transition function, the equilibrium melting temperature comes from group contributions and interactions between structural groups which are largely affected by odd-even co-monomers [53]. From the microstructure perspectives, as shown in Figure 1.9, the odd-even effect on Tm (zig-zag fluctuation) is attributed to the different interplanar spacing, d-spacing, of crystalline cell ( $d \sim 1/\sin \theta$ ), and molecular conformations (different ratios of trans- and gauche-related conformations) [53], [51]. With further increase in carbon chain length of co-monomers, Tm increases continuously but becomes less dependent or independent of odd-even co-monomers because smaller ester density in longer repeating units behaves more like linear polyethylene (orthorhombic crystal) [53], [52]. Previous studies also show, with same carbon number in repeating units, a polyester synthesized from C6 diol with C6 diacid exhibits higher Tm and melting enthalpy than polyester synthesized from C7 diol and C5 diacid.
Figure 1.10. Tensile modulus of polyesters synthesized from 1,12-dodecanedioic acid with C2-C10 diols. (All tensile specimens were prepared by press-molding. Data from ref. [51])

Figure 1.11. Tensile modulus of polyesters synthesized from 1,5-pentaneidol with C9, C10, and C12 diacids. (All tensile testing specimens were prepared by press-molding. Data from ref. [52])
The odd-even effects were also observed in tensile modulus similar to Tm zig-zag trend; co-polyesters with odd carbon number in repeating units had lower moduli than even carbon number in repeating units, which is attributed to the different crystallinity as discussed above. As Figure 1.10 shows, tensile moduli of polyesters synthesized from C12 diacids with C5-C10 diols exhibited zig-zag trend [51]. Furthermore, the tensile moduli of polyesters synthesized from 1,5-pentanediol with C9, C10, and C12 diacids increase from 254 MPa to 344 MPa with carbon number of diacids, which is attributed to the increase in crystallinity as shown in Figure 1.7 [52].

1.7 Current 1,5-Pentanediol-based aliphatic, and aromatic polyesters

![Figure 1.12](image.png)

**Figure 1.12.** Aliphatic polyesters synthesized from 1,5-pentanediol with various diacids, m=2-10.

Aliphatic polyesters were previously synthesized using various aliphatic dicarboxylic acids with different chain length (carbon number: 4, 5, 6, 7, 9, 10, 12) copolymerized with 1,5-pentanediol [52] as depicted in Figure 1.12. As discussed above, odd-even effects may have influence on aliphatic polyesters thermal transitions, microstructures, and mechanical properties. In addition, poly (pentylene adipate) (PPA)
exhibited the worst thermal stability, which may account for the relatively lower molecular weight of PPA than other aliphatic polyesters during melt polymerization [52]. These aliphatic polyesters have comparable tensile properties to linear low-density polyethylene, however, their hydrolytic instability and low melt temperatures (20 – 60°C) may limit their applications.

![Figure 1.13. Polymer structures of aromatic polyesters synthesized from various diols with terephthalic acid, m=2-6.](image)

Aromatic polyesters are copolymers of aliphatic diols with aromatic diacids and include poly (ethylene terephthalate) (PET), poly (trimethylene terephthalate) (PTT), poly (butylene terephthalate) (PBT), poly (pentamethylene terephthalate) (PPT), poly (hexamethylene terephthalate) (PHT), etc, as described in Figure 1.13. They are characterized by their superior thermo-mechanical properties. However, PPT has not found wide applicability due to its unacceptably low melting temperature and resulting inferior mechanical properties. Previous studies show that terephthalate esters exhibited decreasing Tm and glass transition temperatures with increasing diol carbon length (carbon number=2, 4, 5, 6, 10), except that PPT had a lower Tm than terephthalate esters based on C4 and C6 diols [54], [55]. In addition, PPT crystallizes slowly from melt state under both non-isothermal and isothermal crystallization conditions; the higher
crystallinity (Xc) can be acquired at lower cooling rates at non-isothermal crystallization (Xc=17.3% at 5°C/min cooling vs Xc=0.7% at 15°C/min cooling) and half crystallization time is longer at higher isothermal crystallization temperatures (t₁/₂=3.9 min at 60°C, Xc=21% vs t₁/₂=17.4 min at 100°C, Xc=22%) [56].

![Graph showing Young's modulus changes](image)

**Figure 1.14.** Young’s modulus changes with number of methylene groups in diols for (●) terephthalate series; (▲) isophthalate series; (■) copolyester series; (Figure derived from ref. [55])

Compared to injection-mold specimens of PET, PTT and PBT, PPT has lower modulus (0.65 vs 1.1-3.0 GPa), tensile strength (21 vs 50-70 MPa) but higher elongation (450% vs 4-500%) [56]. Similarly, as Figure 1.14 shows, elastic moduli of terephthalate esters compression films decreased with diol chain length increasing from C2 to C10 [55],
which may be attributed to microstructures (crystallinity, crystalline thickness) of different polyesters. While aromatic polyesters usually have high mechanical properties, the continuous aromatic ester sequences in the polymer backbone make these polymers resistant to degradation.

1.8 Biodegradation of polyesters

![Figure 1.15. PBAT aliphatic-aromatic polyesters. m represents mole fraction of aliphatic units and n represents mole fraction of aromatic units.](image)

Aliphatic-aromatic polyesters may combine acceptable mechanical properties and degradability for degradable or compostable thermoplastics applications. As an example, poly (butylene adipate-co-terephthalate) structure is depicted in Figure 1.15. Biodegradation of aliphatic-aromatic polyesters may involve three stages: biodeterioration, biofragmentation, and assimilation, with consideration of abiotic factors (mechanical, light, thermal, chemical degradation) [57]. Long polymer chains are first disintegrated into small segments (monomer, dimer, or oligomers), followed by the assimilation of the decomposed polymer by means of microbials and its mineralization which creates CO2, and H2O (with CH4). The biodegradation rate depends on various factors including the aromatic contents, degradation environment (e.g. temperature, microorganisms), molecular weight, etc. For example, the higher aromatic contents are,
the higher the melting temperature and crystallinity, the lower biodegradation rate; degradation rate of PBAT decreases from 1.2 to 0.6 mg/(week cm²) when aromatic content increased from 34% to 48% [58]. This is because biodegradation proceeds more preferentially in amorphous regions and rigid chains with low mobility are difficult to penetrate into microorganisms [59]. The degradation is also affected by environment temperature. The temperature between the Tm of polymers and degradation testing temperature, Tt ((ΔTmt=Tm-Tt), indicates the chain mobility. Previous study shows the biodegradability of poly (hexylene adipate-co-terephthalate) (PHAT) with 60% terephthalic acid exhibited 50% weight loss, however, PBAT with 60% terephthalic acid didn’t degrade within 16 weeks. This can be explained by the lower melting temperature of PHAT than PBAT at the same aromatic content, thus smaller ΔTmt and higher mobility of PHAT. Over wide range of PHAT and PBAT compositions, the biodegradation rate decreases with the increasing ΔTmt [60].

![Figure 1.16. Structures of PBAT aromatic sequence length = 3, three continuous BT linkages connected to aliphatic units on both ends.](image)

After primary disintegration (e.g. by hydrolysis) of long co-polyesters into small segments, the degradation rate of residual oligomers may depend on the continuous aromatic unit length. Aromatic model oligomers (poly (propylene terephthalate)s, PPT with 1-6 repeating units) were studied in soil, composting environment, and water [61].
In soil at ambient temperature, only PPT with 1 and 2 repeating units were degraded within 8 weeks. In composting environment, not only PPT oligomers with 1-2 repeating units readily degraded within 12 weeks, but oligomers with 5-6 repeating units also degraded and shifted to shorter oligomers with 3-4 repeating units. This may be attributed to relatively high temperature (60°C), higher microorganism activities, or other active components in composting environment facilitated the degradation. Based on these model oligomers, in statistic aliphatic-aromatic co-polyesters, aromatic sequence length (number-average block length) less than 3 is determined for readily biodegradability. Figure 1.16 shows the aromatic sequence length of PBAT equals to 3. Furthermore, PBAT can be totally degradable in thermophilic strain which is isolated from compost material, even if it contains approximately 9% contents with an aromatic sequence length >=3 [62].

The previous research will guide us to choose co-polyester compositions for good thermo-mechanical properties and meanwhile promising biodegradability.
CHAPTER 2

OBJECTIVES

According to the discussions in Chapter 1, 1,5-pentanediol has not been widely investigated and applied in polyesters due to its high cost and uncertain properties in final products. With the advent of low-cost 1,5-pentanediol, investigation of its use in polyesters is timely and warranted. Our objectives include two major applications, thermosets and thermoplastics as described below.

Object 1: Biomass-based 1,5-pentanediol as a replacement for 1,6-hexanediol for polyester polyols, coatings, and adhesives

Objective 1 is to apply biobased 1,5-pentanediol (Bio-PDO) for coatings and hot melt adhesives applications to replace petroleum-based 1,6-hexanediol (HDO). I first synthesized low molecular weight polyester polyols using Bio-PDO and HDO respectively and formulated these polyols into coating and adhesive formulations to compare the properties of Bio-PDO-based and HDO-based coatings and adhesives. The effects of impurities commonly found in biobased monomers on polyol functionality and thermal properties were also investigated.

Object 2: Biodegradable high molecular weight poly (pentylene adipate-coterephthalate): synthesis, thermos-mechanical properties, microstructures and biodegradation.
Objective 2 is to design, synthesize and characterize PDO-based aliphatic-aromatic polyesters for the applications in biodegradable plastics. By utilizing melt polymerization, chain extension or thin-film polymerization, high molecular weight poly (pentylene adipate-co-terephthalate) polyesters were successfully synthesized. The thermal transitions, microstructures, and biodegradability in soil were investigated. The new polyesters were compared with petroleum-based poly (butylene adipate-co-terephthalate) and low-density polyethylene.
CHAPTER 3

BIO-BASED 1,5-PENTANEDIOL AS A REPLACEMENT FOR PETROLEUM-DERIVED 1,6-HEXANEDIOL FOR POLYESTER POLYOLS, COATINGS, AND ADHESIVES

This chapter was adapted with permission from Lei Zheng, Daniel J. McClelland, Kelsi M.S. Rehmann, Kevin J. Barnett, George W. Huber, John Klier. Bio-based 1,5-Pentanediol as a Replacement for Petroleum-derived 1,6-Hexanediol for Polyester Polyols, Coatings, and Adhesives. ACS Sustainable Chemistry & Engineering, 2022, 10, 18, 5781-5791. L. Z. contributed to conceptualization, data curation, formal analysis, investigation, methodology, validation, visualization, and writing; J. K. and G. W. H. contributed to conceptualization, project administration, supervision, and writing; D. J. M. and K. J. B. contributed to conceptualization, resources, and writing; K. M.S.R. contributed to conceptualization, validation, and writing.

3.1 Abstract

Amorphous and semi-crystalline polyester polyols based on a novel, low cost, bio-based 1,5-pentanediol (Bio-PDO) were synthesized and formulated into solvent-borne coatings and hot melt adhesives. Bio-PDO may provide a lower cost, more sustainable and non-petroleum-based alternative to polyols based on 1,6-hexanediol (HDO). The polyester polyols were characterized for end group composition, monomer incorporation and thermal transitions. Bio-PDO-based coatings exhibited similar
performance, including hardness, flexibility, adhesion strength, and solvent resistance, to the coatings based on petroleum-derived HDO. Bio-PDO-based adhesives exhibited lower green strength (initial adhesion strength) and longer open time (workable time to bond substrates) than HDO-based adhesives. The effects of common bio-based impurities, including lactones and mono-alcohols (delta-valerolactone and tetrahydrofurfuryl alcohol as examples of impurities), on polyester polyols were investigated. Hydroxyl functionalities of polyols were controlled by the excess diols in monomer feeds and were not impacted largely by the delta-valerolactone levels. High-level tetrahydrofurfuryl alcohol terminated the polyester ends with unreactive functionality. Deleterious effects on polyol hydroxyl functionality are not expected at the low impurity levels (<2 wt%) found in leading Bio-PDO processes.

3.2 Introduction

1,6-hexanediol (HDO) is a commonly used monomer in polyester polyols with applications in adhesives, elastomers and coatings including hot melt adhesives, powder coatings, solvent-borne coatings, water-based coatings, and UV-cure coatings [28], [29]. The HDO market is expected to grow up to $1.4 billion by 2025 at a compound annual growth rate (CAGR) of 8% [26]. Polyesters containing HDO impart cured coatings with desired flexibility and formability [30] [31] [28], behave as flow modifiers in powder coatings to improve surface levelling [32], and are formulated into adhesives to generate adhesion strength. HDO is commercially produced from benzene through numerous reaction steps with low conversion (~60%), high separation and recycle costs, which use flammable solvents and release N₂O as a byproduct [25]. Biomass-derived monomers are
drawing increased attention from researchers due to reduced reliance on petroleum feedstocks and improved sustainability. For example, 1,3-propanediol produced via microbial glucose fermentation has been used in solvent borne [63], water borne, powder [64], [65], and UV-cure [66] coatings to replace HDO and neopentyl glycol. [67] Non-crystalline polyols synthesized with 1,3-propanediol were also evaluated in hot melt adhesive formulations where mixtures of crystalline and non-crystalline polyols imparted adhesives with tunable green strength and final strength. [68] Compared with longer chain diols (e.g. 1,5-pentanediol and 1,6-hexnaediol), 1,3-propanediol may provide coatings with higher hardness, lower flexibility and lower hydrolysis resistance. [66], [67], [69]

Polymer thermal properties are extremely important for coatings and adhesives applications. In similar formulations, the lower the glass transition temperature (Tg) of polymer soft segments, the more flexible and the softer the coatings and adhesives [28], [63], [70], [71]. Previous studies showed an inverse relationship between carbon atom sequence length of linear diol or diacid monomers and their polymer Tg [72], [73]. In addition, Tg is affected by the polymer structure, for example, poly (1,3-propylene adipate) exhibited lower Tg than poly (ethylene adipate) and poly (1,4-butylene adipate) [74], likely due to weaker interactions among poly (1,3-propylene adipate) polymer chains. Therefore, the replacement of HDO with PDO may slightly change the Tg of their polyesters because of combined factors including carbon atom sequence length and interchain interaction. On the other hand, PDO based semi-crystalline polyesters, such as poly (pentamethylene terephthalate) and poly (pentamethylene adipate) exhibited lower melting temperatures, lower melting enthalpies and slower crystallization rates than HDO
based counterparts [72], [75]. Crystallization rates, crystallization enthalpies, and crystallite contents affect the green strength and open time of hot melt adhesives [68], [76], [77]. The faster the polymers crystallize, the greater the green strength and the shorter the open time.

PDO has not been widely studied as a diol monomer in polyols for coatings and adhesives due to its limited availability and high cost. PDO is currently produced by glutaric acid hydrogenation [33]. The 5-carbon glutaric acid is only made in limited quantities as a byproduct during KA oil (cyclohexanone and cyclohexanol) oxidation to adipic acid. No current process exists to produce PDO on purpose. Recently, we have reported a new low cost process to produce bio-based PDO (Bio-PDO) from furfural. [34], [2]. An economic analysis shows that this route can produce Bio-PDO at costs 30-50% lower than the price of HDO. [2], [1] However, bio-based monomers may contain various impurities, including lactones, mono-alcohols, and secondary alcohols, depending on catalyst types, temperatures, reaction times and purification processes. [78], [79], [38]. For example, 4-490 ppm gamma-butyrolactone and 816-1123 ppm 2-(4’-hydroxybutoxy) tetrahydrofuran were observed in 1,4-butanediol synthesized using microbial organisms. [80] 0-1.25% delta-valerolactone existed in Bio-PDO, [38] and mono-alcohols, such as 1-propanol, 2-propanol and 1-hexanol, were observed in biobased 1,3-propanediol and 1,6-hexanediol. [81], [82] The effect of these impurities on polyols reactivity and properties are largely unknown. Polyester polyols could potentially be terminated by mono-alcohols, reducing their reactive functionalities, which could cause imperfections in final polyurethane networks and lower mechanical properties [83]. Secondary hydroxyl groups are less reactive than primary hydroxyl groups, and thus the majority of secondary
hydroxyl groups may locate at chain ends [84], which could result in lower reactivity for further polycondensation with polyisocyanates and limit the molecular weight of polyurethanes [85]. Lactones can be polymerized via ring-opening polymerization associated with several mechanisms, such as anionic, coordination, cationic polymerizations [86], which cause polymers with different functional end groups including hydroxyl groups, ester groups, ether groups [87], [88].

Only a limited number of studies have employed PDO as a component of polyols, most of which were for polycarbonate-derived polyurethanes. Polycarbonate polyols containing PDO or mixture of PDO with HDO have been commercialized by Ube Industries, Ltd, and Caffaro Industrie S.p.A. because of their superior performance in high-value products. For example, PDO was used as a building block in polycarbonate polyols and a chain extender in polyurethane elastomers with high transparency, flexibility, water resistance, chemical resistance, and excellent mechanical properties. [38], [35], [36], [37] 1,5-PDO based polycarbonate polyols were also formulated into high-performance polyurethane coatings with excellent abrasion resistance and aging resistance. [39] However, (bio-based) PDO has not been widely applied in polyesters for the applications in coatings and adhesives with limited studies available in the literature. Among these, fully bio-based polyesters composed of isosorbide, 2,5-furandicarboxylic acid, and succinic acid, were described in coil coating formulations and cured coatings demonstrated tunable flexibility and hardness. [69] Kinetic modeling, process simulation, optimization and sustainability evaluation of polyfuranoates and succinates containing Bio-PDO as sole diol were investigated; the results suggested optimum process
temperature to synthesize polyesters with number-averaged molecular weight of 4.1-4.7 KDa for coil coating applications [89].

The objective of this paper was to prepare and test amorphous and semi-crystalline polyester polyols from Bio-PDO and HDO and evaluate their properties in thermoset coatings and adhesives. This is the first reported study of Bio-PDO as the main diol in coatings and adhesives and the first study on the effect of the potential impurities such as lactones and mono-alcohols on polyester polyols; delta-valerolactone and tetrahydrofurfuryl alcohol are chosen as examples of impurities. Successful demonstration of PDO’s substitution potential may provide a lower cost, more sustainable and non-petroleum-based alternative to polyols based on HDO.

