

10-2021

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Abstract

Polyurethanes (PU) are an important class of materials used in various applications across industries. With increased global interest in sustainable and environmentally benign packaging, there is high demand to replace traditional petroleum-based materials with renewable, bio-derived sources. This research developed PU adhesives for multilayer flexible food packaging using *Physaria fendleri* oil (formerly *Lesquerella fendleri*) and *Ricinus communis* (Castor oil), each possessing naturally occurring hydroxyl functional groups. *Physaria* oil has, on average, hydroxyl functionality on two of the three fatty acids compared to all three for Castor oil; therefore systematically varying the concentration of each oil and maintaining a constant crosslink density for each adhesive facilitates an understanding of the effect of *Physaria* oil's unreacted hydrocarbon sidechain on physical properties in biobased adhesives. The results of this study determined that the peel resistance of polyethylene and polyethylene terephthalate substrates adhered with adhesives containing varying amounts of *Physaria* and castor oils possessed average peel strengths of 6–8 N relatively independent of composition. Furthermore, the glass transition temperatures were measured to be within the range of –25 to –44 °C with higher concentrations of the hydrocarbon sidechain resulting in lower Tgs. These physical properties indicate their use in multilayer food packaging adhesive applications where isocyanate PU adhesives are still commonplace. Understanding the PU adhesive network structure-property relationships will help develop the next generation of bio-derived PU adhesives with additional sources of renewable feedstocks for food packaging applications.

Keywords

Biobased, Plant oil, Adhesive, Packaging, Multilayer

Disciplines

Agronomy and Crop Sciences | Food Chemistry | Food Processing | Food Science | Human and Clinical Nutrition

Comments

This article is published as Ivey, A., Talbert, J., Evangelista, R., Vorst, K., Curtzwiler, G., Influence of a hydrocarbon side chain on the performance of *Physaria fendleri*-Castor oil polyurethane packaging adhesives. *Cleaner Engineering and Technology*, 2021, 4(100216); doi: 10.1016/j.clet.2021.100216.

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Influence of a hydrocarbon side chain on the performance of *Physaria fendleri*-Castor oil polyurethane packaging adhesives[☆]

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ARTICLE INFO

Keywords:
Biobased
Plant oil
Adhesive
Packaging
Multilayer

ABSTRACT

Polyurethanes (PU) are an important class of materials used in various applications across industries. With increased global interest in sustainable and environmentally benign packaging, there is high demand to replace traditional petroleum-based materials with renewable, bio-derived sources. This research developed PU adhesives for multilayer flexible food packaging using *Physaria fendleri* oil (formerly *Lesquerella fendleri*) and *Ricinus communis* (Castor oil), each possessing naturally occurring hydroxyl functional groups. *Physaria* oil has, on average, hydroxyl functionality on two of the three fatty acids compared to all three for Castor oil; therefore systematically varying the concentration of each oil and maintaining a constant crosslink density for each adhesive facilitates an understanding of the effect of *Physaria* oil's unreacted hydrocarbon sidechain on physical properties in biobased adhesives. The results of this study determined that the peel resistance of polyethylene and polyethylene terephthalate substrates adhered with adhesives containing varying amounts of *Physaria* and castor oils possessed average peel strengths of 6–8 N relatively independent of composition. Furthermore, the glass transition temperatures were measured to be within the range of –25 to –44 °C with higher concentrations of the hydrocarbon sidechain resulting in lower T_g s. These physical properties indicate their use in multilayer food packaging adhesive applications where isocyanate PU adhesives are still commonplace. Understanding the PU adhesive network structure-property relationships will help develop the next generation of bio-derived PU adhesives with additional sources of renewable feedstocks for food packaging applications.

1. Introduction

With increased demand in cost-effective sustainability and safety, there is a need to replace petroleum-based coatings and adhesives with safer and renewable resources (Deka and Karak, 2009). Plant extract oils are abundant, cost-effective, sustainable, and possess inherent chemical functional groups that provide a greener chemistry alternative (Islam et al., 2014). There is vast potential for plant oils to replace components in petroleum-based adhesives since monomers, fine chemicals, and polymers can be derived from these renewable resources (Maassen et al., 2016). However, most oil extracts require chemical modification prior to direct replacement of traditional petroleum feedstocks (Islam et al., 2014).

