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Waterborne Polyurethane/Acrylic Adhesive Blends from *Physaria fendleri* Oil for Food Packaging Applications

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Abstract: Environmental concerns and the diminishing acceptability of using petrochemical polymers require innovative synthetic approaches to materials for essential polymeric technologies such as adhesives. Biobased plant oils have been suggested as replacements for petrochemical monomers in polyurethane formulations. A variety of seed oil extracts from plants contain naturally occurring functional groups such as hydroxyl and glycidyl ether, which can be utilized in polyurethane synthesis. Most studies of bioderived polyurethane adhesives occur in solventborne systems and with chemically modified oils. However, rising concerns and manufacturing limitations of volatile organic compounds in solventborne systems warrant investigation into more sustainable and alternatives that are easier to handle. In this work, we synthesized waterborne polyurethanes comprised of oil derived from *Physaria fendleri* seed (naturally occurring hydroxyl functionality), hexamethylene diisocyanate, toluene diisocyanate, and dimethyl propionic acid. Acrylate copolymers were synthesized via emulsion polymerization comprised of different butyl and methylmethacrylate monomer ratios. These polymers were formulated into waterborne polyurethane/acrylic adhesive blends. The resulting formulations possess a commercially comparable peel strength of >6 N and are suggested for use in resealable food packaging applications. This study demonstrates the utility of oil derived from *Physaria fendleri* seeds in waterborne adhesive applications, adding value with bioderived materials and increasing sustainability of polyurethane adhesives.

Keywords: waterborne; biobased; polyurethane; acrylate; adhesive; packaging

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1. Introduction

Consumer demand for goods is continuing to expand, increasing the potential for landfill and environmental accumulation. As of 2017, 8.3 billion metric tons of plastics have been produced and only 21% was reclaimed for recycling or incineration. Packaging comprises one of the largest market of plastics and is a major contributor to solid waste in landfills and marine environments [1]. In 2018, 28% of the total municipal solid waste (292 million tons) consists of containers and packages [2]. It has been determined that flexible packaging and multilayer/ multicomponent plastic materials comprise 72% of the plastic pollution leaking into the environment [3]. Plastic packaging has the shortest service lifetime of all plastics [1]; thus, utilizing sustainably sourced, degradable packaging, and diverting plastic waste from landfills and marine environments is crucial. This presents a significant challenge to brand owners and manufacturers to consider end-of-life practices and package composition in addition to consumer safety.

The total packaging market is anticipated to eclipse $1 trillion by 2024 [4] with 59% of all plastic production being comprised of monolayer flexible and multilayer/ multimaterial plastics [3]. Flexible food packaging is projected to have the highest growth rate in the packaging sector with a compounded annual growth rate (CAGR) of ~6% from 2020–2027 [5].

The global bioplastics and biopolymers market is expected to grow at a CAGR of 21.7% and reach $27.9 billion by 2025 [6]. Such significant anticipated market growth necessitates innovative technology development that facilitates improving environmental and human health to avoid regrettable substitutes to petroleum polymers. The inability for a single material to adequately protect food pre-consumer requires multiple types of, often immiscible, polymers to be adhered together using petroleum-based adhesives. Even if the substrates were compostable (e.g., poly(lactic acid), poly(butylene succinate), poly(hydroxyalkanoate)), the adhesive renders the structure not compostable. This is a major limitation of current adhesive technologies as traditional multilayer films are difficult to recycle and are not compostable, leading to excessive landfill accumulation and nuisance litter.

The majority of the adhesives market is petrochemically derived. However, environmental concerns about toxic byproduct production (e.g., urea and phenol formaldehyde) during polymer synthesis and curing along with use of solvent and associated volatile organic compound regulations limits expansion [7]. Furthermore, consumers are demanding more sustainable material alternatives to current products, and this demand leads to new approaches. Materials are also being explored to produce polymers for high value applications. Polyurethanes are an important class of polymers that possess mechanical strength and chemical resistance properties that afford its utility in applications including foams, adhesives, and coatings. Traditional polyurethane adhesives require a polyol (e.g., polyester or polyether based), isocyanate and other additives. This type of adhesive has been thoroughly studied in solventborne systems [8–14], though there are concerns of environmental contamination with volatilization of the carrier solvent. Instead, research efforts have focused upon the use of water as the adhesive delivery vehicle.