3.3 Experimental section

3.3.1 Materials

Bio-based 1,5-pentanediol (Bio-PDO) was provided by Pyran, Inc. Other chemicals used for this paper along with the manufacturers include: 1,5-pentanediol (Petro-PDO, Acros Organics), 1,6-hexanediol (HDO, Sigma-Aldrich), neopentyl glycol (NPG, Sigma-Aldrich), 2-methyl-1,3-propanediol (2M13PDO, Sigma-Aldrich), trimethylolpropane (TMP, Sigma-Aldrich), adipic acid (AA, Sigma-Aldrich), isophthalic acid (IPA, Sigma-Aldrich), terephthalic acid (TPA, Sigma-Aldrich), 1,2-cyclohexanedicarboxylic anhydride (predominantly cis, HHPA, Sigma-Aldrich), dimethyl carbonate (DMC, Sigma-Aldrich), δ-valerolactone (DVL, Sigma-Aldrich), tetrahydrofurfuryl alcohol (THFA, Sigma-Aldrich), 2,4,4-trimethylhexamethylene diisocyanate (THDI, TCI), titanium tetrabutoxide (TBT, Sigma-Aldrich), polypropylene
glycol (Mn=2000Da, Alfa Aesar), dibutyltin dilaurate (Sigma-Aldrich), methyl amyl ketone (MAK, Sigma-Aldrich), butanol (Sigma-Aldrich), dipropylene glycol monomethyl ether (Sigma-Aldrich), aromatic 100 (Solvents & Petroleum Service), poly (tetrahydrofuran) (Mn=1000 Da, Sigma-Aldrich), methylene diphenyl diisocyanate (Acros Organics), Tolonate™ HDT 90 (Vencorex), Dynacoll® 7250 (Evonik), Dynacoll® 7380 (Evonik), Resimene 747 (Prefere Melamines)

3.3.2 Synthesis

As shown in Table 3.1, five classes of polyester polyols and one class of polycarbonate polyol were synthesized for the applications in coatings and adhesives. Detailed monomer feed ratios are summarized Table 3.8. In each of the five classes of polyesters, Bio-PDO-based and HDO-based polyols were synthesized. For the polycarbonate polyols, Bio-PDO-based and Petro-PDO-based polyols were synthesized. Structures of Bio-PDO-based polyols are shown in Figure 3.1. To study the effects of impurities, model polyesters were synthesized using Petro-PDO with increasing amount of DVL (δ-Valerolactone) or THFA (tetrahydrofurfuryl alcohol), with detailed monomer feed ratios summarized in Table 3.9.

Table 3.1. Compositions of polyols for coatings and adhesives

<table>
<thead>
<tr>
<th>Class</th>
<th>Sample</th>
<th>Polymer composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bio-PDO-PU</td>
<td>Bio-PDO/NPG/HHPA/THDI</td>
</tr>
<tr>
<td></td>
<td>HDO-PU</td>
<td>HDO/NPG/HHPA/THDI</td>
</tr>
<tr>
<td>2</td>
<td>Bio-PDO-AA-HHPA</td>
<td>Bio-PDO/AA/HHPA</td>
</tr>
<tr>
<td></td>
<td>HDO-AA-HHPA</td>
<td>HDO/AA/HHPA</td>
</tr>
<tr>
<td>3</td>
<td>Bio-PDO-Branched</td>
<td>Bio-PDO/2M13PDO/TMP/IPA/TPA</td>
</tr>
<tr>
<td></td>
<td>HDO-Branched</td>
<td>HDO/2M13PDO/TMP/IPA/TPA</td>
</tr>
<tr>
<td>4</td>
<td>Bio-PDO-AA</td>
<td>Bio-PDO/AA</td>
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<tr>
<td></td>
<td>HDO-AA</td>
<td>HDO/AA</td>
</tr>
<tr>
<td>5</td>
<td>Bio-PDO-AA-IPA</td>
<td>Bio-PDO/AA/IPA</td>
</tr>
<tr>
<td></td>
<td>HDO-AA-IPA</td>
<td>HDO/AA/IPA</td>
</tr>
<tr>
<td>6</td>
<td>Bio-PDO-PC</td>
<td>Bio-PDO/HDO/DMC</td>
</tr>
</tbody>
</table>
All polyesters were synthesized in 500 mL reactor vessels via esterification reaction. All raw materials were charged into reactor and nitrogen was purged for 30 mins followed by increasing the temperature to 170°C to melt the raw materials under stirring. The titanium butoxide (TBT) catalyst (1 wt% based on diacids) was added after the temperature reached 170°C with continuous stirring, followed by a stepwise temperature increase to 200°C to avoid possible discoloration and evaporation of monomers. Water formed during the esterification was removed by distillation. Water was continuously collected to monitor the extent of reaction. When 90% of the theoretical mass of water was collected, nitrogen was reconnected to help remove the remaining water until the desired acid numbers (tested by titration) were approached. To synthesize Bio-PDO-PU and HDO-PU, polyester polyol intermediates were first synthesized from Bio-PDO or HDO, NPG and HHPA following the above procedure, and then extended.
with trimethyl hexamethylene diisocyanate at 110 °C for 2.5 hours. Polycarbonate polyols synthesis followed similar procedures (Supporting information).

3.3.3 Preparation of Coatings

After synthesis, Bio-PDO-PU, HDO-PU, Bio-PDO-AA-HHPA, HDO-AA-HHPA were formulated into 2K thermoset coatings using Tolonate™ HDT 90 (hexamethylene diisocyanate trimer) as a crosslinker, which is employed in automotive topcoat formulations for use on elastomeric and metal substrates. [90], [91] The acyclic monomers (Bio-PDO, HDO, and AA), cyclic monomers (HHPA) and isocyanate moieties in polyols impart coatings with flexibility and hardness. HHPA also provides cured coatings with UV-resistance which is required by topcoat coatings. Bio-PDO-Branched and HDO-Branched were formulated into coil coatings. The diols in branched polyols (Bio-PDO, HDO and 2-methyl-1,3-propanediol) provide coatings with flexibility while isophthalic acid provides good weathering properties. The branched polyester polyols with medium molecular weights also improve flexibility and cracking resistance of coil coatings. [92], [93] Polycarbonates, Bio-PDO-PC and Petro-PDO-PC, were formulated into 2K thermoset polyurethane coating formulations designed for internal pipeline coatings with excellent adhesion strength, abrasion resistance and aging resistance due to the carbonate groups. [39] The main coating compounds are summarized in Table 3.2, and detailed information is shown in Table 3.10-3.12.
Table 3.2. Coating Formulations

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Petro-HDOF1</th>
<th>Bio-PDOF1</th>
<th>Petro-HDOF2</th>
<th>Bio-PDOF2</th>
<th>Petro-HDOF3</th>
<th>Bio-PDOF3</th>
<th>Petro-PDOF4</th>
<th>Bio-PDOF4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diol of Interest</td>
<td>HDO</td>
<td>Bio-PDO</td>
<td>HDO</td>
<td>Bio-PDO</td>
<td>HDO</td>
<td>Bio-PDO</td>
<td>HDO</td>
<td>Bio-PDO</td>
</tr>
<tr>
<td>HDO-PU</td>
<td>1.39</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Bio-PDO-PU</td>
<td>/</td>
<td>1.39</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>HDO-AA-HHPA</td>
<td>/</td>
<td>/</td>
<td>8.99</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>HDO-Branched</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>16.1</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Bio-PDO-Branched</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>16.1</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Petro-PDO-PC</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>5</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Bio-PDO-PC</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>5</td>
<td>/</td>
</tr>
<tr>
<td>Tolonate™ HDT 90</td>
<td>1.08</td>
<td>1.08</td>
<td>2.00</td>
<td>2.00</td>
<td>/</td>
<td>/</td>
<td>0.70</td>
<td>0.70</td>
</tr>
<tr>
<td>THDI</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>3.40</td>
<td>3.40</td>
</tr>
<tr>
<td>Resimene 747</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>1.63</td>
<td>1.63</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

3.3.4 Preparation of Moisture-curable Hot Melt Adhesives

Moisture-curable adhesive formulations [94] are summarized in Table 3.3. HDO-based polyesters or Bio-PDO-based polyesters were mixed with commercial polyols (polypropylene glycol, Dynacoll® 7250 and Dynacoll® 7380) at 130°C, followed by reacting with excess methylene diphenyl diisocyanate under nitrogen environment for 3 hrs. The mixture of semi-crystalline, amorphous polyester polyols, and liquid polyether polyols provide adhesive formulations with the needed green strength, adhesion strength, appropriate open time and flowability.
Table 3.3. Formulations of Moisture-curable Hot Melt Adhesives

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Petro-HDO Formulation</th>
<th>Bio-PDO Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDO-AA-IPA</td>
<td>3</td>
<td>/</td>
</tr>
<tr>
<td>Bio-PDO-AA-IPA</td>
<td>/</td>
<td>3</td>
</tr>
<tr>
<td>Polypropylene glycol</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>Dynacoll® 7250</td>
<td>1.75</td>
<td>1.75</td>
</tr>
<tr>
<td>HDO-AA</td>
<td>3.94</td>
<td>/</td>
</tr>
<tr>
<td>Bio-PDO-AA</td>
<td>/</td>
<td>3.94</td>
</tr>
<tr>
<td>Dynacoll® 7380</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Methylene diphenyl diisocyanate</td>
<td>1.56</td>
<td>1.56</td>
</tr>
</tbody>
</table>

3.3.5 Characterizations

Hydroxyl values (OHv) and acid values (Av) were tested according to ASTM D4274 Method D and ASTM D4662 Method A. ¹H NMR spectra were recorded on a Bruker Avance-III 400 MHz to characterize polymer compositions. Deuterated chloroform was used as solvent and tetramethylsilane as internal reference with signal at 0 ppm.

Thermal transitions were determined using differential scanning calorimetry (DSC) (TA Instruments Q200) with a nitrogen flow rate of 50 mL/min. The DSC temperature calibration was performed using Indium's melting point. The samples were equilibrated at -70°C for 2 mins, heated to 100°C at a rate of 5°C/min, cooled to -70°C at a rate of 5°C/min and heated to 100°C at a rate of 5°C/min. Tg, Tm and melting enthalpy were calculated from second heating ramp of DSC. Maximum of melting peaks were recorded as Tm and melting enthalpies were integrated from linear baseline.
The polyester structures were characterized by matrix-assisted laser desorption/ionization time-of-flight MALDI-TOF mass spectrometry. Polyester samples were dissolved at 10 mg/mL in tetrahydrofuran. Matrix 2,5-dihydroxybenzoic acid was dissolved at 20 mg/mL in tetrahydrofuran. The matrix and polyester sample were mixed at a ratio of 10:1, and 0.5 μL was spotted onto a stainless-steel target and dried in air. The sample was ionized by the smart beam laser (355 nm), and mass spectra were acquired from 5000 laser shots in reflection mode over the range of 900-4500 m/z. MALDI-TOF analysis was performed using a ultrafleXtreme (Bruker Scientific, Billerica MA) mass spectrometer.

The crosslinked coatings were measured using compositional and mechanical tests. To measure gel content of crosslinked coatings, the initial weight of coatings was recorded (m1). The free-standing coating films were immersed in MAK for 72 h; the MAK was refreshed three times. Next, the swollen films were taken out from the solvent and heated at 70ºC for 24 h. The weight of dried films was taken (m2). The gel content was calculated according to eq 1. The gel content was measured in triplicate for each coating and standard deviation was calculated.

\[
\text{Gel content (\%)} = \frac{m_2}{m_1} \times 100\% \quad (1)
\]

The hardness of each coating was measured using pencil hardness tester (Gardco) and pendulum hardness tester (QBY film pendulum hardness tester, AliExpress) based on ASTM D3363 and GB 1730. The coating hardness ranged from 9B, 8B to B, HB, F to 9H, which correspond to the softest to the hardest coatings. For pendulum hardness test, the films were placed on the panel table with the pendulum (120g) on the top of the film. The pendulum was deflected and released at 5º, and the number of oscillations until an
angle of 2° was reached where counted using an electronic counter. The harder the films, the larger the oscillation numbers. Flexibility was tested by a conical mandrel bend tester (BYK) based on ASTM D522. Coatings were recorded as “pass the test” if there is no cracking on coating surfaces with ½ inch far from the small end of the mandrel. Solvent resistance test was conducted according to ASTM D4752. Cured coatings were rubbed with a weight (1 kg) wrapped with a cotton cloth (Avalanche Brands, Selbyville, DE) that was saturated with methyl ethyl ketone (MEK). One forward and back rub was considered as one rub cycle, and rate was 1 rub/s. The total number of cycles required for the coatings to be completely removed from the substrate was recorded. Adhesion strength of coatings on substrates were tested according to ASTM D3359 Method B. The percent of coatings removed was recorded to compare the adhesion strength of different coating samples. These tests were conducted in triplicate for each sample and standard deviation was calculated.

Green strength, which evaluates the bond strength of adhesion before curing, was tested according to ASTM D3165. Adhesive precursors (adhesives before curing) were applied to bond two ABS (acrylonitrile butadiene styrene) substrates immediately after mixing the adhesive ingredients for 3 h under nitrogen, and to create a 2 cm by 1 cm bonded area. The thickness of adhesives was controlled to be the same for each specimen (around 0.5mm) by applying the same force on upper layer of ABS strip. After 10 mins, the specimens were clamped onto an Instron machine and pulled on two ends of specimens at a rate of 1.27 mm/min. The load per unit shearing area at failure was recorded as green strength. The nature of this failure was recorded as cohesive failure when the failure occurs within the adhesives or as adhesive failure when the failure
occurs between the adhesives and substrates. The tests were conducted in triplicate for each specimen and standard deviation was calculated. Open time, which evaluates the workable time of adhesives for bonding substrates, was tested according to modified ASTM D4497. 12 cm by 9 cm ABS sheets and 5 cm by 0.5 cm ABS strips were prepared. After the adhesive ingredients were mixed at 130°C for 3 h, adhesive precursors were applied onto an ABS sheet to create a 12 cm by 3 cm adhesive film. Immediately after the films were created, timer started. Every 30 s, one ABS strip was laid on top of the cooling film to generate 3 cm by 0.5 cm bond area and was pressed with 1 kg weight. The shortest time that the ABS strips cannot be bonded on the films was recorded as open time.

3.4 Results and discussion

3.4.1 Synthesis and Structural Characterization

By controlling the reaction time, HDO-based and Bio-PDO-based polyester polyols have similar hydroxyl values and acid values, as shown in Table 3.4. Similarly, Petro-PDO-based and Bio-PDO-based polycarbonate polyols have similar functional groups. The substitution of HDO (or Petro-PDO) with Bio-PDO allows the introduction of biomass content (21%-47%) in polyols without major changes in polyester structures and compositions as indicated by 1H NMR spectra (Figure 3.7-3.9).
Table 3.4. Biomass Content ($\Phi_{\text{bio}}$), Hydroxyl Values (OH$_v$), Acid Values (A$_v$) and Glass Transition Temperatures (Tg) and Melting Temperature (Tm) of Biomass-based and Petroleum-based Polyols

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Phi_{\text{bio}}$ (%)</th>
<th>OH$_v$ (mg KOH/g)</th>
<th>A$_v$ (mg KOH/g)</th>
<th>Tm (°C)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polyester polyols</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bio-PDO-PU</td>
<td>23.6</td>
<td>172.0</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>HDO-PU</td>
<td>0</td>
<td>163.0</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Bio-PDO-AA-HHPA</td>
<td>44.8</td>
<td>70.0</td>
<td>1.8</td>
<td>/ -49±0.4</td>
<td>/ -52±0.2</td>
</tr>
<tr>
<td>HDO-AA-HHPA</td>
<td>0</td>
<td>64.0</td>
<td>4.0</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Bio-PDO-Branched</td>
<td>21.1</td>
<td>45.0$^{b}$</td>
<td>6.2</td>
<td>/ 23±8</td>
<td>/ 29±3</td>
</tr>
<tr>
<td>HDO-Branched</td>
<td>0</td>
<td>41.0$^{b}$</td>
<td>8.2</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Bio-PDO-AA</td>
<td>46.8</td>
<td>31.7</td>
<td>1.0</td>
<td>34/41 (64J/g)</td>
<td>/</td>
</tr>
<tr>
<td>HDO-AA</td>
<td>0</td>
<td>34.3</td>
<td>0.8</td>
<td>54 (87J/g)</td>
<td>/</td>
</tr>
<tr>
<td>Bio-PDO-AA-IPA</td>
<td>44.6</td>
<td>53.8</td>
<td>0.3</td>
<td>/ -44±0.7</td>
<td>/</td>
</tr>
<tr>
<td>HDO-AA-IPA</td>
<td>0</td>
<td>47.5</td>
<td>0.6</td>
<td>/ -45±1.3</td>
<td>/</td>
</tr>
<tr>
<td><strong>Polycarbonate polyols</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bio-PDO-PC</td>
<td>41.7</td>
<td>237.0</td>
<td>0</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Petro-PDO-PC</td>
<td>0</td>
<td>257.0</td>
<td>0</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

a: $\Phi_{\text{bio}}$ was calculated from eqs 3.5-3.8

b: Hydroxyl values were tested by $^1$H NMR using benzoic acid as inner standard as shown in Figure 3.10-3.11.

### 3.4.2 Thermal Transitions (Tg, Tm) of Polyols

Comparing linear polyesters, Bio-PDO-AA-HHPA vs HDO-AA-HHPA, and Bio-PDO-AA-IPA vs HDO-AA-IPA, the substitution of Bio-PDO for HDO slightly increased glass transition temperature (Tg: -49±0.4 vs -52±0.2 °C, and -44±0.7 vs -45±1.3°C). This is because the shorter PDO is less flexible than HDO. HDO-Branched polyester had a higher Tg than the Bio-PDO-Branched polyester (29±3 vs 23±8°C), which can be attributed to more trimethylolpropane incorporated into HDO-Branched than Bio-PDO-Branched polyester (9.8% vs 8.6% ester groups from trimethylolpropane based on total
ester groups, Figure 3.10 and 3.11). The difference in the level of incorporated trimethylolpropane may have resulted from the uncontrolled monomer evaporation in different reaction temperature profiles and nitrogen flow rates. More rigorous controls on synthesis conditions may be required. The melting temperatures of Bio-PDO-AA polyesters observed in this study were 34 and 41°C, which were close to values of 35.7 and 41.8°C reported previously [95]. Bio-PDO-AA exhibited lower melting temperatures and melting enthalpies than HDO-AA likely due to the odd-even effect, which interrupts the arrangements of polymer chains in Bio-PDO-AA polyester [73].

3.4.3 Coating Results

After coatings were cured at elevated temperature, hardness, flexibility, adhesion strength, and solvent resistance tests were conducted to compare the properties of HDO based and Bio-PDO based coatings. Petro-PDO-based and Bio-PDO-based polycarbonate polyols were formulated into pipeline coating formulations. The coating properties are summarized in Table 3.5.