The demand for adhesives is anticipated to rise globally by 3.6% per

year until 2024 and polyurethanes are an important class (Adhesives Market Report - World). Polyurethanes (PU) are commonly used in various applications such as foams, plastics, composites, films, sealants, coatings, inks, and adhesives and have been extensively studied with a variety of compositions (Akindoyo et al., 2016). Currently, water-based *Ricinus communis* (castor) oil PU adhesives are often the most desirable for food packaging because of the low toxicity solvent (water). However, water-based PU adhesives often exhibit poor coatability (wetting) and low adhesive force (Qiao et al., 2016). Therefore, there is a need for an environment-friendly, high performance adhesive for more demanding applications and substrates.

Previous use of vegetable or plant oils for PU applications generally required various synthetic strategies to introduce hydroxyl groups into the fatty acid chain via the carbon-carbon double bonds (Akindoyo

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<https://doi.org/10.1016/j.clet.2021.100216>

Received 18 February 2021; Received in revised form 28 June 2021; Accepted 15 July 2021

Available online 16 July 2021

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et al., 2016). Therefore, plant oil extracts containing naturally occurring functional groups are of particular interest to reduce cost and maintain simplicity. For example, hydroxyl functional containing oils such as *Physaria fendleri* (*Physaria*) oil with *Physaria* uerolic acid (C20:1OH) are valuable alternatives to petroleum-based and other natural oils that require several synthetic steps prior to incorporation into PU formulations. *Physaria* and castor oil possess similar chemical structures due to the β , γ – unsaturated hydroxyl functional group on a hydrocarbon chain, however, the hydroxyl functionality of castor oil is on average three compared to two for *Physaria* oil (Thames et al., 1994). Castor oil also is mainly grown and processed in India and the oil is imported to the United States (U.S.), whereas *Physaria* is grown in the southwest region of the U.S. which could be an important economic factor in commercial use (Brahim et al., 1996).

Previous research modified the hydroxyl groups of *Physaria* oil through transesterification (Thames et al., 1994), dehydration (Thames et al., 1997), and methacrylation/acrylation (Thames et al., 1996). These chemical modifications of the oil enabled formulations that targeted industrial coatings such as air-dry primers and ultraviolet-cured coatings. *Physaria* oil was hypothesized to introduce hydrophobicity and flexibility to industrial coatings due to the hydrophobic side chain. To provided adequate performance, each study required fillers and additives that were not designed nor approved for direct food contact applications.

This research formulated plant-based PU adhesives comprised of unmodified *Physaria* (formerly *Lesquerella fendleri*) and Castor oils for use as the adhesive in multilayer food packaging applications. The influence of the hydrocarbon side chain on the physical properties were studied by systematically varying castor (no hydrocarbon side chain, OH f~3) and *Physaria* oil (contains hydrocarbon side chain, OH f~2) content maintaining the total equivalents of trifunctional molecules (polyhexamethylene diisocyanate and castor oil) to minimize crosslink density differences between formulations. This enables isolation of the influence of *Physaria* oil's hydrocarbon side chain without the confounding variable of crosslink density in each adhesive formulation. We hypothesize that the hydrocarbon side chain of *Physaria* oil will produce formulations with decreased glass transition temperature and increase adhesion between hydrophobic substrates.

2. Materials and methods

2.1. Materials

Refined, bleached, and deodorized *Physaria fendleri* oil (*Physaria*) (hydroxyl number = 216.6 mg KOH/g) was prepared by USDA National Center for Agricultural Utilization Research, Peoria, IL as described previously (Evangelista, 2009). Castor oil (hydroxyl number 156–165 mg KOH/g) was used as received from Alfa Aesar. (Gurunathan et al., 2015). Hexamethylene diisocyanate (HDI) and poly (hexamethylene diisocyanate) (PHDI) were obtained from Sigma Aldrich. Isosorbide and dibutyltin dilaurate (DBTDL) were received from TCI, and methyl ethyl ketone (MEK) was obtained from Fisher Scientific. All materials were used as received.