To form a waterborne polyurethane adhesive, a linear thermoplastic polyurethane is generally synthesized with hydrophilic groups either in the backbone or as side groups (dimthylol propionic acid, acrylic based, poly(ethylene glycol), etc.). Ionic species can be either cationic (e.g., ammonia) or anionic (e.g., carboxylate). Both pendant and backbone approaches can produce highly stable dispersions, which can be used as the foundation for strong adhesives. Waterborne adhesive systems have been prevalently studied with petrochemically derived polyurethanes [15–24]. However, consumers and brand owners have pushed to shift the industry towards waterborne biobased polyurethanes derived from naturally sourced polyols [25–29]. Polyurethane synthesis has been demonstrated with a number of biobased sources [30–32], including seeds [33–36], legumes [37–39], and vegetables [40–43]. However, many of these oils must be functionalized with hydroxyl groups to be suitable for polyurethane synthesis. This step adds additional complexity and cost in the integration of biobased polyols as feasible petrochemical alternatives. Castor oil and oil from *Physaria fendleri* seeds do not require chemical modification prior to use in adhesive formulations due to existing alcohol groups on the polymer backbone and are of particular interest in expanding the biobased chemicals economy. Castor oil has been thoroughly studied in waterborne adhesive applications [44–48]. Several studies utilize and enhance the cross-linking capability of castor oil to achieve adhesion properties desired for various substrate types and applications [49,50]. However, castor oil production creates ricin as a toxic byproduct, raising concerns for its widespread use in biobased adhesives that are in direct food contact applications.

Oil production from the seeds of *Physaria fendleri* does not produce ricin and is both cost efficient ($1–2/kg) and does not divert food sources, which is a growing concern for some brand owners. The chemical structure of oil from *Physaria fendleri* seed (known as *Lesquerella fendleri* oil) is similar in composition to castor oil, although the average hydroxyl functionality is two compared three for castor oil. Using oil from *Physaria fendleri* seed in adhesive formulations is expected to add hydrophobicity and flexibility to coatings and adhesives due to the hydrocarbon side chain. Our previous work also demonstrated that the hydrocarbon side chain depresses the measured glass transition temperature with increasing concentration in a solventborne adhesive formulation [14]. Unlike castor oil, oil from *Physaria fendleri* has not been thoroughly studied, though a few works on

its utility in biobased foams [51,52] and industrial coatings [53,54] exist. Many of these studies modify the fatty acid chain, focusing more on structure than application. Recently Ivey et al., used both oil from *Physaria fendleri* seed and castor oil, alongside hexamethylene diisocyanate, polyhexamethylene diisocyanate, isosorbide, and dibutyl tin dilaurate to form a flexible food packaging adhesive for multilayer structures. Here, we translate this work into a waterborne system, mitigating volatile organic compound (VOC) concerns in the aforementioned solventborne system.

To translate the solventbone system into a waterborne adhesive, we synthesized the polyurethane by reacting oil from *Physaria fendleri* seeds with a mixture of difunctional isocyanates (toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI)), and dimethyl propionic acid (DMPA)). Both TDI and HDI were included to balance the impact of aliphatic and aromatic molecular structures on adhesive performance. The polyurethane was then suspended in water followed by emulsion polymerization of an acrylate copolymer (butyl acrylate for elasticity and methyl methacrylate for rigidity). The introduction of polyurethane into a waterborne acrylic latex was anticipated to increase the adhesive strength due to the hydrogen bonding between the polar groups of the polyurethane. Different isocyanates, polyurethane reaction times, and ratios of reagents were analyzed to optimize the formulation for adhering common food packaging materials. The adhesive was utilized to adhere two poly(ethylene terephthalate) films, as previous work suggested similar formulations can be used for re-sealable food packaging applications. The resulting biobased polyurethane adhesive demonstrated comparable performance to the solventborne formulations by Ivey et al. [14]. The results of this study demonstrate that the addition of *Physaria fendleri* oil to polyurethane chemistries provides a unique opportunity for non-food source oils to enter the market for waterborne bio-based adhesives for sustainable food packaging.