Table 3.5. Gel Content, Hardness, Flexibility, Adhesion Strength, Solvent Resistance and Tg of Cured Coatings Prepared from Petroleum-derived and Biomass-derived polyols

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Gel Content (wt%)</th>
<th>Pencil hardness</th>
<th>Pendulum hardness (Cycles)</th>
<th>½-inch mandrel test at -15°C</th>
<th>Adhesion to steel (% Peeled off)</th>
<th>MEK double rubs</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petro-HDOF1</td>
<td>94±0.3</td>
<td>B-2B</td>
<td>362±5</td>
<td>Pass</td>
<td>0</td>
<td>&gt;250</td>
<td>27±2</td>
</tr>
<tr>
<td>Bio-PDOF1</td>
<td>95±0.3</td>
<td>B-2B</td>
<td>367±6</td>
<td>Pass</td>
<td>0</td>
<td>&gt;250</td>
<td>33±2</td>
</tr>
<tr>
<td>Petro-HDOF2</td>
<td>87±0.2</td>
<td>&lt;6B</td>
<td>67±9</td>
<td>Pass</td>
<td>72±23</td>
<td>192±91</td>
<td>-25±0.2</td>
</tr>
<tr>
<td>Bio-PDOF2</td>
<td>87±0.3</td>
<td>&lt;6B</td>
<td>62±13</td>
<td>Pass</td>
<td>75±22</td>
<td>180±64</td>
<td>-25±0.8</td>
</tr>
<tr>
<td>Petro-HDOF3</td>
<td>89±1</td>
<td>F</td>
<td>N/A</td>
<td>Pass</td>
<td>0</td>
<td>&gt;250</td>
<td>40±0.3</td>
</tr>
<tr>
<td>Bio-PDOF3</td>
<td>92±0.1</td>
<td>F</td>
<td>N/A</td>
<td>Pass</td>
<td>0</td>
<td>&gt;250</td>
<td>37±1.3</td>
</tr>
<tr>
<td>Petro-PDOF4</td>
<td>N/A</td>
<td>N/A</td>
<td>65±7</td>
<td>Pass</td>
<td>20</td>
<td>N/A</td>
<td>-9±0.5</td>
</tr>
<tr>
<td>Bio-PDOF4</td>
<td>N/A</td>
<td>N/A</td>
<td>73±4</td>
<td>Pass</td>
<td>20</td>
<td>N/A</td>
<td>-10±1.0</td>
</tr>
</tbody>
</table>
3.4.3.1 Gel Content

Gel content of cured coatings was tested to evaluate the crosslinking density of coatings. The mole ratios of isocyanate/hydroxyl group (NCO/OH) in Petro-HDOF1 and Bio-PDOF1 were both close to 1.2. The higher hydroxyl value in polyester Bio-PDO-PU compared to HDO-PU (172 mgKOH/g vs 163 mgKOH/g) increased the gel content in cured coatings, 95±0.3% in Bio-PDOF1 compared to 94±0.3% in Petro-HDOF1, and increased the glass transition temperatures, 33±2ºC of Bio-PDOF1 coatings compared to 27±2ºC of Petro-HDOF1 coatings. The increases in gel content and Tg as NCO/OH values are consistent with previous studies where the gel contents increased from 75.22% to 98.71% with the increase of NCO/OH from 0.4 to 0.95. [96] In Petro-HDOF2 and Bio-PDOF2, the mole ratios of NCO/OH were close to 0.9 and gel contents of both coatings were 87%. This is because the gel contents are dependent on the stoichiometry of the crosslinking agents. The mole ratios of methoxymethyl groups to hydroxyl groups were close to 3.0 for the Petro-HDOF3 and Bio-PDOF3 with gel content of 89±1% and 92±0.1% respectively. The higher hydroxyl value of polyester Bio-PDO-Branched versus HDO-Branched (45 mgKOH/g vs 41 mgKOH/g) increased the crosslinked fractions in cured coatings from Bio-PDOF3. Comparing Bio-PDO-based and HDO-based coatings prepared from these three formulations, large differences in gel content were not observed, indicating that biomass-derived polyols provide sufficient functional groups for crosslinking and form similar crosslinked networks with HDO-based coatings.

3.4.3.2 Hardness, Flexibility, Adhesion Strength, and Solvent Resistance.

Hardness of coatings was evaluated by pencil hardness and pendulum hardness tests. By controlling the compositions and structures of polyesters, three groups of
coatings from soft (pencil hardness smaller than 6B) through medium (B-2B) to relatively hard (F) were acquired. In each group of coating, large difference in pencil hardness pendulum hardness were not observed, indicating the substitution of HDO with Bio-PDO didn’t affect the coating hardness. The HDO-PU and Bio-PDO-PU based coatings had higher hardness than HDO-AA-HHPA and Bio-PDO-AA-HHPA based coatings because of the higher urethane content. All coatings passed ½ inch mandrel bend test at -15°C and therefore exhibited good low-temperature flexibility. Higher amounts of isocyanate and melamine crosslinking agents used in the 1st and 3rd formulations contributed to the stronger adhesion of HDO-PU, Bio-PDO-PU, HDO-Branched and Bio-PDO-Branched based coatings than HDO-AA-HHPA and Bio-PDO-AA-HHPA based coatings, which came from the stronger interactions between O atoms, N atoms and melamine cycles with metal substrates via electrostatic and Lewis acid-base interactions [97]. The lower crosslinking density (gel content) and poorer adhesion of HDO-AA-HHPA and Bio-PDO-AA-HHPA based coatings also caused lower solvent resistance than HDO-PU and Bio-PDO-PU based coatings [98], [99]. The results show Bio-PDO coatings have similar properties with petroleum-derived HDO-based coatings, which provide the opportunity to directly substitute Bio-PDO-based polyols for HDO-based polyols without sacrificing coating performance. The Petro-PDO and Bio-PDO also provide polycarbonate-based coatings with similar hardness, flexibility, and adhesion strength.

3.4.4 Moisture-curable Hot Melt Adhesive Results

HDO-AA, Bio-PDO-AA, HDO-AA-IPA and Bio-PDO-IPA were formulated into adhesive formulations (Table 3.3) to investigate the effects of HDO-based and Bio-PDO-
based polyols on adhesives. The thermal properties, green strength, and open time were compared for the HDO and Bio-PDO based adhesives.

### 3.4.4.1 Thermal Properties of Adhesives

The thermal properties of adhesives before and after curing were tested to investigate the effects of HDO-based polyols and Bio-PDO-based polyols on thermal transitions of adhesives, as shown in Figure 3.2 and Figure 3.3. Before curing, HDO-based adhesive prepolymer showed much higher melting enthalpy than Bio-PDO-based adhesive prepolymer (20.5 J/g vs 3.2 J/g based on 2nd heating ramp), which was attributed to the higher melting enthalpy of HDO-AA polyester than Bio-PDO-AA polyester existing in adhesive formulations respectively. HDO-based HMA prepolymer exhibited a melting temperature of 45°C, which is close to the melting temperature of HDO-AA polyester (with melting temperature of 54.4°C as shown in Table 3.4). For Bio-PDO-based adhesive prepolymer, the melting transition around 25°C was also observed in the 1st heating curve (Figure 3.12), which comes from the corresponding polyester Bio-PDO-AA (with melting temperatures of 34/41°C). The absence of a melting peak around 25°C in the 2nd heating curve may be due to the slow crystallization during the cooling process because Bio-PDO has an odd number of carbons. [74] For both HDO-based and Bio-PDO-based HMA prepolymer, melting temperatures around 60°C (62°C and 66°C respectively) were observed, which may come from the Dynacoll® 7380 with a melting temperature of 70°C. Similarly, previous studies showed that melting temperatures and crystallinities of 1,3-praopanediol-based hot melt adhesives were lower than corresponding polyester diols added into adhesive formulations. [76]
After curing two weeks, the melting enthalpy of HDO-based adhesives decreased to 12.5 J/kg from 20.5 J/kg. Similar suppression effects were also observed in a previous study [76]. However, the suppression effect was not observed in Bio-PDO-based adhesives; the melting enthalpy increased to 12.3 J/kg from 3.2 J/kg after curing; crystallization enthalpy slightly increased to 5.7 J/kg from 4.2 J/kg. The melting transition around 22°C appeared in the 1st and 2nd heating curves (Figure 3.13). These results may indicate cured adhesives facilitate Bio-PDO-based adhesives forming ordered packing structures.

The glass transition temperatures of cured HDO-based and Bio-PDO-based adhesives are -38°C and -42°C respectively, indicating good low-temperature flexibility. Therefore, the results show that HDO-based adhesive prepolymer had higher melting enthalpy and crystallization enthalpy, indicating higher crystalline contents, than Bio-PDO-based adhesive prepolymer.
Figure 3.2. DSC thermograms of HDO-based hot melt adhesives, upper two curves: cooling mode, lower two curves: 2nd heating mode.
**Figure 3.3.** DSC thermograms of Bio-PDO-based hot melt adhesives, upper two curves: cooling mode, lower two curves: 2<sup>nd</sup> heating mode.

**Table 3.6.** Green Strength and Open Time of Petroleum-derived and Biomass-derived Hot Melt Adhesives

<table>
<thead>
<tr>
<th></th>
<th>Green strength (MPa)</th>
<th>Open time (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDO-based HMA</td>
<td>0.973±0.07 (Adhesive failure)</td>
<td>5</td>
</tr>
<tr>
<td>Bio-PDO-based HMA</td>
<td>0.058±0.01 (Cohesive failure)</td>
<td>10</td>
</tr>
</tbody>
</table>
3.4.4.2 Green Strength and Open Time

To further investigate the industrial properties of adhesives, green strength, and open time were tested to evaluate the applicability of Bio-PDO-based adhesives and compare with HDO-based adhesives. HDO-based adhesive prepolymer exhibited higher green strength and shorter open time than Bio-PDO-based hot melt adhesive prepolymer (0.973±0.07 MPa vs 0.058±0.01 MPa and 5mins vs 10mins in Table 3.6), which is probably due to higher melting enthalpy (indicating higher crystalline content) and faster solidification of HDO-based adhesive prepolymer. These results were consistent with previous studies that higher green strength was acquired from adhesives with larger crystalline content [77]. Therefore, it is possible that the green strength of Bio-PDO-based adhesives can be enhanced through formulating Bio-PDO-based polyesters with higher crystallization capacity, such as poly (1,5-pentylene azelate), poly (1,5-pentylene sebacate) or poly (1,5-pentylene dodecanedioate) [95]. The HDO-based adhesive prepolymer exhibited adhesive failure while Bio-PDO-based adhesive prepolymer exhibited cohesive failure. Bio-PDO-based polyesters may provide the adhesive formulators with options to tune the green strength and open time of adhesives suitable for different applications.

3.4.5 Effects of DVL and THFA Impurities on Polyols

While the results presented in Tables 3.4 and 3.5 show that Bio-PDO can exhibit near-identical properties to HDO in polyester polyols and likely minimal impact of impurities on thermoset coating properties, a more in-depth analysis was conducted on the effect of biomass-specific impurities on polyester polyols. In this study, delta-valerolactone (DVL) and tetrahydrofurfuryl alcohol (THFA) were chosen as model
compounds for lactones and mono-alcohols. These model compounds were studied in great excess to the concentrations typically reported in bio-monomer feeds in order to observe an outsized impact on potential effects on polymer properties. Polyesters were synthesized with Petro-PDO and increasing amount of DVL and THFA as summarized in Table 3.7. Thermal transitions are summarized in Table 3.13.

**Table 3.7.** Hydroxyl Values (OH$_v$) and Acid Values (A$_v$) of Petro-PDO-based Polyester Polyols with Increasing DVL and THFA

<table>
<thead>
<tr>
<th>Sample</th>
<th>F$_{impurity}$ (wt%)</th>
<th>OH$_v$ (mg KOH/g)</th>
<th>A$_v$ (mg KOH/g)</th>
<th>Equi weight (Da)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDOH0</td>
<td>0%</td>
<td>66</td>
<td>0.3</td>
<td>846</td>
</tr>
<tr>
<td>PDOH5D</td>
<td>5%DVL</td>
<td>60</td>
<td>~0</td>
<td>935</td>
</tr>
<tr>
<td>PDOA0</td>
<td>0%</td>
<td>23.6</td>
<td>4.0</td>
<td>2033</td>
</tr>
<tr>
<td>PDOA2D</td>
<td>2%DVL</td>
<td>24.7</td>
<td>3.9</td>
<td>1962</td>
</tr>
<tr>
<td>PDOA5D</td>
<td>5%DVL</td>
<td>18.6</td>
<td>3.9</td>
<td>2494</td>
</tr>
<tr>
<td>PDOA7D</td>
<td>7%DVL</td>
<td>31.7</td>
<td>3.1</td>
<td>1612</td>
</tr>
<tr>
<td>PDOA10D</td>
<td>10%DVL</td>
<td>25.8</td>
<td>1.5</td>
<td>2070</td>
</tr>
<tr>
<td>PDOA5T</td>
<td>5%THFA</td>
<td>31.3</td>
<td>2.5</td>
<td>1660</td>
</tr>
<tr>
<td>PDOA7T</td>
<td>7%THFA</td>
<td>43.8</td>
<td>4.0</td>
<td>1174</td>
</tr>
</tbody>
</table>

Several mechanisms were proposed for the polymerization of DVL. DVL can be initiated by diols to form hydroxyl end groups through acyl-fission (Scheme 1) [100], or initiated by metal alkoxides (e.g. titanium butoxide) to generate alkyl ester end groups (Scheme 2), which can further undergo esterification or transesterification to form longer-chain polyesters [87], [101]. The diacids or anhydrides can further react with hydroxyl groups on the ring opened DVL to form ester linkages. Mono-alcohols, such as THFA, react with diacids and generate unreactive termination on polyester polyols.
3.4.5.1 MALDI-TOF Spectra

We conducted MALDI-TOF experiments to determine the incorporation of DVL. Polymer end group (e.g. hydroxyl groups, carboxyl groups), and repeating unit structures can be determined by MALDI-TOF reflected modes through assigning m/z values to specific, predicted polymer structures [102], [103]. The polymer structures of PDOA2D are shown in Figure 3.4, which were determined via the peaks in mass spectra shown in Figure 3.5. For the PDOA2D sample, polyesters were either terminated with hydroxyl groups on two ends (peak A), with one OH group and one COOH group (peak B), or unterminated cyclic polyesters (peak C). Polyester diols containing DVL appeared at peak A’, and polyesters containing DVL with one OH group and one COOH group appeared at peak B’. In addition to these polyester structures, peak E may represent monohydroxylic oligomers that came from the initiation of DVL by TBT (Scheme 2). Similar results were also observed in a previous study where minor amount of
monohydroxylic polymers were generated from the initiation of β-butyrolactone by
titanium alkoxide, thus reducing the loading of titanium alkoxide catalyst may diminish
this side reaction [104]. All structures were also observed in other samples, PDOA0,
PDOA5D, PDOA7D, and PDO10D, as shown in Figure 3.16, 3.18-3.20. Polyesters
containing THFA exhibited mono-alcohol THFA terminal groups (Figure 3.24-3.26).
Therefore, MALDI-TOF results confirmed the DVL and THFA were incorporated into
polyester backbones.
Figure 3.4. Polyester structures existing in PDOA2D sample, cations are Na$^+$.
3.4.5.2 Hydroxyl Functionality

Hydroxyl functionalities are important for polyols in coatings and adhesives as they are required for further reaction with crosslinkers and chain extenders. The OH theoretical value can be calculated from eq 3.2, when the conversion is 1, and feed monomers consisted of $N_A$ moles of Petro-PDO and $N_B$ moles of adipic acid (or with cyclohexanedicarboxylic anhydride). The derivation is shown in eqs 3.8-3.11.

\[
\text{OH}_{v,\text{theory}} = \frac{56100 \times 2}{\frac{N_A}{N_B} \times M_0 + 18} \quad (3.2)
\]

Where $\frac{N_A}{N_B}$ represents the ratio of diol and diacid (or with anhydride) units in synthesized polyesters, and $M_0=107$ for PDOA polyesters and $M_0=114.7$ for PDOH polyesters. When DVL existed in the feed monomers, DVL was polymerized into
polyester backbones as indicated by MALDI-TOF results. Thus, DVL can be hypothetically considered as a type of hydroxy acid that is capable of polymerizing with diols and diacids or anhydride. In this case, \( N_A \) and \( N_B \) are the ratio of \( 2n(\text{diol})+n(\text{DVL}) \) to \( 2n(\text{diacid w/ anhydride})+n(\text{DVL}) \), where \( n \) represents moles of monomers that are incorporated into polyesters. Due to chemical shifts of DVL overlapped with Petro-PDO and adipic acid in \(^1\text{H} \) NMR spectrum (Figure 3.27 and 3.28), the ratio of \( 2n(\text{diol})+n(\text{DVL}) \) to \( 2n(\text{diacid w/ anhydride})+n(\text{DVL}) \) can be calculated from eq 3.3 and eq 3.4, where \( I_a, I_b, I_c, \) and \( I_g \) were acquired from \(^1\text{H} \) NMR spectra of PDOH0, PDOH5D, PDOA0, PDOA2D, PDOA5D, PDOA7D and PDOA10D samples as shown in Figures 3.27 and 3.28.

\[
\frac{N_A}{N_B} = \frac{2n(\text{diol})+n(\text{DVL})}{2n(\text{diacid w/ anhydride})+n(\text{DVL})} = \frac{I_a+I_b}{I_c} \quad (3.3)
\]

\[
\frac{N_A}{N_B} = \frac{2n(\text{diol})+n(\text{DVL})}{2n(\text{diacid w/ anhydride})+n(\text{DVL})} = \frac{I_a+I_b}{I_c+I_g} \quad (3.4)
\]

\( \frac{N_A}{N_B} \) values are summarized in Table 3.14. Hydroxyl values from theoretical calculation and experiments are plotted in Figure 3.6. In the range of \( \frac{N_A}{N_B} \) investigated here, the theoretical hydroxyl values (red points) and experimental hydroxyl values (black points) are both linearly related to \( \frac{N_A}{N_B} \). The deviations (within 14\%) of experimental OH values from theoretical values may come from cyclization, polymerization of DVL in different mechanisms, and uncompleted reactions (remaining carboxyl groups). Also, we did not observe a strong correlation between hydroxyl values and the DVL content in feed monomers, which indicates the esterification reaction among diols and diacids dominates the DVL polymerization with diols. Therefore, within the range of DVL investigated in this study, the hydroxyl values of polyesters are still
mainly controlled by diols and diacids. And DVL is not expected to materially suppress reactive hydroxyl end groups.

![Figure 3.6](image)

**Figure 3.6.** Hydroxyl (OH) values as a function of $\frac{N_A}{N_B}$

### 3.5 Conclusions

Amorphous and semi-crystalline polyester polyols were successfully synthesized using HDO and Bio-PDO via esterification and transesterification. Bio-PDO-based polyols had similar hydroxyl values and acid values with HDO-based polyols, which indicated the biomass-derived polyols retained reactive functionalities in levels similar to HDO-based polyols. The amorphous Bio-PDO-based polyesters had comparable Tg to
HDO-based polyesters. The semi-crystalline Bio-PDO-based polyesters exhibited lower melting temperatures and melt enthalpies than HDO-based polyesters due to the odd-even effect. Bio-PDO-based coatings exhibited similar gel content, hardness, flexibility, adhesion strength and solvent resistance, compared with HDO-based coatings. Bio-PDO-based adhesives showed lower green strength, longer open time probably due to the interrupted crystalline domains in adhesive prepolymers, compared to 1,6-HDO-based adhesives.