2. Materials and Methods

2.1. Chemicals

Oil from *Physaria fendleri* seeds was provided by USDA-ARS-NCAUR (Peoria, IL, USA) as in our previous work [14,55], hexamethylene diisocyanate (≥98%, TCI America, Tokyo, Japan), toluene diisocyanate (97%, Alfa Aesar, Haverhill, MA, USA), dimethylolpropionic acid (98%, Sigma Aldrich, St. Louis, MO, USA), methyl ethyl ketone (≥99%, Fischer Chemical, Zurich, Switzerland), potassium persulfate (≥99%, Fischer Chemical), butyl acrylate (≥99%, ACROS Organics, Geel, Belgium), methyl methacrylate (99%, Alfa Aesar), sodium dodecyl sulfate (≥99%, Sigma Aldrich), trimethylamine (≥99%, Fischer Chemical).

2.2. Preparation of a Physaria Fendleri Polyurethane Dispersion

Oil from *Physaria fendleri* seeds (30 g, 0.0699 mol of OH groups), 11.6 g of isocyanate (0.0667 mol), and 4.2 g of DMPA (0.0313 mol) were added to a three-necked flask equipped with a condenser, and the reaction was carried out at 75 °C for 3 h under a dry nitrogen atmosphere. The reaction was then cooled to 65 °C and 30 g of MEK was added to reduce the viscosity of the polymer and the solution was stirred vigorously with a stirbar. Triethylamine was added to the polymer solution for neutralization (3.4 g) then the neutralized solution was added slowly into water under high shear (250 g). Residual methyl ethyl ketone was removed via rotovap resulting in a solids content of ~15%. The dispersions were opaque pale yellow in appearance.

2.3. Preparation of Polyurethane and Acrylic Latex Adhesive

To make the acrylic portion, sodium dodecyl sulfate (3 g) and potassium persulfate (1 g) were dissolved in 414 g of distilled water. Butyl acrylate (BA) and methyl methacrylate (MMA) were then added in an 8:2 weight ratio then stirred vigorously using a stirbar. The BA:MMA ratio was selected to achieve the desired glass transition temperature (see Results and Discussion section). A definite amount of the polyurethane dispersion was added to a vacuum sealable flask. The acrylate pre-emulsion amount was calculated to

achieve the desired ratio of polyurethane to acrylate. The calculated amount of acrylate pre-emulsion was added in with the polyurethane dispersion. The system was purged under nitrogen for 30 min at room temp under constant stirring then heated to 80 °C for 4 h. After 4 h of polymerization, the reaction was chemically and thermally quenched with 0.5% hydroquinone solution in an ice bath. Specific formulation composition for each adhesive is in Table 1. Samples for bulk characterization were prepared by drying the emulsions at room temperature in a plastic well plate.

Table 1. Adhesive formulations including isocyanate ratios, acrylate monomer ratio, and polyurethane/acrylate ratio in the final dispersion.

Formulation #	PU Reaction TDI:HDI Ratio	Acrylate Emulsion BA:MMA Ratio	Final Dispersion PU:Acrylate Ratio
1	1:0	8:2	1:0
2	1:0	8:2	2:1
3	1:0	8:2	1:1
4	1:0	8:2	1:2
5	8:1	8:2	1:0
6	8:1	8:2	2:1
7	8:1	8:2	1:1
8	8:1	8:2	1:2
9	4:1	8:2	1:0
10	4:1	8:2	2:1
11	4:1	8:2	1:1
12	4:1	8:2	1:2

2.4. Preparation of Laminated Poly(Ethylene Terephthalate) Films

Poly(ethylene terephthalate) (PET) film was procured from a commercial supplier and corona treated using an Enercon (Enercon Industries Corporation, Menomonee Falls, WI, USA) Compak Series 2000 corona treater. Each adhesive formulation was applied to an individual piece of corona treated PET film using a 4 mil wet draw down bar. The drawdowns were allowed to dry for a few minutes at ambient temperature before the top layer of corona treated polyethylene terephthalate was applied. Pressure was applied evenly over the two layers to complete the lamination. The samples were conditioned at room temperature for one week prior to characterization. The adhesive had a milky appearance directly after application commonly associated with emulsions, but became transparent after conditioning (Figure 1).

Figure 1. Optical image of peel strength test strips demonstrating optical clarity of adhesive.

2.5. Characterization

2.5.1. Gel Permeation Chromatography

Synthesized polyurethane samples were characterized using to gel permeation chromatography (Agilent 1200 HPLC with a refractive index and multiple wavelength detectors, in chloroform) to determine the molecular weight as a function of time. Each polymer type was dissolved in chloroform at a concentration of 5 mg/mL then injected on the columns (Agilent PL1110-6504 and PL1110-6515) using a flow rate of 1 mL/min HPLC grade chloroform. Molecular weight and molecular weight distribution was calculated with ASTRA® 8.0.2.5 software (Wyatt Technology, Santa Barbara, CA, USA).

2.5.2. Differential Scanning Calorimetry

Differential scanning calorimetry (TA Instruments Q2000, New Castle, DE, USA) in modulated mode −85–60 °C, stabilize at 1 °C/min, then 5 °C/min ramp) was used to measure the glass transition temperature of each polymer and adhesive formulation.

2.5.3. Infrared Spectroscopy

Fourier transform infrared spectroscopy (Thermo Nicolet 6700 FT-IR, Waltham, MA, USA) was used to measure molecular structure changes and interactions. Each spectrum collection consisted of 32 scans done with a diamond Golden Gate ATR assembly and a DTGS detector with a 2 cm^{-1} resolution.

2.5.4. Peel Strength

The peel strength of the polyurethane adhesive was quantified according to ASTM D1876-08 Standard Test Method for Peel Resistance of Adhesives [56]. Three test stripes per adhesive formulation were analyzed for peel strength on a Mark-10 EMS303 (Johnson Scale and Balance Company, Pine Brook, NJ, USA) test stand equipped with a 22 N load cell. The test strips were 2.5 cm × 30 cm PET adhered to PET. Samples were tested at an angle of 180° with a crosshead speed of 0.253 mm/min.

3. Results and Discussion

The adhesive formulations were comprised of a mixture of two components: a polyurethane and a polyacrylate copolymer. Figure 2 displays the molecular structure of individual reactants forming the polyurethane dispersion and polyacrylate copolymer. We hypothesized that blending polyacrylate copolymer and polyurethane chemistries would enable increased control over wetting and physical properties. PU samples were prepared with a range of TDI:HDI ratios to determine the influence of different isocyanate structures on the adhesive properties in biobased formulations. TDI was selected as the primary component due to its high reactivity and relatively rigid molecular structure. As a result, TDI was expected to increase the rigidity of the polymer. HDI is an aliphatic molecule and is more flexible than TDI. Therefore, it was reasoned that controlling TDI/HDI composition can partially control physical properties in the polyacrylate copolymer/polyurethane adhesive blends. The acrylate component included butyl acrylate (BA) and methyl methacrylate (MMA). Similar to the isocyanates, methyl methacrylate in the polymer is anticipated to provide higher rigidity while butyl acrylate would increase the rubbery/elastic response. A ratio of 8 parts BA to 2 parts MMA produced an acrylate was selected to achieve a glass transition temperature close to −30 °C, which is in the middle of the range of glass transition temperatures for the PU component. We hypothesize that changing the BA:MMA ratio would decrease T_g corresponding to an increase in BA, and an increase in overall T_g corresponding to an increase in MMA. Both the change in the glass transition temperature and the intermolecular interactions are anticipated to influence the adhesive physical properties and substrate wetting.

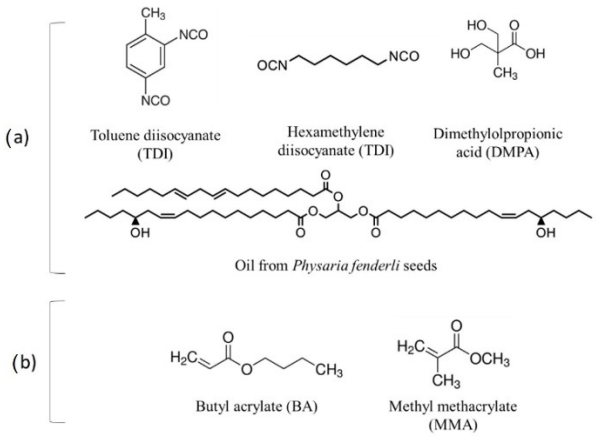

Figure 2. Molecular structure of components forming (**a**) polyurethane dispersion, (**b**) acrylate copolymer.