The effects of biomass-specific impurities such as lactones and mono-alcohols were studied with the use of DVL and THFA as model compounds respectively. DVL was incorporated into the polyester backbone via ring-opening polymerization, confirmed by MALDI-TOF. The majority of polyols had reactive hydroxyl groups on both ends, which were mainly controlled by esterification over DVL polymerization. When polymers were synthesized with DVL impurities (up to 2 wt% DVL based on Petro-PDO), difference in hydroxyl values and thermal properties of polyesters were not observed. When THFA was added into monomer feeds in large amounts (>5 wt%), polyesters were end capped with THFA, resulting in lower molecular weights and higher hydroxyl functionalities. These results indicate that low levels (<2 wt%) of these bio-based impurities didn’t deleteriously affect PDO-based polyols. Bio-based polyols based on the current technology described above do not suffer from these limitations. Therefore, Bio-PDO provides a lower cost, sustainable and non-petrochemical alternative to HDO in thermoset coatings.
3.6 Appendix of Chapter 3

Polymer compositions

Table 3.8. Compositions of Polyols for Coatings and Adhesives

<table>
<thead>
<tr>
<th>Class</th>
<th>Sample</th>
<th>Polymer composition</th>
<th>Monomer mole ratio in feeds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bio-PDO-PU</td>
<td>Bio-PDO/NPG/HHPA/THDI</td>
<td>1: 1: 1: 0.14</td>
</tr>
<tr>
<td></td>
<td>HDO-PU</td>
<td>HDO/NPG/HHPA/THDI</td>
<td>1: 1: 1: 0.14</td>
</tr>
<tr>
<td>2</td>
<td>Bio-PDO-AA-HHPA</td>
<td>Bio-PDO/AA/HHPA</td>
<td>1.3: 0.4: 0.6</td>
</tr>
<tr>
<td></td>
<td>HDO-AA-HHPA</td>
<td>HDO/AA/HHPA</td>
<td>1.3: 0.4: 0.6</td>
</tr>
<tr>
<td>3</td>
<td>Bio-PDO-Branched</td>
<td>Bio-PDO/2M13PDO/TPA</td>
<td>0.291: 0.689: 0.09: 0.998: 0.002</td>
</tr>
<tr>
<td></td>
<td>HDO-Branched</td>
<td>HDO/2M13PDO/TPA/TPA</td>
<td>0.291: 0.689: 0.09: 0.998: 0.002</td>
</tr>
<tr>
<td>4</td>
<td>Bio-PDO-AA</td>
<td>Bio-PDO/AA</td>
<td>1.2: 1</td>
</tr>
<tr>
<td></td>
<td>HDO-AA</td>
<td>HDO/AA</td>
<td>1.2: 1</td>
</tr>
<tr>
<td>5</td>
<td>Bio-PDO-AA-IPA</td>
<td>Bio-PDO/AA/IPA</td>
<td>1.3: 0.5: 0.5</td>
</tr>
<tr>
<td></td>
<td>HDO-AA-IPA</td>
<td>HDO/AA/IPA</td>
<td>1.3: 0.5: 0.5</td>
</tr>
<tr>
<td>6</td>
<td>Bio-PDO-PC</td>
<td>Bio-PDO/HDO/DMC</td>
<td>0.7: 0.7: 1</td>
</tr>
<tr>
<td></td>
<td>Petro-PDO-PC</td>
<td>PDO/HDO/DMC</td>
<td>0.7: 0.7: 1</td>
</tr>
</tbody>
</table>

Table 3.9. Compositions of polyols with increasing impurities

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer composition</th>
<th>Monomer mole ratio in feeds</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDOH0</td>
<td>PDO/AA/HHPA</td>
<td>0.4: 0.6: 1.2</td>
</tr>
<tr>
<td>PDOH5D</td>
<td>PDO/AA/HHPA/5% DVL</td>
<td>0.4: 0.6: 1.23: 0.02</td>
</tr>
<tr>
<td>PDOA0</td>
<td>PDO/AA</td>
<td>1: 1.1</td>
</tr>
<tr>
<td>PDOA2D</td>
<td>PDO/AA/2% DVL</td>
<td>1: 1.11: 0.02</td>
</tr>
<tr>
<td>PDOA5D</td>
<td>PDO/AA/5% DVL</td>
<td>1: 1.11: 0.05</td>
</tr>
<tr>
<td>PDOA7D</td>
<td>PDO/AA/7% DVL</td>
<td>1: 1.11: 0.07</td>
</tr>
<tr>
<td>PDOA10D</td>
<td>PDO/AA/10% DVL</td>
<td>1: 1.11: 0.1</td>
</tr>
<tr>
<td>PDOA5T</td>
<td>PDO/AA/5% THFA</td>
<td>1: 1.11: 0.05</td>
</tr>
<tr>
<td>PDOA7T</td>
<td>PDO/AA/7% THFA</td>
<td>1: 1.11: 0.07</td>
</tr>
</tbody>
</table>
Coating formulations based on polyester polyols

Table 3.10. 2K Thermoset Coating Formulations

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Petro-HDO Formulation 1 (Petro-HDOF1)</th>
<th>Bio-PDO Formulation 1 (Bio-PDOF1)</th>
<th>Petro-HDO Formulation 2 (Petro-HDOF2)</th>
<th>Bio-PDO Formulation 2 (Bio-PDOF2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diol of Interest</td>
<td>HDO Parts by weight (g)</td>
<td>Bio-PDO Parts by weight (g)</td>
<td>HDO Parts by weight (g)</td>
<td>Bio-PDO Parts by weight (g)</td>
</tr>
<tr>
<td></td>
<td>Component 1</td>
<td></td>
<td>Component 2</td>
<td></td>
</tr>
<tr>
<td>HDO-PU</td>
<td>1.39</td>
<td>/</td>
<td>1.39</td>
<td>/</td>
</tr>
<tr>
<td>Bio-PDO-PU</td>
<td>/</td>
<td>1.39</td>
<td>/</td>
<td>1.39</td>
</tr>
<tr>
<td>HDO-AA-HHPA</td>
<td>/</td>
<td>/</td>
<td>8.99</td>
<td>/</td>
</tr>
<tr>
<td>Tinuvin 644</td>
<td>0.05</td>
<td>0.05</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>Tinuvin 123</td>
<td>0.01</td>
<td>0.01</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>0.05</td>
<td>0.05</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>butyrate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibutyltin dilaurate</td>
<td>0.02</td>
<td>0.02</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>Methyl amyl ketone</td>
<td>0.74</td>
<td>0.74</td>
<td>4.79</td>
<td>4.79</td>
</tr>
<tr>
<td>Component 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tolonate™ HDT 90</td>
<td>1.08</td>
<td>1.08</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>Methyl amyl ketone</td>
<td>1.17</td>
<td>1.17</td>
<td>4.40</td>
<td>4.40</td>
</tr>
</tbody>
</table>

Note: Component 1 and component 2 were prepared separately and were mixed for 5 mins at room temperature right before applying coatings on to steel panels (Q-panel, Q-Lab) using a drawdown tool (Gardner Co.) to generate 50 µm thick films. The coated panels were cured at 130ºC for 1 h and equilibrated at room temperature for one week before testing.
### Table 3.11. Coil Coating Formulations

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Petro-HDO Formulation 3 (Petro-HDOF3)</th>
<th>Bio-PDO Formulation 3 (Bio-PDOF3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diol of interest</td>
<td>HDO Parts by weight (g)</td>
<td>Bio-PDO Parts by weight (g)</td>
</tr>
<tr>
<td>HDO-Branched</td>
<td>16.10</td>
<td>/</td>
</tr>
<tr>
<td>Bio-PDO-Branched</td>
<td>/</td>
<td>16.10</td>
</tr>
<tr>
<td>(60 wt% in solvents)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resimene 747</td>
<td>1.63</td>
<td>1.63</td>
</tr>
<tr>
<td>TEGO 425</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>Nacure 1051</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>Butanol</td>
<td>0.52</td>
<td>0.52</td>
</tr>
<tr>
<td>Dipropylene glycol</td>
<td>1.38</td>
<td>1.38</td>
</tr>
<tr>
<td>monomethyl ether</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aromatic 100</td>
<td>1.55</td>
<td>1.55</td>
</tr>
</tbody>
</table>

Note: First, Bio-PDO-Branched and HDO-Branched polyesters were reduced with Aromatic 150 and dipropylene glycol monomethyl ether at the ratio of 1:1. The reduced polyesters have nonvolatile of 60%. Then, the reduced polyesters were mixed with Resimene 747 (hexamethoxymethyl melamine formaldehyde resin) and other ingredients. The coatings were applied on to aluminum panels (Q-panel, Q-Lab) by using a drawdown tool (Gardner Co.) to generate 50 µm thick films. The coated panels were cured at 200ºC for 2 mins and equilibrated at room temperature for one week prior to coating tests.

**Synthesis of polycarbonate polyol.**

Polycarbonate polyols were synthesized in a 250 mL reactor attached with a Vigreux column on top to remove by-product methanol and reflux dimethyl carbonate. The reactor was charged with half of the feed dimethyl carbonate, and all HDO, Bio-PDO or Petro-PDO and titanium butoxide (1 wt% based on dimethyl carbonate), and then heated up to 80ºC. After all components melted, the temperature was increased to 140ºC very slowly to keep the reflux in the Vigreux column and head temperature less than 65ºC. The remaining dimethyl carbonate was added into the reactor when the reflux in the Vigreux column decreased. Then, the temperature was increased to 170ºC very slowly to maintain reflux in Vigreux column and a head temperature less than 65ºC. After the reflux stopped, the Vigreux column was removed, followed by completing the
reaction under slow nitrogen gas flow until the desired molecular weight, acid value, and hydroxyl value were reached.

**Coating formulations and results based on polycarbonate polyols**

**Table 3.12. Internal Pipeline Coating Formulations**

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Petro-PDO Formulation 4 (Petro-PDOF4)</th>
<th>Bio-PDO Formulation 4 (Bio-PDOF4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diol of interest</td>
<td>Components 1</td>
<td></td>
</tr>
<tr>
<td>Petro-PDO-PC</td>
<td>5.00</td>
<td>/</td>
</tr>
<tr>
<td>Bio-PDO-PC</td>
<td>/</td>
<td>5.00</td>
</tr>
<tr>
<td>Poly(tetrahydrofuran)</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>Cellulose acetate butyrate</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>Dibutyltin dilaurate</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Methyl amyl ketone</td>
<td>11.70</td>
<td>11.70</td>
</tr>
<tr>
<td>Component 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimethyl hexamethylene diisocyanate</td>
<td>3.40</td>
<td>3.40</td>
</tr>
<tr>
<td>Tolonate™ HDT 90</td>
<td>0.70</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Note: Polycarbonate based coatings were prepared following the same procedure with 2K thermoset coatings described above.

**1H NMR spectrum**
Figure 3.7. 1H NMR spectra of (a) HDO-AA and (b) Bio-PDO-AA. The chemical shifts of CH2 groups in the HDO unit (a, b, d, e) and AA unit (c, d) appeared at 3.67, 4.06, 1.66, 1.39, 2.32, 1.66 ppm, respectively. When the HDO unit was replaced with Bio-PDO unit, the chemical shifts did not change.
Figure 3.8. 1H NMR spectra of (a) HDO-AA-HHPA and (b) Bio-PDO-AA-HHPA. The chemical shifts of CH2 groups in the HDO unit (b, d, e) and AA unit (c, d) appeared at 4.06, 1.66, 1.55-1.24, 2.32, 1.66 ppm, respectively. The chemical shifts of CH2 (g) in the HHPA unit appeared at 2.11-1.94 and 1.84-1.72 ppm due to the conformation of axial-equatorial-cis-HHPA. The chemical shifts of CH2 (h) in the HHPA unit and CH2 (e) in HDO units overlapped at 1.54-1.25 ppm. The chemical shift of CH (f) in HHPA unit...
appeared at 2.81 ppm and 2.60 ppm which may result from the conformation of HHPA containing polymers. When the HDO unit was replaced with Bio-PDO unit, the chemical shifts did not change. Calculated from the ratio of peak intensity g (Ig) to c (Ic), the mole ratios of HHPA to AA in polyesters synthesized from HDO and Bio-PDO are 1.55 and 1.51 respectively. These ratios are close to the ratio (1.5) in monomer feeds.
Figure 3.9. 1H NMR spectra of (a) HDO-AA-IPA and (b) Bio-PDO-AA-IPA. For HDO-AA-IPA polyester, the chemical shifts of CH2 groups in the HDO unit (a, b, b’, d, d’, e) and AA unit (c, d) appeared at 3.67, 4.07, 4.36, 1.66, 1.82, 1.37-1.46, 2.32, 1.66 ppm. Aromatic protons (i, j, k) appeared at 8.69, 8.24, 7.54 ppm. When the HDO unit was replaced with Bio-PDO unit, the chemical shifts did not change.
Figure 3.10. 1H NMR spectra of HDO-Branched polyol in chloroform with benzoic acid as inner standards. Peak a represents the protons near hydroxyl end groups when diols (2-methyl-1,3-propanediol or 1,6-hexanediol) terminates on polyesters. X represents the unknown protons. Due to only 0.2% terephthalic acid in monomer feeds, the terephthalic acid units are not shown in the polymer structures. The ratios of $I_d'/I_d$ and $I_e'/I_e$ are 0.45, from which the ratio of incorporated 2-methyl-1,3-propanediol to 1,6-hexanediol is 1.8. The ratio of protons near ester groups from trimethylolpropane to the protons near all ester groups ($I_b'/(I_b'+I_b)$) is 0.098. The mass of benzoic acid and polyester are 1mg and 1.064mg respectively. Therefore, $\text{OH}_v=\frac{(1/122)\times(1/5.27) \times (1/2) \times 56.1 \times 1000}{1.064}=41 \text{ mgKOH/g polymer}$.
Figure 3.11. 1H NMR spectra of Bio-PDO-Branched polyol in chloroform with benzoic acid as inner standards. Peak a represents the protons near hydroxyl end groups when diols (2-methyl-1,3-propanediol or 1,5-pentanediol) terminates on polyesters. X represents the unknown protons. Due to only 0.2% terephthalic acid in monomer feeds, the terephthalic acid units are not shown in the polymer structures. The ratios of Id’/Id and Ie’/Ie are 0.45, from which the ratio of incorporated 2-methyl-1,3-propanediol to 1,5-pentanediol is 1.8. The ratio of protons near ester groups from trimethylolpropane to the protons near all ester groups (Ib’/(Ib+Ib)) is 0.086. The mass of benzoic acid and polyesters are 1mg and 2.718mg respectively. Therefore, OHv=((1/1.88) × (1/122) × (1/2) × 56.1 × 1000)/2.718=45 mgKOH/g polymer.

Biomass content (Øbio) calculation

Øbio values of Bio-PDO-AA, Bio-PDO-AA-HHPA and Bio-PDO-AA-IPA were calculated from the eqs A3.1-A3.3 by referencing peak intensities in Figures 3.7-3.9. Øbio values of HDO-PU, Bio-PDO-PU, HDO-Branched, Bio-PDO-Branched, Petro-PDO-PC and Bio-PDO-PC were calculated from monomer feed ratios.

\[
\begin{align*}
\Phi_{\text{Bio-PDO-AA-HHPA}} &= \frac{1}{3}(I_a+I_b)\times 5 + \frac{1}{2}(I_f+I_{f'})\times 8 + \frac{1}{2}I_c\times 6 \quad (3.5) \\
\Phi_{\text{Bio-PDO-AA}} &= \frac{5}{5}(I_a+I_b)\times 6 \quad (3.6)
\end{align*}
\]
\[ \varnothing_{\text{Bio-PDO-AA-IPA}} = \frac{\frac{1}{2} (l_a + l_b + l_{br}) \times 5}{\frac{1}{2} (l_a + l_b + l_{br}) \times 5 + 5 \times 8 + \frac{1}{2} \times 6} \quad (3.7) \]

DSC thermograms

Figure 3.12. DSC thermogram of Bio-PDO-based hot melt adhesive before curing

Figure 3.13. DSC thermogram of Bio-PDO-based hot melt adhesives after curing
Figure 3.14. DSC thermogram of HDO-based hot melt adhesives before curing

Figure 3.15. DSC thermogram of HDO-based hot melt adhesives after curing
MALDI-TOF spectrum of DVL containing and THFA containing polyesters

Figure 3.16. (a) Mass spectrum for sample PDOA0 (b) zoom-in mass spectrum
Figure 3.17. (a) Mass spectrum for sample PDOA2D (b) zoom-in mass spectrum
Figure 3.18. (a) Mass spectrum for sample PDOA5D (b) zoom-in mass spectrum
Figure 3.19. (a) Mass spectrum for sample PDOA7D (b) zoom-in mass spectrum
Figure 3.20. (a) Mass spectrum for sample PDOA10D (b) zoom-in mass spectrum
Figure 3.21. Polyester structures existing in PDOH0 and PDOH5D, cations are Na⁺
Figure 3.22. (a) Mass spectrum for PDOH0, (b) zoom-in mass spectrum
Figure 3.23. (a) Mass spectrum for sample PDOH5D (b) zoom-in mass spectrum
Figure 3.24. Polyester structures existing in PDO5T and PDO7T samples, cations are Na⁺
Figure 3.25. (a) Mass spectrum for PDO5T (b) zoom-in spectrum
Figure 3.26. (a) Mass spectrum for PDO7T (b) zoom-in spectrum

Effects of DVL on thermal transitions
Table 3.13. Thermal transitions of Petro-PDO-based Polyester Polyols with Increasing DVL

<table>
<thead>
<tr>
<th>Sample</th>
<th>F_impurity (wt%)</th>
<th>Tm, °C (ΔHm, J/g)</th>
<th>Tc, °C (ΔHc, J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDOA0</td>
<td>0%</td>
<td>33/40 (62)</td>
<td>11 (62)</td>
</tr>
<tr>
<td>PDOA2D</td>
<td>2%DVL</td>
<td>32/39 (61)</td>
<td>11 (61)</td>
</tr>
<tr>
<td>PDOA5D</td>
<td>5%DVL</td>
<td>32/38 (58)</td>
<td>6 (56)</td>
</tr>
<tr>
<td>PDOA7D</td>
<td>7%DVL</td>
<td>31/38 (61)</td>
<td>7 (59)</td>
</tr>
<tr>
<td>PDOA10D</td>
<td>10%DVL</td>
<td>31/38 (60)</td>
<td>7 (58)</td>
</tr>
</tbody>
</table>