The PU-acrylate blend adhesives were characterized with FTIR spectroscopy to identify the characteristic bands representative of both polyurethane and acrylate groups. The spectrum for the 1:1 PU:PA blend was compared to the spectra for pure polymers (Figure 3). This sample was selected as a representation for all PU-acrylate blend formulations as the spectrum of each formulation had minimal variations due to the similar composition. Both the acrylate and PU spectra possess a carbonyl peak at 1725 cm^{-1}; however, the acrylate produces a sharper carbonyl peak and the PU is broader which coincides with previous reports in the literature [57]. The PU spectrum also possesses a broad N-H peak at 3300 cm^{-1} and a vinyl peak at 1550 cm^{-1}. The 1:1 PU:A blend exhibits a combination of the characteristic peaks of the PU and acrylate.

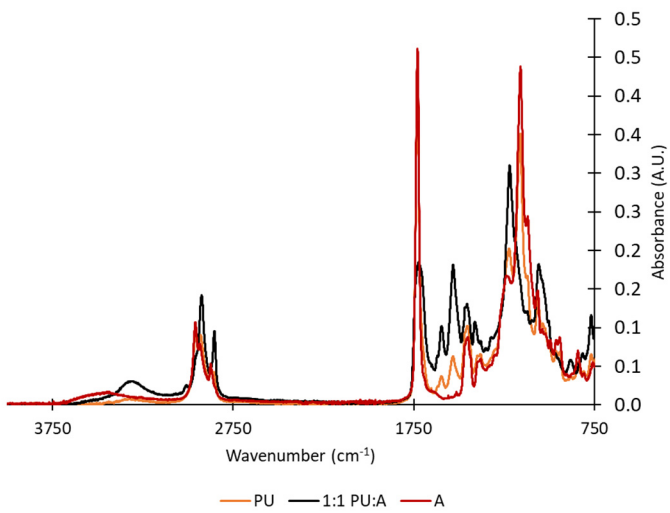

Figure 3. FTIR spectra of the polyacrylate (A), 1:0 TDI:HDI polyurethane (PU) at time 3 h, and their blend (1:1 PU:A).

To understand how reaction time and isocyanate ratio impact PU molecular weight growth, the molecular weight as a function of time was measured via gel permeation chromatography at 0.2, 1, 2 and 3 h (Figure 4). The PU sample with only TDI increased molecular weight more quickly when compared to the samples using mixtures of TDI and HDI. The polymer synthesized with the 4:1 ratio of TDI to HDI did not increase molecular weight as a function of time and was also the lowest molecular weight suggesting rapid growth followed by rapid termination reactions. We attribute the difference in molecular weight growth to the documented lower reactivity of HDI compared to TDI [58], which may dramatically inhibit chain growth. More research is needed to understand the molecular weight growth differences as a function of catalyst concentration and reaction

time/temperature. An important observation, however, was that the samples containing TDI alone and both TDI and HDI demonstrated a visible change in viscosity with elapsed reaction time. While the HDI samples were less prone to forming a highly viscous material (as sometimes occurred with the TDI), the viscosity still increased over time.

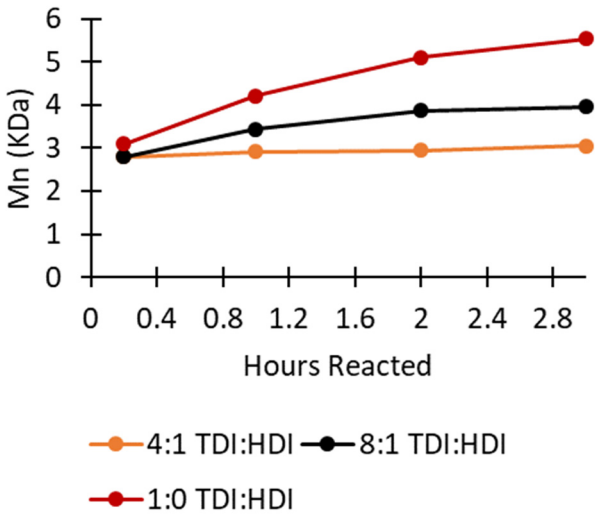

Figure 4. Gel Permeation chromatography measurements of polyurethanes containing differing isocyanate compositions and reaction times.

The three different PU polymers were then blended with poly(butyl acrylate-co-methyl methacrylate) in varying mass ratios. It is generally understood from the Fox equation [59] (Equation (1)) that the observed glass transition temperature (T_g) of a miscible polymer mixture is dependent upon the ratio of the two components and will be in-between the T_gs of the individual components. T_g is also known to play a significant role in adhesive strength. Past studies on epoxy adhesives indicated that, in general, higher T_g polymers had increased lap shear strength [60]. It should be noted that these results are not necessarily universal for all adhesives, as they only explored epoxy polymers with T_g values above room temperature.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}, \quad (1)$$

Differential scanning calorimetry was utilized to determine the impact of PU:A ratio on T_g of the adhesive as applied. The T_g of the synthesized polyurethanes increased with the reaction time, which is indicative of increased molecular weight. This trend was observed for all the PU-polyacrylate blends (Figure 5). There were no time points for the poly(butyl acrylate-co-methyl methacrylate) as it reacted for four hours in all scenarios therefore, this is displayed as a line for ease of comparison (Figure 5a). Since the polyacrylate's T_g is within the range of the PU, it is reasonable that the T_g's of the blends do not practically increase or decrease relative to PU and polyacrylate components. Future work exploring the impact of changing the BA:MMA ratio could reveal more about the influence of acrylate selection on the adhesive performance, especially for formulations with and 1:2 ratio of PU:A. Considering the PU alone, the TDI:HDI ratio does not influence T_g after a one hour reaction. After 3 h, there is a significant difference however, as the 1:0 TDI:HDI ratio yields a T_g of −18.5 °C, and the 4:1 ratio yields a T_g of −7 °C. The fact that the PU with the most HDI had the highest T_g was unexpected but remained consistent across all blends. The glass transition temperature of all blends was between −50 to −10 °C, indicating that all adhesives are in a rubbery state at room temperature. The PU-polyacrylate blends follow the Fox equation for predicting glass transition temperature of polymer mixtures by weight. The largest deviation between the blend T_g predicted by the Fox Equation and the measured T_g was 4.4%. The majority of samples were within 2% of the predicted blend T_g.