**Thermal transitions.** To study the impact of lactones and mono-alcohols on melting and crystallization of polyesters, DSC was conducted on Petro-PDO-based polyesters as shown in Table 3.13. For polyesters PDOA0, PDOA2D, PDOA5D, PDOA7D and PDOA10D, crystallization temperatures and crystallization enthalpies tested by cooling DSC curves were slightly decreased when >5% DVL was added into monomer feeds; however, melting temperatures and melting enthalpies tested by the 2nd heating DSC curves were similar, indicating DVL segments caused polyesters to crystallize slower during cooling process. In addition, a step change in crystallization temperatures and crystallization enthalpies was observed when DVL was added from 2% to above 5%. This step change may indicate DVL was not randomly incorporated into polyester backbones, but this was not confirmed in this study. Previous study shows that DVL was used as a comonomer to effectively reduce polycaprolactone melting temperature and enthalpy, with applications in antifouling paint. [105] The effects of these impurities will depend on the impurity concentration and are not expected to provide noticeable impact on thermal properties at low concentrations.
Effects of DVL on hydroxyl group functionality

Theoretical hydroxyl values \( (OH_{v,\text{theory}}) \) of polyols can be estimated according to eq 3.8 where number-average molecular weight \( (M_n) \) can be calculated from eq 3.9, Carother’s equation (eq 3.10) and Pinner’s extension (eq 3.11).

\[
OH_{v,\text{theory}} = \frac{56100 \times 2}{M_n} \quad (3.8)
\]

\[
M_n = DP \times M_o + 18 \quad (3.9)
\]

\[
DP = \frac{2}{2-pf_{avg}} \quad (3.10)
\]

\[
f_{avg} = \frac{2N_B f_B}{N_A + N_B + N_C} \quad (3.11)
\]

Where DP is the degree of polymerization, \( M_o \) is the molecular weight of repeat units, \( p \) is the fraction of conversion of deficient groups (carboxyl groups here), \( f_{avg} \) is the average functionality of monomers. The feed monomer could be a ternary mixture of \( N_A \) moles of diols, \( N_B \) moles of diacids \( (f_B = 2) \) and \( N_C \) moles of mono-alcohols.
Figure 3.27. 1H NMR spectra of PDOH0 (PDO/AA/HHPA) and PDOH5D (PDO/AA/HHPA/5%DVL). The 1H NMR spectrum of polyesters PDOH5D is the same with polyesters PDOH0 because the chemical shifts of DVL partially overlapped with PDO and AA. The chemical shifts of CH$_2$ groups in the PDO unit (b, d, e) and AA unit (c, d) appeared at 4.06, 1.66, 1.59-1.39, 2.32, 1.66 ppm. The chemical shifts of CH$_2$ (g) in the HHPA unit appeared at 2.05 and 1.78 ppm due to the conformation of axial-equatorial-cis-HHPA. The chemical shifts of CH$_2$ (h) in the HHPA unit and CH$_2$ (e) in PDO units overlapped at 1.59-1.39 ppm. The chemical shift of CH (f) in HHPA unit appeared at 2.81 ppm and 2.60 ppm which may result from the conformation of HHPA containing polymers. The chemical shifts of DVL partially overlapped with PDO and AA. Calculated from the ratio of peak intensity g (Ig) to c (Ic) in Figure 3.4, the mole ratios of HHPA to AA in polyester PDOH0 (PDO/AA/HHPA) and PDOH5D (PDO/AA/HHPA/5%DVL) is 1.54 and 1.45 respectively, which are close to the ratio (1.5) in monomer feeds. The slightly smaller value, 1.45, in polyester PDOH5D than polyester PDOH0 is attributed to the larger Ic from CH$_2$ (c) in DVL unit.
Figure 3.28. $^1$H NMR spectra of polyester PDOA0 (PDO/AA), PDOA2D (PDO/AA/2%DVL), PDO5D (PDO/AA/5%DVL), PDO7D (PDO/AA/7%DVL) and PDO10D (PDO/AA/10%DVL).
Table 3.14. $\frac{N_A}{N_B}$ values, $OH_{v,\text{theory}}$ values, and $OH_{\text{exp}}$ values

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_b$</th>
<th>$I_a$</th>
<th>$I_c$</th>
<th>$2I_g$</th>
<th>$\frac{N_A}{N_B}$</th>
<th>$OH_{v,\text{theory}}$</th>
<th>$OH_{\text{exp}}$</th>
<th>$OH_{\text{exp}} - OH_{v,\text{theory}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDOH0</td>
<td>7.38</td>
<td>1</td>
<td>2.98</td>
<td>4.36</td>
<td>1.142</td>
<td>64.05</td>
<td>66</td>
<td>1.949</td>
</tr>
<tr>
<td>PDOH5D</td>
<td>7.81</td>
<td>1</td>
<td>3.25</td>
<td>4.54</td>
<td>1.131</td>
<td>59.53</td>
<td>60</td>
<td>0.468</td>
</tr>
<tr>
<td>PDOA0</td>
<td>17.56</td>
<td>1</td>
<td>17.74</td>
<td>4</td>
<td>1.046</td>
<td>23.60</td>
<td>23.6</td>
<td>0.002</td>
</tr>
<tr>
<td>PDOA2D</td>
<td>18.29</td>
<td>1</td>
<td>18.5</td>
<td>0</td>
<td>1.043</td>
<td>21.84</td>
<td>24.7</td>
<td>2.856</td>
</tr>
<tr>
<td>PDOA5D</td>
<td>20.89</td>
<td>1</td>
<td>21.21</td>
<td>0</td>
<td>1.032</td>
<td>16.50</td>
<td>18.6</td>
<td>2.100</td>
</tr>
<tr>
<td>PDOA7D</td>
<td>15.88</td>
<td>1</td>
<td>16.00</td>
<td>0</td>
<td>1.055</td>
<td>27.94</td>
<td>31.7</td>
<td>3.761</td>
</tr>
<tr>
<td>PDOA10D</td>
<td>16.97</td>
<td>1</td>
<td>17.1</td>
<td>0</td>
<td>1.051</td>
<td>25.91</td>
<td>25.8</td>
<td>-0.105</td>
</tr>
</tbody>
</table>

$I_b$, $I_a$, $I_c$, and $I_g$ are summarized from Figure 3.27 and 3.28. $\frac{N_A}{N_B}$ was calculated from eqs 3.3 and 3.4. $OH_{v,\text{theory}}$ was calculated from eq 3.2. $I_g$ was calculated from the g peaks at 2.07 ppm only because g peaks at 1.78 ppm overlap with d peaks as shown in Figure 3.27.

The hydroxyl values increase as the THFA concentration in the monomer feeds increase (Table 3.7). This trend follows eqs A3.4-A3.7, where with the increase of mono-alcohols, degree of polymerization (DP) decreases and hydroxyl values increase. However, a quantitative relation between hydroxyl values with THFA concentrations was not developed because the actual THFA fractions in synthesized polyesters were not quantified. The decreased molecular weight indicates polyols were terminated by unreactive groups from mono-alcohols as confirmed by MALDI-TOF in Figure 3.24-3.26. These unreactive groups could introduce pendent “dangling chain” segments into crosslinked polymer films and thus weakening the mechanical properties of final films.
DSC data

**Figure 3.29.** DSC curve of HDO-AA polyester

**Figure 3.30.** DSC curve of Bio-PDO-AA polyester
Figure 3.31. DSC curve of HDO-based hot melt adhesives before curing

Figure 3.32. DSC curve of HDO-based hot melt adhesives after curing
Figure 3.33. DSC curve of Bio-PDO-based hot melt adhesives before curing

![DSC curve of Bio-PDO-based hot melt adhesives before curing](image)

Figure 3.34. DSC curve of Bio-PDO-based hot melt adhesives after curing

![DSC curve of Bio-PDO-based hot melt adhesives after curing](image)

FTIR data

![FTIR spectrum of cured coatings of Bio-PDOF1 and Petro-HDOF1](image)

Figure 3.35. FTIR spectrum of cured coatings of Bio-PDOF1 and Petro-HDOF1. Free isocyanate groups at 2270 cm\(^{-1}\) and hydroxyl groups of polyols around 3500 cm\(^{-1}\) were not observed in cured coatings. Absorption bands at 1520 cm\(^{-1}\) are C-N stretching and N-H bending, absorption bands at 3380 cm\(^{-1}\) are N-H stretching, indicating the coatings were cured completely.
Figure 3.36. FTIR spectrum of Bio-PDO-AA-HHPA polyol (red curve) and cured coatings of Bio-PDOF2 (black curve). Absorptions bands at 3500 cm\(^{-1}\) are O-H stretching from hydroxyl groups of polyester polyols. After curing, absorption bands at 3380 cm\(^{-1}\) are N-H stretching, and absorption bands at 1520 cm\(^{-1}\) are C-N stretching and N-H bending, which proved isocyanate crosslinkers reacted with polyester polyols. Free isocyanate groups at 2270 cm\(^{-1}\) and hydroxyl groups of polyols around 3500 cm\(^{-1}\) were not observed in cured coatings, indicating the coatings were cured completely.

Figure 3.37. FTIR spectrum of HDO-AA-HHPA polyol (red curve) and cured coatings of Petro-HDOF2 (black curve).
Figure 3.38. FTIR spectrum of Bio-PDO-Branch polyol (red curve) and cured coatings of Bio-PDOF3 (black curve). Absorptions bands at 3500 cm$^{-1}$ are O-H stretching from hydroxyl groups of polyester polyols. After curing, absorption bands at 1540 cm$^{-1}$ are C=N ring stretching vibrations that came from melamine-formaldehyde crosslinkers. Broad absorption bands at 3380 cm$^{-1}$ may came from the water adsorbed on coatings. O-H stretching was not observed in cured coatings, indicating all polyol hydroxyl groups were crosslinked.

Figure 3.39. FTIR spectrum of HDO-Branch polyol (red curve) and cured coatings of Petro-HDOF3 (black curve).
Figure 3.40. FTIR spectrum of Bio-PDO-based hot melt adhesive (HMA) and HDO-based hot melt adhesive (HMA) after curing two weeks. Absorption bands at 3380 cm⁻¹ are N-H stretching. Free isocyanate groups at 2270 cm⁻¹ and hydroxyl groups of polyols around 3500 cm⁻¹ were not observed, indicating adhesives were cured completely after two weeks.
CHAPTER 4

BIODEGRADABLE HIGH MOLECULAR WEIGHT POLY (PENTYLENE ADIPATE-CO-TEREPHTHALATE): SYNTHESIS, THERMO-MECHANICAL PROPERTIES, MICROSTRUCTURES, AND BIODEGRADATION

4.1 Abstract

In this chapter, high molecular weight aliphatic-aromatic polyester, poly (pentylene adipate-co-terephthalate) PPAT, was successfully synthesized via thin-film polymerization and chain extension. The effects of reaction conditions on molecular weight such as temperature and catalyst were investigated. PPAT polyesters were characterized for polymer compositions, number-average unit length, thermal transitions, and rheological properties. PPAT compression molded films were characterized for microstructures such as crystallinity and long period, and tensile properties to correlate micro and macro properties. PPAT compression molded films exhibited 1-1.5 times higher tensile modulus than poly (butylene adipate-co-terephthalate) (PBAT) and comparable with LDPE. Meanwhile, the biodegradability of PPAT in soil is comparable and even higher than PBAT within 70 days. Therefore, PPAT is a promising bio-based and biodegradable candidate to replace low-density polyethylene (LDPE) in flexible packaging films.

4.2 Introduction

Low density polyethylene (LDPE) is one of the most used thermoplastics in flexible packaging applications due to its appropriate mechanical properties and low cost.
However, polyethylene is produced from fossil resources and cannot be readily degraded and recycled. In the last several decades, people are attempting to recycle thermoplastics to reduce the waste and the dependence on non-renewable sources. Only a small fraction (<10%) of plastics is recycled and majority of them are discarded in landfills. These plastics, particularly flexible plastic wastes, are accumulated in natural environment and finally cause environmental issues [10]. Therefore, there is an increasing demand for the biobased, degradable, and recyclable plastics.

**Table 4.1.** Comparison of Mechanical Properties of PBAT and Polyethylene Blown Films

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Melt flow index (g/10min)</th>
<th>Melt temp (°C)</th>
<th>Tensile strength at break (MPa)</th>
<th>Secant modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE (Packaging)</td>
<td>0.85-1</td>
<td>108-124</td>
<td>35-45</td>
<td>120-200</td>
<td>400-700</td>
</tr>
<tr>
<td>LDPE (Packaging)</td>
<td>2-12</td>
<td>107-113</td>
<td>10-31</td>
<td>170-200</td>
<td>150-500</td>
</tr>
<tr>
<td>PBAT</td>
<td>2.7-4.9</td>
<td>110-120</td>
<td>35/44</td>
<td>95/80</td>
<td>560/710</td>
</tr>
</tbody>
</table>

Note: The mechanical properties were tested using blown films. The data of LLDPE and LDPE are extracted from DOW datasheet and PBAT data is from BASF datasheet.

Thanks to the cleavable ester groups, polyesters are promising candidates to replace polyethylene due to their biodegradability, recyclability, and potentially biobased feedstocks. Aliphatic-aromatic polyesters are an increasingly important class of co-polymers due to the combination of superior thermo-mechanical properties, biodegradability and recyclability. Among them, PBAT polyester has been commercialized and applied in the flexible packaging industry. However, PBAT does not fully meet the application requirements due to its lower tensile modulus than polyethylene, non-biobased nature, and slow degradation rate in aquatic environments.
Basic properties of LDPE, LLDPE and PBAT blown films are summarized in Table 4.1, showing the moduli of PBAT films are still insufficient, even if the tensile strength may be unnecessarily higher than LDPE and LLDPE for flexible packaging applications. The lower moduli demand thicker films of PBAT than polyethylene to withstand the same loading. Alternatively, PBAT is blended with starch or PLA to strengthen the mechanical properties for wider applications, however, at the expense of increased cost and processing complexity. To be competitive with LDPE, a modulus of at least 1.5x of current PBAT is required (to allow for thinner films similar to those found in LDPE packaging).

In addition, PBAT is currently synthesized using monomers from fossil resources. Biobased diacid, 2,5-furandicarboxylic acid was evaluated to replace terephthalic acid in PBAT to produce poly (butylene adipate-co-furandicarboxylate) (PBAF). The thermal properties and mechanical properties generally decreased with the butylene furandicarboxylate (BF) molar fraction increasing from 0% to 30% and started to increase when BF molar fraction greater than 60% [106]. When BF mole fraction was increased up to 60%-90%, PBAFs exhibited moduli of 44-111 MPa, moderate strength (30-42MPa) and high elongation at break (310-470%), which indicates PBAF may need larger amount of furandicarboxylate content (>60mol%) to achieve acceptably high modulus. Biobased poly (butylene succinate-co-furandicarboxylate) PBSFs were also investigated, and the composition dependences of thermal properties and mechanical properties (tensile modulus and tensile strength) exhibited similar trends with PBAF, while PBSFs generally had higher modulus than PBAFs at the same BF fractions, which may be attributed to the higher crystallinity of PBSFs [106] [107]. Further study shows
that PBAF degraded faster than PBSF in composting environment due to its lower crystallinity, and PBSF with 60% butylene furandicarboxylate (BF) fraction passed biodegradation requirement, i.e. 90% biodegradation in 180 days [108]. The obvious biodegradation of PBSF (60% BF) may came from the hydrophilic furan ring than, which favored the attack of extracellular enzymes, and facile segmental motion [109].

Thanks to the emergence of low cost biobased 1,5-PDO (Bio-PDO), Bio-PDO-based polymers have very recently attracted attention from researchers to replace petroleum-derived diols. Currently, biobased poly (pentylene adipate-co-terephthalate) (PPAT), poly (pentylene succinate-co-terephthalate) (PPST), poly (pentylene furanoate) (PPF), poly (ethylene furandicarboxylate-co-pentylene furandicarboxylate) (PEPF) have been synthesized and investigated. The crystallinity of PPAT and PPST increased with aromatic terephthalic acid fraction. When pentylene terephthalate (PT) comprised more than 45 mol% of the polymer repeating units (higher “aromatic content”) higher modulus and tensile strength were achieved [110], [111]. Compared with PPST, PPAT exhibited superior crystallization ability and lower glass transition temperatures. However, the PPAT synthesized in the previous work suffered low molecular weight, indicated by low intrinsic viscosity, causing the insufficient overall mechanical properties including tensile strength and elongation for real applications. The previous PPAT failed to achieve the target value of approximately 1.5x modulus of current PBAT polymers which is required to produce films of similar thickness as polyethylene.
Figure 4.1. Possible mechanism for brittle-to-ductile transition: (a) low molecular weight polymers, (b) high molecular weight polymers, lc: thickness of crystalline lamellar, la: thickness of interlamellar region (Figure derived from ref. [112])

The importance of molecular weight and required PPAT design parameters can be further understood by analogy to structure property relationships of analogous semi-crystalline thermoplastics. In design of PPAT polymers it is important to maintain high modulus (arising from high crystallinity) while preserving ductile behavior for stretching, toughness and impact resistance.

First, polymers require sufficient ductility for real applications, and thus need high molecular weight and appropriate crystallinity. The mechanical properties of polyethylene have been widely investigated and provide a useful set of guiding principles. A material is brittle at low Mw and becomes ductile above a critical Mw. The nature of the brittle to ductile transition may be related to the interlamellar thickness (la) of polyethylene (Figure 4.1); over a wide range of molecular weight, the polyethylene was
either brittle or in the transition region when the interlamellar thickness was less than 60-70 Å [113]. This is because ductile deformation requires adequate elastically active disordered chains in the interlamellar regions to connect the crystallites. Disordered chains that are “cross linked” by molecular entanglement provide this desired behavior. In addition, polymers may undergo a transition from ductile to brittle behavior as crystallinity increases and it is necessary to design packaging grade polymers to avoid this from taking place. For example, when polyethylene at Mw=71KDa, a transition from brittle to ductile behavior occurred when the crystallinity changed from 75% to 64%, while at higher molecular weights, the material was still ductile even at higher crystallinity levels.

Second, crystallinity plays an important role in tensile modulus. The improvement in mechanical properties (e.g. modulus and tensile strength) will allow further downgauging of film thickness to reduce cost and improve sustainability. The minimum mechanical requirements are inversely proportional to film thickness [114], particularly, mono layer film stiffness, determined by modulus × thickness, needs to satisfy minimum mechanical requirements. Currently PBAT blown film needs to be thicker than polyethylene for the same end usage because of lower elastic modulus of PBAT. This causes much higher cost for PBAT films and restricts the adoption in the marketplace. In the ductile deformation region of polyethylene, the initial modulus is directly proportional to crystallinity level, modestly affected by interlamellar thickness (the thicker the interlamellar region, the lower the modulus), and weakly dependent on the crystallite thickness [113].
From the polyester composition perspective, more aromatic content increases crystallinity and tensile modulus. For example, the crystallinity of PPAT increases from 5.6% to 14% and tensile modulus increases from 69 to 200 MPa when aromatic content increases from 45 mol% to 85 mol% [110]. In addition, crystallinity is affected by the processing conditions of polymers. Polyethylene crystallinity and lamellar thickness increase under isothermal crystallization conditions, which are well controlled by crystallization temperature and time [115]. Uniaxial stretching is another way to improve crystallinity by aligning polymer chains under external force [116], [117]. A more practical processing method is film blowing; polymer melts are processed under both temperature gradients and external force to evolve desired microstructures (e.g. crystallinity, orientation) [118]. Molecular weight has large effects on crystallization kinetics. After a certain molecular weight, crystallinity may decrease with molecular weight, and therefore, tensile modulus decreases [112], [119]. Thus, by designing polymer composition and optimizing processing parameters, the tensile modulus can be enhanced to meet film thickness and downgauging requirements.

The ultimate tensile strength of polyethylene films increased with molecular weight and approach a maximum, which highlight the importance of noncrystalline interlamellar regions where entanglements, knots, and loops exist [113], [120]. Similar dependence of mechanical property on molecular weight and crystallinity was also observed in linear polyesters. For poly(ω-hydroxy tetradecanoic acid) and poly(ω-pentadecalactone) with Mw of 53K to 110KDa and 250K to 481KDa respectively [121],
The ultimate tensile strength (recalculated from the sample dimensions after stretching) increased with molecular weight and approached to a maximum value because more entanglements in longer polymers contribute to higher tensile strength. Higher molecular weight creates more entanglements in polymer amorphous regions which contributes to strain hardening of materials [122]. A model was proposed to correlate the tensile stress at break ($\sigma_B$) and number-averaged molecular weight ($M_n$) as described in the equation ($\sigma_B \sim (\rho \left( \frac{1}{M_c} - \frac{1}{M_n} \right)^{5/6}$), where $M_c$ is the critical entanglement molecular weight [123]. Therefore, polyesters will be synthesized aiming for a high molecular weight ($> M_c$) to generate ductile materials for flexible packaging applications.

In this chapter, the initial target is to synthesize higher molecular weight PPAT with 60 mol% terephthalic acid (based on total acids) to improve their mechanical properties. For initial comparison, we achieved PPAT compression films with 1.5 times modulus than PBAT to replace low-density polyethylene, meanwhile maintaining acceptable biodegradability. We recommend future work, where we expect the mechanical properties of PPAT blown films to have 1.5 times modulus than PBAT blown films and comparable with LDPE blown films.

4.3 Experimental section
4.3.1 Materials

1,5-pentanediol (PDO, 98%), glycerol, adipic acid (AA), terephthalic acid (TPA), titanium(IV) isopropoxide (Ti), phosphoric acid (P), 4,4’-methylene diphenyl diisocyanate (MDI).

4.3.2 Synthesis

First, poly (pentylene adipate-co-terephthalate)s were synthesized in a 500 mL reactor via esterification and transesterification reactions. The monomer feed mass is shown in Table 4.5. PDO, glycerol, adipic acid, terephthalic acid, and 37.5 wt% of Ti catalysts were charged into reactor with slow nitrogen flow, followed by increasing temperature to 175°C and starting agitation. The temperature was increased to 230°C in increments of 5°C/30mins. After terephthalic acid was melted and 90% of the theoretical water was collected, the rest of the catalysts (and P if using) were fed into the oligomers. Then, 0.5 mbar vacuum was applied and the polycondensation was initiated. The temperature was increased to 250°C in increments of 5°C/30min. When the weight-average molecular weight was increased to 32KDa, the reaction was stopped, and the polymer melts were cooled under fast nitrogen flow.

To further increase the molecular weight, PPAT polyesters with medium MW were further advanced in thin-film polymerization and chain extension reactions. To perform thin-film polymerization, 2.5g PPAT was transferred to a 50 mL flat bottom flask. Then, the flask was heated in an oil bath that was preheated to set temperature, and PPAT was melted to generate about 1.6 mm film. Subsequently, 0.01 – 0.02 mbar vacuum was applied to continue the polycondensation reaction. To perform chain
extension reaction, 20g PPAT polyesters were loaded into a melt blender that was preheated to 200°C, and then 0.5 wt%, 1 wt%, and 1.5 wt% MDI were slowly added to allow the chain extension for 15 mins before collecting the samples.

4.3.3 Characterizations

1H NMR spectra were recorded on a Bruker Avance-Ⅲ 400 MHz spectrometer to characterize polymer compositions. Deuterated chloroform was used as solvent and tetramethylsilane as internal reference with signal at 0 ppm. Acid values were tested by dissolving 1-2 g polymers in chloroform and titrate with 0.1 N KOH methanol solution with phenolphthalein indicators. Polyester molecular weight (weight-average: Mw, number-average: Mn) and polydispersity were characterized by gel permeation chromatography (GPC) operated at 40°C using 2,2,2-Trifluoroethanol as eluent at a flow rate of 1 mL/min on an Agilent 1200 series system with a refractive index detector. PMMA was used as standards. Polymers were dissolved in TFE solvent at 3 mg/mL, and then filtered through 0.45 µm PTFE filter prior to injecting to GPC columns.

Thermal transitions were determined using differential scanning calorimetry (DSC) (TA Instruments Q200) with a nitrogen flow rate of 50 mL/min. The DSC temperature calibration was performed using Indium's melting point. The samples were heated to 200°C from 25°C at a rate of 10°C/min, cooled to -50°C at a rate of 10°C/min and heated to 200°C at a rate of 10°C/min. Tg was calculated from second heating ramp of DSC. Maximum of melting peaks were recorded as Tm.

The linear viscoelastic properties of PPAT were characterized by a rotational rheometer in parallel plate with 8 mm diameter and 0.4 mm gap. All measurements were
conducted at 160°C under nitrogen environment. Dynamic frequency sweep was performed with a frequency at 0.1 to 150 Hz and controlled strain of 1.3%.

Microstructures were tested by Wide-angle X-ray scattering (WAXS), small-angle X-ray scattering (SAXS) and soil-state NMR. SAXS and WAXS measurements were performed on a Ganesha SAXS-LAB instrument. The incident beam was Cu Kα radiation (λ = 0.1542 nm). The incident beam was collimated with a two-aperture system. The measurements were performed in vacuum at room temperature. SAXS and WAXS patterns were recorded as a function of the scattering vector (q = 4π sin(θ)/λ) using a two-dimensional detector (Pilatus 300K), where λ is the X-ray wavelength and 2θ is the scattering angle. Long period (Lp) of polyesters was calculated from plot of I*q^2 vs q (Lp=2π/q_max). Solid-state NMR spectra were recorded on a Bruker 600MHz Avance-III operating at single 1H 90° pulse, followed by acquisition of Free Induction Decay signal (FID). The acquisition consisted of 4 dummy scans followed by 64 accumulated scans at a 2 s/scan recycle delay. 30-40 mg polymers were cut into small pieces and loaded into the NMR sample tubes. Only the first 240 µs of data were used for fitting Gaussian-Exponential-Exponential equation, from which crystallinity is calculated [124].

Mechanical properties were tested by Instron. Uniform polymer films were prepared by heat press machine at 180C. All films had similar thickness of 0.5 mm and were cut into dumbbell-shaped specimens (3.8*1.6*0.5 mm) followed by annealing at room temperature one week prior to tensile testing. 3-5 specimens of each polymer films were drawn at a rate of 1.27 mm/min, and stress-strain curves were recorded. Tensile
modulus (within 2% strain), tensile strength and elongation at break with standard deviations were calculated.

Biodegradation test in soil. The biodegradation was conducted at University of Wisconsin by Min Soo Kim from George Huber’s Group. The biodegradation test of synthesized polyesters was built according to ASTM D5988 which is the standard for determining aerobic biodegradation of plastic materials in soil. The soil preparation followed the ASTM D5988-18 and a mixture of soil aliquots collected into three different regions was used to ensure microbial biodiversity. The mixed soil was sieved to obtain particle sizes smaller than 2 mm. Nine square samples of 1 inch x 1 inch and thickness around 0.9mm were subjected to soil degradation in a closure maintained at ambient temperature (21±1°C). The container base was covered with soil; samples of each material were placed on this layer being subsequently covered with approximately 2 cm of soil. Every 7~10 days, each sample was measured for the CO2 produced by microorganisms. Figure 4.2 shows the schematic view of the biodegradation test in soil according to ASTM D5988.
Figure 4.2. The schematic view of the biodegradation test setup according to ASTM D5988.

\[
\text{Biodegradation (\%)} = \frac{\text{CO}_2\text{test} - \text{CO}_2\text{blank}}{\text{CO}_2\text{theoretical}} \times 100
\]

where \(\text{CO}_2\text{blank}\) is the amount of \(\text{CO}_2\) evolved from only soil without the tested material.

We set-up the fifteen desiccators for 4 materials (PPAT-32K, PPAT-1.5% MDI, PBAT, and cellulose) and blank having only soil, in triplicates according to the ASTM D5988.
4.4 Results and Discussion

Scheme 1. Melt polymerization, thin-film polymerization, and chain extension to synthesize high molecular weight PPAT.

4.4.1 Synthesis of High molecular Weight PPAT

Scheme 1 describes the reaction route for high molecular weight PPAT through esterification/polycondensation, followed by thin-film polymerization or chain extension. We first synthesized PPAT polyesters in a 400g scale via esterification and polycondensation. The monomer feeds, catalysts (Ti/P, and Ti) and resulting molecular weight (MW) are summarized in Table 4.6. The molecular weights of 30-40KDa were achieved, similar to the previous study [125]. However, longer reaction time caused the polymers to depolymerize, and generated carboxyl groups as indicated by the increase in acid values (8.54-10.85 mg KOH/g polymer Table 4.7). This is because, during melt polymerization, the MW is manipulated by simultaneous polymerization and depolymerization. High temperature reduced the viscosity of polymer melts and therefore
facilitated the mass transfer of by-products (i.e., 1,5-pentanediol). However, high temperature also caused degradation. Previous studies show PBAT degraded at 180-200°C probably due to hydrolysis or β-C-H hydrogen transfer, similar to polybutylene terephthalate and polypropylene terephthalate, generating COOH and chain-terminating groups (e.g. allyl, butenyl ester end groups) [126], [127], [128], as shown in Figure 4.3. These chain-terminating end groups further caused the decrease in Mw [128]. Therefore, PPAT polyesters with medium Mw were collected before degradation for further post polymerization as discussed below.

**Figure 4.3.** PTT thermal degradation via β-C-H hydrogen transfer under non-oxidative conditions (derived from Ref. [128]).
Figure 4.4. Molecular weight increases with thin-film polymerization time by using Ti/P as catalysts at different temperatures for 1.6 mm films. The vacuum is controlled at 0.01-0.02 mbar for all reactions.

Inspired by PBAT synthesis which involve multiple reactors, steps and use coupling agent to improve production and quality [129], PPAT polyesters were subjected to post polycondensation. We employed two methods to further boost molecular weights, (a) thin-film polymerization and (b) chain extension reaction shown in Scheme 1. For thin-film polymerization, the thin-layer films largely reduced mass transfer path of by-product (1,5-pentanediol), and therefore allowed polycondensation reaction to continue and molecular weight to increase. Previous studies on polyethylene terephthalate synthesis show higher temperature, higher vacuum, and thinner films facilitated the diffusivity of by-products in polymer melts [130]. However, overly high temperature...
 (>240°C) and long reaction time caused the degradation of polypropylene terephthalate and polybutylene terephthalate, and increased carboxyl groups [130], [131], [127]. Therefore, the effects of reaction temperatures on polycondensation of PPAT were explored. PPAT polyesters synthesized with Ti/P catalysts were subjected to thin-film polymerization at 230°C, 240°C and 250°C. Weight-average molecular weight (Mw) change with reaction time and temperature is shown in Figure 4.4. The rate of Mw increase at 240°C is greater than at 230°C because higher temperature facilitated the mass transfer of by-product and increased the polycondensation rate. After certain reaction times (7 hrs at 230°C, 5 hrs at 240°C and at 250°C), Mw started to decrease, indicating depolymerization prevailed. When the reaction was conducted at 250°C, the increase of Mw with time was not obvious, indicating 250°C caused severe degradation of PPAT. As Table 4.7 shows, the acid values of degraded PPAT after treated at 230°C, 240°C and 250°C are all higher than initial PPAT, which confirm the degradation.
Figure 4.5. Molecular weight increases with thin-film polymerization time by using different catalysts (Ti, Ti/P) at 230°C for 1.6mm films. The vacuum was controlled at 0.01-0.02 mbar for all reactions.

Figure 4.6. Appearance of PPAT synthesized using Ti/P (left), and Ti alone (right).

MW of PPAT synthesized from Ti/P after thin-film polymerization for 7 hrs may be insufficient for real applications. To further improve MW, we studied the effects of different catalysts including Ti/P and Ti alone. Phosphoric acid was used in melt polymerization as thermal stabilizer and inhibited discoloration of final products at elevated temperatures [132]. We found, as Figure 4.5 shows, phosphoric acid as a co-
catalyst largely decreased the transesterification rate, compared to Ti as catalysts. This is because phosphoric acid reacted with Ti catalyst and inhibited the catalyst activity. Previous studies show phosphorous compounds with acidic OH groups formed adducts with various catalysts, such as titanium butoxide, antimony triacetate, thus reduced the reactivity of catalysts and reaction rate [133], [134]. In our synthesis, the mole ratio of Ti and P is nearly 1, which formed adducts and largely decreased the reaction rate. Furthermore, the MW of final PPAT synthesized with Ti/P was lower than without P, indicating P may continuously inhibit the MW increase during the whole polycondensation reaction. However, as Figure 4.6 shows, PPAT synthesized from Ti/P exhibited slightly yellow, whereas PPAT synthesized from Ti alone suffered severe discoloration. The decreased catalyst reactivity by P, on the other hand, was found to advantageously restrain side reactions, for example the formation of acetaldehyde, carboxyl end groups and discoloration during PET synthesis [134], [135]. Therefore, the thin-film polymerization illustrates the effects of temperatures and catalysts on reaction kinetics during melt polycondensation. To improve the mass transfer in large scale reaction, a mixer with higher torque may be required to produce PPAT with high Mw in one single reaction. The synthesis of PDO-based high molecular weight polyesters might be more difficult than shorter diol-based polyesters, e.g. PET, PTT, PBT and PBAT, because higher boiling point of PDO may cause lower diffusivity in polymer melts meanwhile higher reaction temperature speeds degradation.

The second method for post-polymerization is chain extension. Isocyanate chemistry has been widely used in coupling agents or compatibilizers to bridge hydroxyl terminated components because reaction rate of isocyanate groups (NCO) with OH is fast.
To perform chain extension reaction, 0.5%, 1% and 1.5% 4,4’-methylene diphenyl diisocyanate (MDI) was used to blend with PPAT-32K at 200°C. The Mw increased from 71KDa to 142KDa with MDI increase, and terminal OH groups were completely consumed when 1.5% MDI was added, as shown by the disappearance of terminal OH at 3.66 – 3.72 ppm in the 1H NMR spectra (Figure 4.23), which confirmed isocyanate groups reacted with PPAT hydroxyl groups.

### 4.4.2 Molecular weight and polymer composition

**Table 4.2.** Aromatic composition (Ø<sub>PT</sub>), Weight-averaged molecular weight (Mw), Polydispersity (PDI), Number-Average Sequence Length (L<sub>n,PT</sub> and L<sub>n,PA</sub>), and Randomness (R) of PPAT

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ø&lt;sub&gt;PT&lt;/sub&gt;</th>
<th>Mw (KDa)</th>
<th>PDI</th>
<th>L&lt;sub&gt;n,PT&lt;/sub&gt;</th>
<th>L&lt;sub&gt;n,PA&lt;/sub&gt;</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPAT-32K</td>
<td>0.624</td>
<td>32</td>
<td>1.8</td>
<td>2.60</td>
<td>1.63</td>
<td>0.999</td>
</tr>
<tr>
<td>PPAT-105K</td>
<td>0.631</td>
<td>105</td>
<td>3.2</td>
<td>2.66</td>
<td>1.61</td>
<td>0.998</td>
</tr>
<tr>
<td>PPAT-145K</td>
<td>0.652</td>
<td>145</td>
<td>4.2</td>
<td>2.80</td>
<td>1.56</td>
<td>0.999</td>
</tr>
<tr>
<td>PPAT-0.5%MDI</td>
<td>0.621</td>
<td>71</td>
<td>2.3</td>
<td>2.59</td>
<td>1.62</td>
<td>1.003</td>
</tr>
<tr>
<td>PPAT-1%MDI</td>
<td>0.619</td>
<td>127</td>
<td>3.6</td>
<td>2.61</td>
<td>1.62</td>
<td>1.001</td>
</tr>
<tr>
<td>PPAT-1.5%MDI</td>
<td>0.621</td>
<td>142</td>
<td>4.1</td>
<td>2.61</td>
<td>1.63</td>
<td>0.998</td>
</tr>
</tbody>
</table>

By utilizing thin-film polymerization and chain extension, it is the first time that high molecular weight PPAT polyesters (71K-145KDa) were successfully synthesized. The GPC curves of all PPAT samples are shown in Figure 4.20 and molecular weights are summarized in Table 4.2. We also observed the PDI increased with Mw, which came from the fact that higher viscosity at higher Mw caused less efficient mixing of polymer melts. The high molecular weight PPAT synthesis may require more powerful reactor and stringent optimization of reaction conditions.
1H NMR spectra of PPAT polyesters are shown in Figures 4.21-4.23, from which the chemical composition, number-average sequence length and randomness are calculated by using equations A4.1-4.4 and results are summarized in Table 4.2. For neat PPAT, with the increase in Mw, $\varnothing_{PT}$ and $L_{n,PT}$ slightly increase. This is because, during polycondensation reaction, hydroxyl end groups from one chain had larger probability to react with terephthalate ester groups near another chain ends (TPA: AA in feeds=3:2) and eliminated by-product diols, thus generated more aromatic units. Unlike neat PPAT, $\varnothing_{PT}$ and $L_{n,PT}$ of chain extended PPAT remained constant due to the different reaction mechanism. All PPAT polyesters have aromatic sequence length ($L_{n,PT}$) less than 3 and randomness close to 1, indicating successful synthesis of random co-polyesters. The $L_{n,PT}$ less than 3 may be critical for the biodegradation because shorter aromatic sequency length (<3) facilitates the degradation in both soil and composting environment [61].