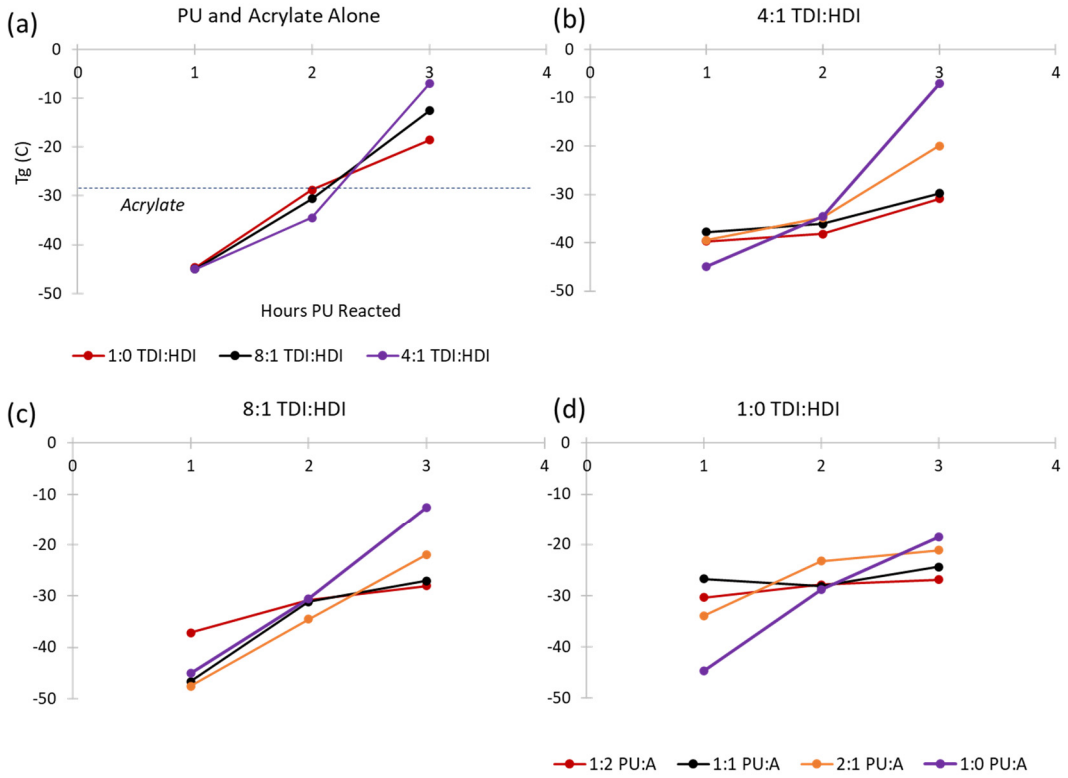

Figure 5. Differential scanning calorimetry data of (**a**) polyurethane and poly(butyl acrylate-co-methyl methacrylate) individually (line), (**b**–**d**) polyurethane-acrylic adhesive blends.

PET laminates were manufactured to understand the influence of each adhesive formulation on the peel strength. In general, many of the ratios possess similar performance (Figure 6). A one-way ANOVA with Bonferroni post-hoc t-test was used to determine statistical differences in the peel strength. Each formulation was compared to other formulations reacted for the same amount of time. Overall, few statistical differences or trends were observed. Regarding only the formulations with 1:0 TDI:HDI, the formulation with 1:0 PU:A reacted for 3 h was statistically higher from all others reacted for the same amount of time. Regarding only the formulations with 2:1 PU:A, the formulation with 4:1 TDI:HDI reacted for 1 h was statistically lower than all others reacted for 1 h. Only one formulation had statistically higher peel strength than all other samples: 4:1 TDI:HDI, 1:0 PU:A, reacted for 3 h. In this case, the PET film failed before the adhesive.

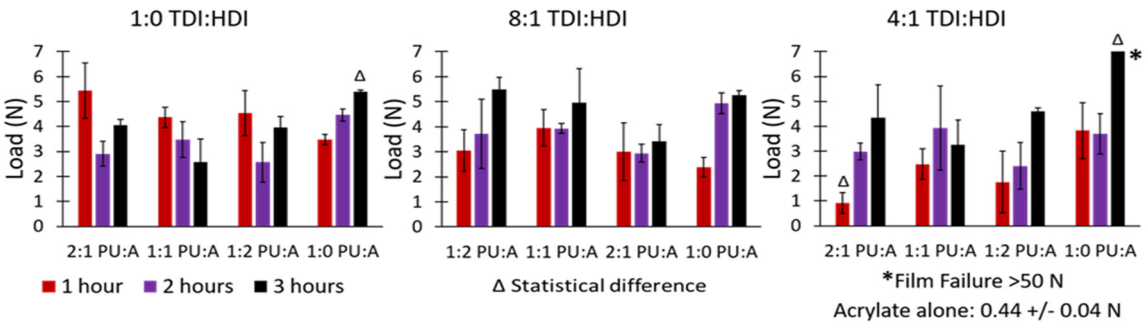

Figure 6. Peel strength for the polyurethane-acrylic adhesive samples on PET plastic.

The peel strength of the formulations with only PU was also considered in the context of molecular weight (Figure 7). For the samples with 1:0 TDI:HDI and 8:1 TDI:HDI, there are clear trends of increasing peel strength with molecular weight. For both formulations,

the 2 h and 3 h time points have statistically higher peel strength than the 1 h time point. However, this trend is not independent of formulation. In other words, the highest molecular weight of the 8:1 TDI:HDI formulation is lower than the lowest molecular weight of the 1:0 TDI:HDI formulation, but the peel strength is significantly higher. The 3 h time point of the 4:1 TDI:HDI is also a major outlier. It has far higher peel strength than all other formulations despite having relatively low molecular weight of 3 kDa. This sample has the highest T_g of all formulations indicating a more rigid adhesive may produce superior results. A few other higher peel strength performers including the 3 h time points of formulations 1 and 5 (see Table 1) have T_g greater than −15 °C. However, there was too much variability in T_g and peel strength data to yield a clear trend.