**Table 4.3.** Melting Temperature (Tm) and Glass Transition Temperature (Tg) of PPAT and PBAT

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tm, °C</th>
<th>Tg, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPAT-32K</td>
<td>82.7</td>
<td>-24</td>
</tr>
<tr>
<td>PPAT-105K</td>
<td>83.7</td>
<td>-22.8</td>
</tr>
<tr>
<td>PPAT-145K</td>
<td>82.6</td>
<td>-18.1</td>
</tr>
<tr>
<td>PPAT-0.5%MDI</td>
<td>80.9</td>
<td>-21.6</td>
</tr>
<tr>
<td>PPAT-1%MDI</td>
<td>75.4</td>
<td>-20.3</td>
</tr>
<tr>
<td>PPAT-1.5%MDI</td>
<td>72.9</td>
<td>-19.7</td>
</tr>
<tr>
<td>PBAT</td>
<td>125</td>
<td>-30</td>
</tr>
</tbody>
</table>
4.4.3 Thermal Transition Temperatures (Tm, Tg) of PPAT Compression Molded Films

To capture the thermal properties of PPAT compression molded films, the melting temperatures were recorded from 1st heating curve of DSC from 25°C to 200°C. DSC curves are shown in Figure 4.24 and A4.6, and results are summarized in Table 4.3. For neat PPAT, when molecular weight increased from 32 to 145 KDa, Tm didn’t change appreciably. For chain extended PPAT, however, Tm decreased from 80.9°C to 72.9°C when MDI increased from 0.5% to 1.5%. The decrease in Tm ascribes to the decrease in crystal lamellar thickness, indicating MDI may interrupt the polymer chain regularity and caused thinner lamella. The Tg of neat PPAT increased from -24°C to -18.1°C with Mw increase from 32KDa to 145 KDa. One reason for the increased Tg is higher aromatic fraction as shown in Table 4.2; according to Fox equation, Tg is dependent on weight fraction of aliphatic and aromatic units. Another reason is the effects of MW. According to Fox and Flory equation [138], higher MW, higher Tg, as observed for both neat PPAT and chain extended PPAT, indicating slower chain mobility with Mw increase [139]. The Tg (-18.1 - -24 °C) and Tm (72.9 – 83.7 °C) indicate PPAT polyesters may have wide temperature window for flexible packaging applications.
As Figure 4.7 shows, PPAT films show diffraction peaks at 7.7, 16, 17.5, 21.8, and 23.3, which are similar to PPT and PPA polyesters. The two peaks at 16 and 17.5 belong to the \{012\}, \{010\} planes, and peaks at 21.8 are assigned to \{110\} plane.
Figure 4.8. Crystallinity (tested by NMR and WAXS) of PPAT compression molded films.

The crystallinities of PPAT compression molded films were calculated from WAXS and NMR relaxometry with results summarized in Tables 4.8 and 4.9. Figure 4.8 shows the change of crystallinity (tested by both WAXS and NMR) with molecular weight. For the same sample, crystallinity tested by solid-state NMR is higher than WAXS, which may be because small crystals with short-range ordering are contributed to crystalline signals in NMR, however, are not visible in WAXS [140]. The crystallinities of either neat PPAT or extended PPAT decreased with the increase in molecular weight, similar to the previous study of poly(aryl-ether-ether-ketone) resins [141]. The compromised crystallinity by molecular weight may be ascribed to slower crystallization kinetics at higher molecular weight. With the same crystallization temperature, nucleation rate and crystal growth rate of polymers are affected molecular weight [142]. We also
observed, with similar molecular weight, neat PPAT films exhibited higher crystallinity
than extended PPAT films, indicating MDI may interrupted polymer regularity in
compression molded films.

Solid-state 1H NMR can detect the distinct T2 relaxation time of each phase
(crystalline, interfacial, and amorphous) to quantify the population and dynamics of each
phase component by fitting a three-phase model. A previous study using the same model
has found semi-crystalline polypropylene has T2 relaxation times of around 8, 55-70, and
430-530 µs for crystalline, interfacial, and amorphous components respectively [124],
similar to our results summarized in Table 4.9. The relaxation time indicates the strength
of 1H-1H dipolar coupling; the shorter the relaxation times, more rigid the components.
With increase in molecular weight, relaxation times of interfacial and amorphous phases
decrease. This may be because higher entanglements in higher molecular weight caused
less segmental mobility and therefore shorter relaxation times.

4.4.5 Rheological Properties
Figure 4.9. Complex viscosity of PPAT and PBAT at 160°C as a function of angular frequency

Figure 4.10. Zero-shear viscosity ($\eta_0$) change with Mw.
Figure 4.9 shows the complex viscosity of PPAT and PBAT polymers at 160°C. Due to the low molecular weight, PPAT-32K didn’t exhibit good rheological properties for real applications. Complex viscosity increases with molecular weight due to the increasing entanglements, similar to the observations in LDPE/HDPE blends [143]. PPAT-105K exhibited lower complex viscosity than PBAT even if they had similar Mw. This may be ascribed to larger PDI of PPAT-105K than PBAT (3.2 vs 2.6) or low molecular weight fraction in PPAT-105K (Figure 4.20). PPAT-145K and PPAT-1.5%MDI (142KDa) exhibited obvious increase in complex viscosity. To further understand the polymer structures, zero-shear viscosity ($\eta_0$) was calculated from Cox-Merz fit (Figure 4.29. and equation A4.6). $\eta_0$ vs Mw plot is shown in Figure 4.10. PPAT with Mw<130KDa, the slope is 3.8, close to 3.4 power for linear polymers ($\eta \sim M^{3.4}$). PPAT-145K and PPAT-1.5%MDI deviated from the linear curve, indicating branching or gel may existed in these two samples and caused much higher $\eta_0$ [144], [145]. A previous study also observed the nylon 6 extended with epoxy linking agents had more than 5 times of increase in $\eta_0$ when MW increased only 1.6 times [145]. This unexpected increase in $\eta_0$ was attributed to the formation of branching structures, which caused the large deviation from 3.4 power law of linear polymers. For the PPAT-145K sample, the local gel may be formed with thin-film polymerization time because 0.17 mol% glycerol (based on PDO) was charged in monomer feeds (Table 4.6). In the PPAT-1.5%MDI, the residual unreacted isocyanate groups may react with urethane groups to form branched structures such as biuret and allophanate structures [146], [77].
Figure 4.11. Storage modulus (G’) and loss modulus (G”) of PPAT-105K at 160°C as a function of angular frequency (ω).

Table 4.4. Crossover Modulus (Gx), Crossover Frequency (ωx) and Relaxation Time (1/ωx) at 160°C

<table>
<thead>
<tr>
<th></th>
<th>Gx (Pa)</th>
<th>ωx (rad/s)</th>
<th>1/ωx (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPAT-105K</td>
<td>133728</td>
<td>175</td>
<td>0.006</td>
</tr>
<tr>
<td>PPAT-145K</td>
<td>25590</td>
<td>0.314</td>
<td>3.185</td>
</tr>
<tr>
<td>PPAT-0.5%MDI</td>
<td>148972</td>
<td>238</td>
<td>0.004</td>
</tr>
<tr>
<td>PPAT-1%MDI</td>
<td>114600</td>
<td>72</td>
<td>0.014</td>
</tr>
<tr>
<td>PPAT-1.5%MDI</td>
<td>19330</td>
<td>0.37</td>
<td>2.703</td>
</tr>
<tr>
<td>PBAT</td>
<td>228300</td>
<td>193</td>
<td>0.005</td>
</tr>
</tbody>
</table>
Figure 4.12. Relaxation time \((1/\omega_x)\) increases with Mw.

To process resins in extrusion and film blowing, Mw and PDI are required to be optimized to balance melt viscosity and elasticity, and to improve resin appearance, melt fracture performance, and melt strength [147]. Therefore, it is critical to understand the effects of Mw and PDI on rheological properties. Storage modulus and loss modulus as a function of angular frequency are shown in Figure 4.11 and Figures 4.30-4.34, from which crossover modulus \((G_x)\), crossover frequency \((\omega_x)\), relaxation time \((1/\omega_x)\) are extracted and summarized in Table 4.4. PBAT and PPAT-105KDa exhibited similar crossover frequency and reptation relaxation times (0.005s and 0.006s), indicating similar chain mobility even if they contain different aromatic content (60% vs 47%). However, PPAT-105K had lower crossover modulus than PBAT (133.7 vs 228.3 KPa), which may

\[
\begin{array}{|c|c|}
\hline
\text{Mw (KDa)} & \frac{1}{\omega_x} (s) \\
\hline
\text{Neat PPAT} & 0.0 \\
\text{PPAT-MDI} & 0.5 \\
\hline
\end{array}
\]

122
be ascribed to the higher PDI, 3.2, of PPAT-105K. Previous studies have shown crossover modulus is strongly dependent on polydispersity (PDI), i.e. for a given polymer assuming plateau modulus is a constant [148], the ratio of plateau modulus to crossover modulus increased with the PDI [149] and Wu’s equation [150] quantified the correlation when PDI less than 3. Similarly, PPAT crossover moduli decreased with Mw and PDI increase.

In addition, Figure 4.12 shows relaxation time \((1/\omega_x)\) increased with Mw because higher Mw inhibited chain mobility. The abrupt increase of \(1/\omega_x\) at Mw around 140KDa may be because of branching structures as discussed above. In addition, higher aromatic content in polymers with higher molecular weights may also contribute to longer relaxation time because the aromatic units behaved as rigid monomers to influence chain dynamics [151]; aromatic content increased from 62.4% to 65.2% in neat PPAT with Mw increase from 32K to 145K, and 0.5% to 1.5% MDI in chain-extended PPAT. The rheological testing indicates PPAT polyesters rheological properties can be tuned by changing molecular weight and PPAT-105K exhibited similar chain mobility as PBAT at 160°C, even if further optimization of PPAT polyesters PDI could improve rheological performance.
4.4.6 Tensile Properties of PPAT Compression Molded Films

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E$ (MPa)</th>
<th>$\delta_y$ (MPa)</th>
<th>$\varepsilon_y$ (%)</th>
<th>$\delta_b$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPAT-32K</td>
<td>96.2±2.3</td>
<td>/</td>
<td>/</td>
<td>7.4±0.1</td>
<td>23±3</td>
</tr>
<tr>
<td>PPAT-105K</td>
<td>75.2±4.8</td>
<td>6.7±0.17</td>
<td>20.8±0.5</td>
<td>16.8±1.1</td>
<td>1073±104</td>
</tr>
<tr>
<td>PPAT-145K</td>
<td>67.5±3.9</td>
<td>6.0±0.12</td>
<td>23.9±1.1</td>
<td>16.6±1.4</td>
<td>1057±54</td>
</tr>
<tr>
<td>PPAT-0.5%MDI</td>
<td>65.5±2.4</td>
<td>5.7±0.16</td>
<td>23.4±2.0</td>
<td>11.4±0.7</td>
<td>1099±55</td>
</tr>
<tr>
<td>PPAT-1%MDI</td>
<td>64.7±3.1</td>
<td>5.5±0.1</td>
<td>20.2±2.4</td>
<td>16.9±3.4</td>
<td>1282±186</td>
</tr>
<tr>
<td>PPAT-1.5%MDI</td>
<td>60.2±1.7</td>
<td>5.8±0.07</td>
<td>25.9±3.1</td>
<td>22.4±0.6</td>
<td>1290±18</td>
</tr>
<tr>
<td>PBAT</td>
<td>54.7± 1.3</td>
<td>7.0±0.31</td>
<td>40.5±4.5</td>
<td>27.3±0.8</td>
<td>1190±2</td>
</tr>
<tr>
<td>LDPE</td>
<td>150.7±8.7</td>
<td>9.2±0.36</td>
<td>76±14.2</td>
<td>19.4±2.4</td>
<td>1096±118</td>
</tr>
<tr>
<td>LLDPE [152]</td>
<td>64±1.5</td>
<td>9.9±0.32</td>
<td>32.7±2.3</td>
<td>~17</td>
<td>1045±33.5</td>
</tr>
</tbody>
</table>

Note: $E$-tensile modulus at 2% strain, $\delta_y$-tensile strength at yield, $\varepsilon_y$ – elongation at yield, $\delta_b$-tensile strength at break, $\varepsilon_b$ -elongation at break.

Figure 4.13. Tensile stress-strain curves of PPAT and PBAT compression molded films. PPAT-145K exhibited similar stress-strain with PPAT-105K.
We first investigated the mechanical properties of PPAT compression molded films to compare with PBAT and LDPE compression molded films as summarized in Table 4.5. Figure 4.13 describes the stress-strain curves of PPAT films and Figure 4.14 shows the tensile strength changes with Mw. For neat PPAT polyesters with Mw of 32KDa, the material was brittle with low elongation at break (23%), which is similar to the previous study [125]. At the molecular above 100KDa, the material exhibited ductile behaviors, and the tensile strength increased to about 17MPa. However, neat PPAT-145K and PPAT-105K exhibited a similar tensile strength. This may be because low molecular weight PPAT fractions existed in both samples (Figure 4.20) and weakened the final tensile strength. Therefore, further optimization of PPAT synthesis conditions is required to narrow the polydispersity. Compared with neat PPAT, tensile strength of PPAT
extended with MDI increased from 11.4 to 22.4 MPa when MDI level increased from 0.5% to 1.5%. With similar molecular weight, PPAT-1.5%MDI (142KDa) exhibited higher tensile strength than neat PPAT-145K, which may be ascribed to intermolecular hydrogen bonding among urethane groups and ester groups [153].

**Figure 4.15.** Tensile modulus of neat PPAT and chain extended PPAT compression molded films. An asterisk (⋆) denotes p<0.05 between samples.

**Figure 4.16.** Tensile modulus as a function of crystallinity (tested by NMR).
Tensile modulus is a critical property that determines applications of different thermoplastics. As Figure 4.15 shows, for either neat PPAT or PPAT extended with MDI, the tensile modulus decreased with the increase in Mw. PPAT extended with MDI exhibited lower moduli than neat PPAT while at similar molecular weight range. As Figure 4.16 shows, the tensile modulus increased with crystallinity for either neat PPAT or chain extended PPAT. The tensile modulus is managed by both amorphous and crystalline phases. Previous studies have shown, polyethylene tensile modulus decreased with crystallinity, which is ascribed to the amorphous phase modulus decreased with crystallinity and lamellar thickness, even if amorphous modulus is 3 orders of magnitude smaller than crystalline phases (2MPa vs 7GPa). The smaller crystal thickness (nearly the same amorphous layer thickness) caused more activated $\alpha_1$ relaxation and increased mobility of amorphous phases and thus a lower amorphous phase modulus and overall modulus [154].
In addition to crystallinity level, the tensile modulus is also affected by interlamellar region because the small deformation mainly occurs in the amorphous region. Figure 4.17 shows the Tensile modulus decreases with Lp increase. Long period (Lp) is the averaged distance between two crystal lamellas (lamellar thickness + amorphous thickness). The Lp values of PPAT films were calculated from small-angle X-ray scattering as shown in Figure 4.27 and results are summarized in Table 4.10. For neat PPAT and extended PPAT, higher molecular weight, larger long period. Furthermore, the Tm of neat PPAT didn’t change largely, whereas Tm of PPAT extended with MDI largely decreased (Table 4.3). The increase in long period (Lp) and decrease in Tm may indicate the averaged distance between crystal lamellas (amorphous thickness) increases, thus causing lower modulus. Similar to the previous study, for various polyethylene with Mw of 40KDa to 351KDa, tensile modulus decreased with interlamellar thickness.
because larger interlamellar region may provide more deformability [120]. In addition, chain extended PPAT with MDI exhibited larger Lp than neat PPAT, indicating chain extender mainly existed in amorphous phases and thinned crystalline layers as shown by the obvious decrease in melting temperature in Table 4.3. The increase in Lp of PBAT blown films after extension with chain extenders was also observed in the previous study [118]. Therefore, the decrease in PPAT moduli with increasing Mw may be ascribed to the combined factors of crystallinity and long period or amorphous layer thickness. These results from compression molded films suggest PPAT mechanical properties (i.e. tensile modulus) can be further enhanced by manipulating microstructures in film blowing process or using additives. Current results show that we have achieved PPAT compression molded films to have higher moduli than PBAT compression molded films and comparable with LDPE compression molded films (PPAT: 60-96MPa, PBAT: 55MPa, LDPE: 64-151 MPa).

Analysis of experimental errors: Primary source of tensile testing errors was experiment. First, all PPAT polyesters had large polydispersity, especially after thin-film polymerization and chain extension. The larger polydispersity caused more inhomogeneous polymer films and thus larger standard deviation particularly for tensile strength and elongation. When 1.5% MDI were added, the standard deviation decreased, which may be ascribed to the hydrogen bonding among urethane groups and ester groups homogenize the films. Second, the procedure to prepare compression molded films is required to be exactly the same for all samples. Temperature and compression pressure
variation can cause the crystallinity change of final films and therefore introducing errors. For example, when compression pressure is 3 MPa (similar to my experiment), crystallinity of polyethylene increased from 20.6% to 23.2% with temperature increase from 135°C to 165°C because higher temperature facilitated crystallization [155]. During my film preparation, temperature and pressure were controlled at 180°C±5°C and 3MPa, thus large influence from compression procedure was not expected.

4.4.7 Biodegradation

![Graph showing biodegradation of PPAT-32K, PPAT-1.5%MDI, and PBAT, according to ASTM D5988-18](image)

**Figure 4.18.** Biodegradability of PPAT-32K, PPAT-1.5%MDI, and PBAT, according to ASTM D5988-18
Biodegradation of PPAT-32K, PPAT-1.5%MDI and PBAT films were investigated in soil at various temperatures. (The experiment and data analysis were done by Min Soo Kim.) Figure 4.18 shows the biodegradation rate of the samples within 90 days. 2.17% of PPAT-32K, 3.74% of PPAT-1.5%MDI, and 2.64% of PBAT degraded within 70 days. This result shows the degradation of PPAT-1.5%MDI is faster than the PBAT in soil. The possible reason is PPAT-1.5%MDI had a lower Tm than PBAT (72 vs 120 °C) and lower crystallinity than PPAT-32K, which allow PPAT-1.5%MDI chains to have more amorphous regions and are more flexible to be degraded.

However, our reference biodegradation rate is lower than other studies. For example, 85.06% of cellulose and 11.14% of PBAT degraded after 90 days at 30°C in soil incorporated with compost according to Saadi et al’s work [156], whereas in our study, 34.52% of cellulose degraded after 84 days and 3.05% of PBAT degraded within 90 days, which may be ascribed to lower soil temperature in our test (21°C).

![Figure 4.18. Biodegradation rate of samples within 90 days.](image)

![Figure 4.19. Evolved CO₂ and biodegradation of PPAT-1.5%MDI and PBAT films at different temperatures (21°C, 28°C, and 34°C).](image)
Thus, to study the effects of temperature on biodegradability, PPAT-1.5%MDI and PBAT films were tested in soil at 28°C and 34°C. Figure 4.19 shows the biodegradation rates of the PPAT-1.5%MDI, PBAT, cellulose and blank samples within 7 days at 28°C and within 8 days at 34°C, respectively. The amounts of CO₂ produced from PPAT-1.5%MDI are 2~3 times at 28 °C and 4 times at 34 °C greater than at 21 °C. The biodegradation of PPAT-1.5%MDI reached to 0.43% and 0.93% at 28 °C within 8 days and 34 °C within 7 days respectively, both of which are faster than at 21°C. Furthermore, it was confirmed that the degree of degradation increased with temperature. The preliminary results show PPAT materials have the potential to be degraded in soil and its biodegradation rate is comparable with PBAT.