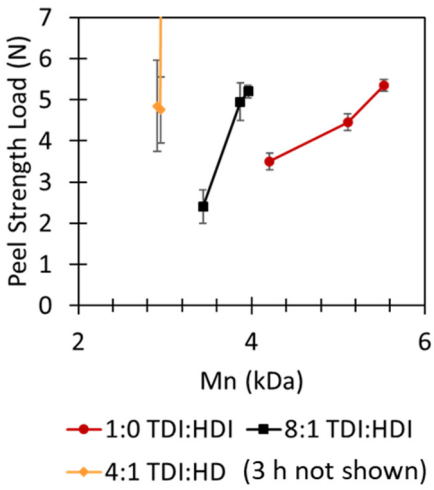

Figure 7. Comparison of molecular weight and peel strength for formulations with only polyurethane. 3 h time point for 4:1 TDI:HDI is out of plot range.

The strength of the samples is generally comparable to our previous study [14] involving a solventborne PU and multiple formulations reached or exceeded a peel strength of 5.78 N, which was the value reported by Karami et al. for a castor-oil based adhesive [61]. It is also competitive to adhesives using polyol blends including castor oil as a cross linker, such as Yang et al. who reported a peel strength of 4.8 kN/m. As such, the work here presents an initial route for developing environmentally friendly waterborne adhesives with competitive performance. Additionally, the inclusion of the polyacrylate copolymer does not appear to influence adhesive strength as the PU samples performing equally well or better (Figure 6). We anticipate that changing the composition of the polyacrylate copolymer will further enable tuning of the peel strength. The ability to tune adhesive properties is crucial to meet the needs for varied packaging applications; Chen et al. demonstrated the impact of formulation on adhesion between plastic and paper layers and the potential detriment of stronger adhesives damaging the paper [62]. Different packaging substrates also present challenges in wettability, which Bao et al. have shown to be an important factor in peel strength [15]. As such, further exploration of different polyacrylate copolymer compositions is the subject of future research.

4. Conclusions

The waterborne adhesive formulations presented in this study show promising results for food packaging applications. The use of oil from *Physaria fendleri* seeds, a previously overlooked option for unmodified bioderived polyols, provides a means to generate a simple polyurethane system without the need for additional modification to the raw components. The adhesive formulations we present only require a few monomers and can be synthesized without numerous complicated steps. Thus, this work provides an opportunity for a new, non-food source bioderived oil to enter the food packaging adhesives market.

The PU component had the largest influence over the adhesive properties with increased reaction time leading to higher molecular weight, higher T_g, and generally higher peel strength. Additionally, the increase of HDI in the PU formulation slows the polymer growth over time but appears to be an important monomer resulting in increased peel strength. The PU-polyacrylate copolymer blends possessed similar peel strength properties for all formulations, but the peel strengths were lower in comparison to the PU on its own. Therefore, future work will seek to optimize both the PU and polyacrylate copolymer components to afford the most tunable adhesive properties based on peel strength, cost, and manufacturing routes.

The work presented here is foundational and is the basis for further developing the biobased economy by introducing the oil from *Physaria fendleri* seeds in waterborne adhesives. The initial results are promising and offer a direction for further study to optimize properties and to determine potential in applications other than food packaging. Future work will refine the adhesive formulations with additional biobased monomers to control properties and synthetic methods. Additional characterization and testing are also needed to develop the formulations for commercial manufacturing in gravure/flexographic equipment such as the impact of drying temperature, drying time, and viscosity. Further evaluation, including water vapor permeability and performance under varying temperatures, would be critical for assessing the potential use of the adhesive in food packaging applications and is the subject of future research. Overall, this serves as an encouraging starting point for in the synthesis of more sustainable food packing adhesive.

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Conflicts of Interest: A patent application was filed in 2020 on the research related to this manuscript. The authors Greg Curtzwiler and Keith Vorst are listed as inventors and Iowa State University Research Foundation is listed as the assignee.

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