4.5 Conclusions

High molecular weight poly (pentylene adipate-co-terephthalate) (PPAT) was successfully synthesized via thin-film polymerization and chain extension. The reaction conditions were explored. In thin-film polymerization, high temperature (250°C) caused the degradation of PPAT and generated carboxyl groups. Titanium-based catalysts provided higher transesterification rates for molecular weight increase than catalysts with the addition of phosphoric acid. In chain extension reaction, 0.5%-1.5% 4,4’-methylene diphenyl diisocyanate was used as coupling agent and final molecular weight increased to 145KDa.
PPAT compression molded films were characterized for tensile properties and exhibited 1-1.5 times higher tensile modulus than poly (butylene adipate-co-terephthalate) (PBAT) compression molded films and comparable with LDPE. The tensile modulus was higher at higher crystallinity level and shorter average distance between lamellas. Moreover, PPAT films exhibited biodegradability comparable or better than PBAT films in soil within 70 days. Therefore, PPAT polyesters are potentially bio-based and biodegradable alternatives of petroleum-based PBAT and non-degradable LDPE.

4.6 Appendix of Chapter 4

Table 4.6. Monomer Feeds and Molecular Weights of PPAT Synthesized in 500mL Reactor

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Recipe 1</th>
<th>Recipe 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,5-PDO</td>
<td>220.2</td>
<td>220.2</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>TPA</td>
<td>118.5</td>
<td>118.5</td>
</tr>
<tr>
<td>AA</td>
<td>69.6</td>
<td>69.6</td>
</tr>
<tr>
<td>Titanium isopropoxide (Ti)</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>Phosphoric acid (P)</td>
<td>0.12</td>
<td>0</td>
</tr>
<tr>
<td>Results</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mw (KDa)</td>
<td>29.2</td>
<td>32-42.7</td>
</tr>
</tbody>
</table>

Table 4.7. Acid values of PPAT before and after thin-film polymerization at different temperatures

<table>
<thead>
<tr>
<th>Polycondensation temperature (°C) /time (hrs)</th>
<th>Acid values (mg KOH/g polymer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial PPAT-29.2K</td>
<td>0.26</td>
</tr>
<tr>
<td>250 (overly heated in 400g scale)</td>
<td>8.54-10.85</td>
</tr>
<tr>
<td>230/12.5</td>
<td>0.58</td>
</tr>
<tr>
<td>240/6.5</td>
<td>0.5</td>
</tr>
<tr>
<td>250/7.5</td>
<td>1.55</td>
</tr>
</tbody>
</table>
Figure 4.20. GPC curves of PPAT and PBAT. TFE GPC using polymethyl methacrylate as standards.

1H NMR spectra of PPAT polyesters

![Chemical structures](image-url)
Figure 4.21. PPAT polyester chemical structures

Figure 4.22. 1H NMR spectra of PPAT-32K, PPAT-105K and PPAT-145K. Chemical shifts at 8.10 ppm, 2.34, and 1.67 ppm are attributed to the methylene groups in benzene (T) and methylene groups from adipic acid monomer (A1, A2). The signals of methylene groups close to ester groups and from PDO monomer were split into four triplets (a4-a1) at 4.07 – 4.42 ppm. Similarly, the rest of methylene groups from PDO monomers were split into signals (b4-b1) at 1.60 – 1.94 ppm and (c3-c1) at 1.39 – 1.60 ppm. The tiny signals at 3.66 – 3.72 ppm come from terminal OH groups.

\[ \phi_{PT}(\text{mol\%}) = \frac{I_T}{I_T + I_A} \times 100\% \]  
(eq 4.1)

\[ L_{n,PT} = 1 + \frac{2I_{a4}}{I_{a3} + I_{a2}} \]  
(eq 4.2)

\[ L_{n,PA} = 1 + \frac{2I_{a1}}{I_{a3} + I_{a2}} \]  
(eq 4.3)

\[ R = \frac{1}{L_{n,PT}} + \frac{1}{L_{n,PA}} \]  
(eq 4.4)
Figure 4.23. 1H NMR spectra of PPAT-0.5%MDI, PPAT-1%MDI and PPAT-1.5%MDI.

DSC data

Figure 4.24. DSC 1st heating curves of PPAT compression films
Figure 4.25. DSC 2nd heating curves of PPAT

Wide-angle X-ray scattering (WAXS) data
Figure 4.26. WAXS and data fitting of PPAT compression films.

Table 4.8. WAXS Fitting Results

<table>
<thead>
<tr>
<th>2θ</th>
<th>7.8</th>
<th>15.9</th>
<th>17.5</th>
<th>21</th>
<th>21.8</th>
<th>23.4</th>
<th>28.2</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPAT-32K</td>
<td>0.0567</td>
<td>0.0517</td>
<td>0.11391</td>
<td>2.94503</td>
<td>0.12387</td>
<td>0.06771</td>
<td>0.0158</td>
<td>0.99871</td>
</tr>
<tr>
<td>PPAT-105K</td>
<td>0.04491</td>
<td>0.03627</td>
<td>0.08034</td>
<td>2.20315</td>
<td>0.07706</td>
<td>0.06423</td>
<td>0.07703</td>
<td>0.99808</td>
</tr>
<tr>
<td>PPAT-145K</td>
<td>0.05713</td>
<td>0.03116</td>
<td>0.07181</td>
<td>2.39219</td>
<td>0.11444</td>
<td>0.03507</td>
<td>0.01686</td>
<td>0.99774</td>
</tr>
<tr>
<td>PPAT-0.5%MDI</td>
<td>0.0452</td>
<td>0.03269</td>
<td>0.07649</td>
<td>2.25984</td>
<td>0.08265</td>
<td>0.04125</td>
<td>0.01304</td>
<td>0.99841</td>
</tr>
<tr>
<td>PPAT-1%MDI</td>
<td>0.04094</td>
<td>0.02819</td>
<td>0.07005</td>
<td>2.2095</td>
<td>0.07501</td>
<td>0.03505</td>
<td>0.01345</td>
<td>0.9981</td>
</tr>
<tr>
<td>PPAT-1.5%MDI</td>
<td>0.05874</td>
<td>0.03924</td>
<td>0.08876</td>
<td>2.90431</td>
<td>0.09029</td>
<td>0.0335</td>
<td>0.01993</td>
<td>0.99804</td>
</tr>
</tbody>
</table>

Small-angle X-ray scattering (SAXS) data
Figure 4.27. $I*q^2$ vs $q$ plot of PPAT polyesters from Small-angle X-ray scattering.

Solid-state NMR data

GEE Curve Fit (Gaussian-Exponential-Exponential)

$$f(x) = A_c e^{-\frac{x^2}{\tau_c}} + A_i e^{-\frac{x}{\tau_i}} + A_a e^{-\frac{x}{\tau_a}} \quad (eq\ 4.5)$$

Where $A_c$, $A_i$, and $A_a$ are the signal amplitudes of the crystalline, interfacial, and amorphous phases respectively, and $\tau_c$, $\tau_i$ and $\tau_a$ are their respective relaxation times.
**Figure 4.28.** GEE fit model for PPAT-32K. Black points are experimental data, while the red curve is the fit.

**Table 4.9.** Solid-state NMR Curve fitting results of signals from PPAT compression molded films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ac</th>
<th>Tc</th>
<th>Ai</th>
<th>Ti</th>
<th>Aa</th>
<th>Ta</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPAT-32K</td>
<td>97169.0</td>
<td>10.8</td>
<td>243588.7</td>
<td>59.6</td>
<td>35844.2</td>
<td>767.9</td>
<td>0.99995</td>
</tr>
<tr>
<td>PPAT-105K</td>
<td>83392.0</td>
<td>10.8</td>
<td>241545.4</td>
<td>55.5</td>
<td>33381.6</td>
<td>507.9</td>
<td>0.99995</td>
</tr>
<tr>
<td>PPAT-145K</td>
<td>70036.9</td>
<td>11.0</td>
<td>221409.5</td>
<td>43.5</td>
<td>34471.0</td>
<td>232.4</td>
<td>0.99996</td>
</tr>
<tr>
<td>PPAT-0.5%MDI</td>
<td>78828.0</td>
<td>10.9</td>
<td>224707.6</td>
<td>51.2</td>
<td>33230.7</td>
<td>383.5</td>
<td>0.99995</td>
</tr>
<tr>
<td>PPAT-1%MDI</td>
<td>50371.0</td>
<td>10.8</td>
<td>162813.7</td>
<td>46.9</td>
<td>26579.6</td>
<td>274.1</td>
<td>0.99993</td>
</tr>
<tr>
<td>PPAT-1.5%MDI</td>
<td>52312.1</td>
<td>10.8</td>
<td>188393.4</td>
<td>46.6</td>
<td>29041.6</td>
<td>271.8</td>
<td>0.99994</td>
</tr>
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</table>
Table 4.10. Crystallinity ($X_c$) and Long period ($L_p$) of PPAT compression molded films

<table>
<thead>
<tr>
<th>Samples</th>
<th>$X_c$ (WAXS)</th>
<th>$X_c$ (NMR)</th>
<th>$L_p$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PPAT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPAT-32K</td>
<td>11.2%</td>
<td>25.8%</td>
<td>95.1</td>
</tr>
<tr>
<td>PPAT-105K</td>
<td>10.2%</td>
<td>23.3%</td>
<td>103.3</td>
</tr>
<tr>
<td>PPAT-145K</td>
<td>10.1%</td>
<td>21.5%</td>
<td>105.8</td>
</tr>
<tr>
<td>Chain extended PPAT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PPAT-0.5%MDI</td>
<td>9.8%</td>
<td>23.4%</td>
<td>104.2</td>
</tr>
<tr>
<td>PPAT-1%MDI</td>
<td>9.1%</td>
<td>21%</td>
<td>112.7</td>
</tr>
<tr>
<td>PPAT-1.5%MDI</td>
<td>8.6%</td>
<td>19.4%</td>
<td>108.3</td>
</tr>
</tbody>
</table>

**Rheology data**

Zero-shear viscosities were calculated from Carreau-Yasuda fit, which is suited for linear low-density polyethylene [147].

**Carreau-Yasuda fit:**

\[
\eta^* = \frac{\eta_0}{(1 + \lambda \omega^a)^{b/a}} \tag{4.6}
\]

Where $\eta_0$ is the zero-shear viscosity, $\lambda$ is a characteristic relaxation time, $a$ and $b$ are exponents.
Figure 4.29. Carreau-Yasuda fit to calculate zero-shear viscosity.

Table 4.11. Zero-shear viscosity and Carreau-Yasuda fitting parameters

<table>
<thead>
<tr>
<th>Samples</th>
<th>( \eta_0 )</th>
<th>( \lambda )</th>
<th>a</th>
<th>b</th>
<th>R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPAT-105K</td>
<td>9155.88973</td>
<td>2.87393</td>
<td>2</td>
<td>0.32107</td>
<td>0.99633</td>
</tr>
<tr>
<td>PPAT-145K</td>
<td>663545.41317</td>
<td>233.24874</td>
<td>2</td>
<td>0.52232</td>
<td>0.99962</td>
</tr>
<tr>
<td>PPAT-0.5%MDI</td>
<td>2463.1065</td>
<td>0.98186</td>
<td>2</td>
<td>0.22546</td>
<td>0.98928</td>
</tr>
<tr>
<td>PPAT-1%MDI</td>
<td>24007.77263</td>
<td>5.45646</td>
<td>2</td>
<td>0.36986</td>
<td>0.99719</td>
</tr>
<tr>
<td>PPAT-1.5%MDI</td>
<td>1.13351E7</td>
<td>14153.13253</td>
<td>2</td>
<td>0.58796</td>
<td>0.99652</td>
</tr>
</tbody>
</table>
Figure 4.30. Storage modulus (G’) and loss modulus (G’”) of PBAT at 160°C

Figure 4.31. Storage modulus (G’) and loss modulus (G’”) of PPAT-145K at 160°C.
Figure 4.32. Storage modulus ($G'$) and loss modulus ($G''$) of PPAT-0.5%MDI at 160°C

Figure 4.33. Storage modulus ($G'$) and loss modulus ($G''$) of PPAT-1%MDI at 160°C
Figure 4.34. Storage modulus ($G'$) and loss modulus ($G''$) of PPAT-1.5%MDI at 160°C.
Conclusions

We have explored the applicability of 1,5-pentanediol (PDO) in thermoset solvent-borne coatings, hot melt adhesives, and biodegradable thermoplastics. PDO is an attractive alternative to petroleum based 1,6 hexanediol (HDO) due to its lower projected cost and renewable nature. For thermoset coatings and adhesives, we synthesized and investigated various low molecular weight polyester polyols using Bio-PDO. Bio-PDO provided coatings with performance, including flexibility, hardness, adhesion strength, and solvent resistance similar to coatings from petroleum-based 1,6-hexanediol (HDO). Bio-PDO-based hot melt adhesives exhibited weaker green strength and longer open time than HDO-based adhesives. We also found lactone impurity (δ-valerolactone as an example) existing in biomass-derived monomers had no large effect on polyol hydroxyl functionality.

For biodegradable thermoplastics, high molecular weight (>100KDa) poly (pentylene adipate-co-terephthalate) (PPAT) was successfully synthesized via thin-film polymerization and chain extension. With 60 mol% aromatic content, PPAT compression molded films exhibited 1.5 times higher tensile modulus than petroleum-based poly (butylene adipate-co-terephthalate) (PBAT) and comparable with low-density polyethylene. Preliminary results also indicate biodegradability of PPAT polyesters was comparable or even higher than PBAT polyesters in soil within 70 days. We also correlated the tensile modulus with crystallinity and long period of PPAT films. The
results suggest tensile modulus of PPAT can be further improved by optimizing the microstructures, crystallinity, and molecular weight.

Future work

1. Apply 1,5-pentanediol-based polyesters to powder coatings

   Thermoset powder coatings are widely applied in general metal coatings, furniture coatings, automotive coatings, architectural coatings and many other areas. Powder coatings are formulated with carboxyl group or hydroxyl group containing polyesters, acrylic polymers, curing agents, catalysts, pigments, flow agents, and other additives. The coating compositions must flow and sufficiently wet substrates when heated to a molten state in order to obtain uniform cured coatings with good appearance.

   Crystalline or semi-crystalline polyesters, commonly composed of aliphatic diols and aliphatic or aromatic diacids, are key components of powder coatings. They provide good melt-state fluidity on substrates and impart sufficient flexibility to the resulting cured coatings. In particular, general metal coatings formulated with amorphous polyesters as major binders and semi-crystalline polyesters as minor binders provide high impact resistance, flexibility, and outstanding weather durability. Amorphous polyesters rich in neopentyl glycol and isophthalic acid, provide coatings with outstanding weatherability [157]. Thanks to the semi-crystalline feature and low melt viscosity, semi-crystalline polyesters such as polyhexylene dodecanedioate and polyhexylene terephthalate provide sufficient flowability for powders on heated substrates [158].

   Although the melting temperature and crystallinity may be affected by odd-even effects (Figures 1.5-1.7), semi-crystalline polyesters based on biomass-derived 1,5-pentanediol
may be promising candidates to replace 1,6-hexanediol-based analogs. Further investigations on the thermal properties, crystallinity, and rheological properties are required.

2. Continue to measure biodegradability of PPAT

High molecular weight PPAT will be subjected to biodegradability test in soil and aquatic environments over a longer period. The final biodegradability will be compared with PBAT.

3. Improve tensile modulus of PPAT by film blowing process and additives

As discussed above, we have achieved PPAT compression films have 1-1.5 times higher tensile moduli than PBAT compression films and comparable level with some polyethylene films (PPAT: 60-96MPa, PBAT: 55MPa, LDPE: 64-151 MPa). To further improve the tensile modulus for wider applications, we will prepare oriented films by film blowing process. During this process, polymer resins are first melted, transported through a heated barrel to the extrusion dies. The molten polymers enter the circle die and air is injected from the die center to radially inflate polymer melts into tube films. The heated tube films are pulled upward, cooled by air flow, and finally collected on top of the blow line. In this process, polymer chains are oriented in two dimensions (draw and transverse) by the air flow and temperature gradient to form optimized microstructures, e.g. crystallinity, oriented factor, etc.

Several key characteristic parameters of polymers need to be optimized for successful processing, including crystallization kinetics, melt viscosity, and melt strength. First, PPAT may suffer slower crystallization rate than PBAT and LDPE. Previous
studies have shown that polypentylene terephthalate (PPT) required higher supercooling (Tm-T) to crystallize than polybutylene terephthalate and polyhexylene terephthalate, meanwhile crystallization rate and spherulite growth rate could be comparable with other polyesters by choosing appropriate crystallization conditions [159]. Recent study shows PPT crystallized more complete from melt state at 5 °C/min cooling rate than faster cooling rates 7.5 – 15 °C/min (Xc=17.3% vs 7-0.7%), and fastest isothermal crystallization occurred at 70°C. Moreover, PPT injection molded films (oriented films) exhibited higher modulus (0.65 vs 0.51 GPa) and elongation (448 vs 22.5%) than compression molded films [56]. For aliphatic polyester, although odd-even effects have influence on thermal properties, polypentylene adipate (PPA) exhibited obvious melt crystallization when cooling at 10 °C/min, indicated by the higher crystallization enthalpy than PPT, 55.3 vs 5.0 J/g [52], [56]. For PPAT copolyesters, the crystallization kinetics are additionally affected by polymer compositions; PPAT with 35 – 63 mol% aromatic units did not exhibit obvious crystallization enthalpy at cooling rate of 10 °C/min, whereas PPAT with 15 mol% and 70-85 mol% crystallized faster [110]. Another method to improve crystallization kinetics is to use nucleating agents. For example, modified starch accelerates PBAT crystallization rates, increase crystallinity, and raise crystallization temperature [160]. Therefore, it is necessary to improve crystallization kinetics of PPAT by either slightly increasing aromatic contents, optimizing processing parameters (crystallization conditions), or introducing nucleating agents. These parameters and information are largely unknown so far and are critical for real applications of PPAT materials.
Second, to be successfully processed in flow blowing equipment, melt strength of PPAT is another important parameter. Polymer resins require sufficiently high melt strength to generate stable bubbles by the air flow so that continuous films can be produced in large scale. To improve melt strength, small amount of long-chain branching agents (e.g. multi-functional epoxy chain extender: Joncryl ADR 4370 from BASF) may be introduced either during the synthesis of PPAT or during post chain extension.
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