Table 1

Plant oil extract based polyurethane adhesive formulations created on equivalents of hydroxyl and isocyanate functional groups.

| Chemical | 0 mol <i>Physaria</i> oil | 1.5 mol <i>Physaria</i> oil | 3 mol <i>Physaria</i> oil | 3.75 mol <i>Physaria</i> oil | 4.5 mol <i>Physaria</i> oil |
|---|---------------------------|-----------------------------|---------------------------|------------------------------|-----------------------------|
| Total Equivalents | | | | | |
| Castor Oil (OH) | 9 | 6 | 3 | 1.5 | 0 |
| <i>Physaria</i> Oil (OH) | 0 | 3 | 6 | 7.5 | 9 |
| Isosorbide (OH) | 2 | 2 | 2 | 2 | 2 |
| Polyhexamethylene diisocyanate (PHDI) (NCO) | 0 | 3 | 6 | 7.5 | 9 |
| Hexamethylene diisocyanate (HDI) (NCO) | 11 | 8 | 5 | 3.5 | 2 |

2.2. Methods

2.2.1. Procedure for formulations

Isosorbide was dissolved in MEK at 4.6 wt% in a 20 mL scintillation vial via planetary mixer at room temperature (FlackTek SpeedMixer, 1500 RPM for 2 min). The isocyanates for each formulation were mixed according to Table 1 and added to the isosorbide, then mixed in the planetary mixer to ensure a homogeneous mixture (1500 RPM for 2 min).

Note that isocyanates are toxic materials, and the appropriate mitigation personal protection equipment should be used when handling (gloves, chemical fume hood, etc.). The corresponding amount of *Physaria* oil and castor oil for each formulation was individually added and mixed via the planetary mixer (1500 RPM for 2 min). DBTDL (5 wt %) was added to the scintillation vial and mixed. After 5 min, each formulation was poured into a polyvinyl alcohol coated Petri dish then conditioned overnight at ambient conditions, followed by an elevated temperature cure at 80°C for 1 h. The samples were removed from the dishes, rinsed with DI water, and dabbed dry to remove residual PVA from the surface of the sample. The samples were dried at 100°C for 5 min. The anticipated general adhesive molecular structure is depicted in Fig. 1.

2.2.2. Preparation of laminated specimens

Two-layer films were prepared using each adhesive formulation in Table 1 to adhere polyethylene terephthalate (PET) film to polyethylene film using an automatic wire coater (Hot Melt Laboratory Coater Laminator, ChemInstruments model HLCL – 1000, Fairfield, OH) equipped with a #20 rod for a targeted wet thickness of 50.8 μm (2 mil). The adhesives were prepared according to Table 1. Each formulation was conditioned at room temperature for 10 min after the addition of catalyst to increase viscosity then added to the reservoir prior to application to the PET film with a wet thickness of 2 mils at a speed of 80 in./min. PE film was adhered to the coated PET film with pressure applied at the point of contact using nip rollers at 80 PSI (see Fig. S1). The samples were then post-cured at 80 °C for 1 h.

2.3. Characterization

2.3.1. Fourier-transform infrared spectroscopy (FT-IR)

Attenuated total reflectance infrared spectra (ATR-IR) were collected using a diamond Golden Gate ATR stage attached to a Nicolet 6700 infrared spectrometer (Waltham, MA) at ambient temperature. Each spectrum was collected with 32 scans and a resolution of 2 cm^{-1} . The Nicolet 6700 infrared spectrometer was then fitted with a vertical sample holder to collect transmission spectra for each adhesive formulation using the same instrumental parameters. All spectra were baseline corrected before analysis with Omnic 8.3 software (Thermo Fisher, Waltham, MA).

2.3.2. Differential scanning calorimetry (DSC)

Adhesive thermal transitions were measured between -70 °C and 250 °C using a Heat/Cool/Heat profile at a rate of 10 °C/min according to ASTM D3418 Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential

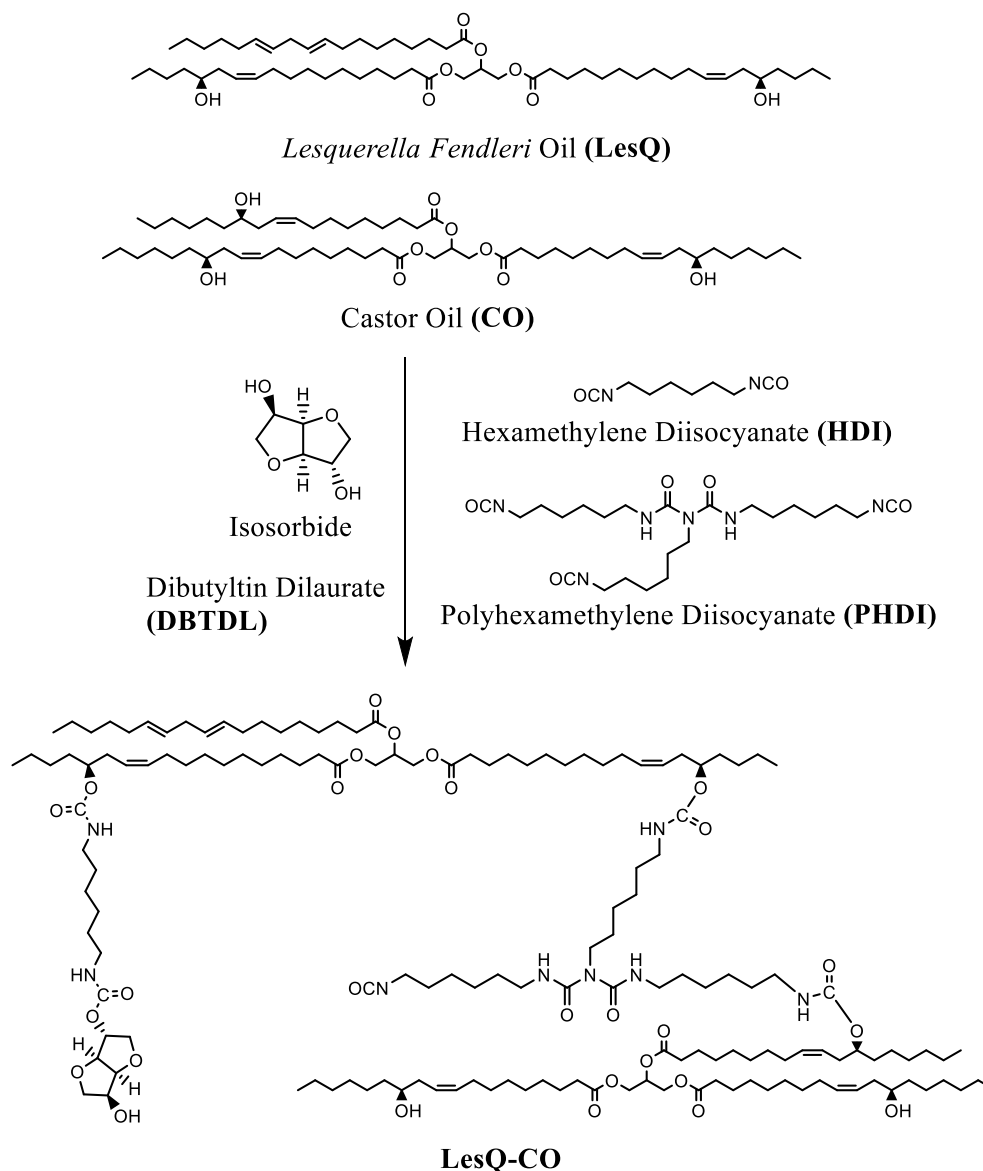


Fig. 1. Plant oil-based polyurethane adhesive reaction scheme.

Scanning Calorimetry with a TA Instruments Q2000 differential scanning calorimeter (New Castle, DE) in a nitrogen atmosphere (ASTM, 2015b). A specimen of each adhesive sample (5–10 mg) was charged into a hermetically sealed aluminum T-zero DSC pan.

2.3.3. Thermogravimetric analysis (TGA)

Mass loss as a function of temperature for each PU adhesive was quantified via thermogravimetric analysis using a TA Instruments Q5000-IR thermogravimetric analyzer (New Castle, DE). The adhesive specimen ($n = 3$) of each sample (5–10 mg) was charged into a platinum pan then heated at 10 °C/min from 25 °C to 600 °C under a nitrogen atmosphere.

2.3.4. Contact angle measurements

Liquid adhesive wettability on PET and PE substrates were evaluated through contact angle measurement with a ramé-hart Model 250 Standard Goniometer (Succasunna, NJ). The microsyringe was filled with the appropriate adhesive formulation (Table 1) and a 22 gauge needle was used to deliver a 2 μ L droplet to the surface. The process was video recorded with DROPimage Advanced v2.8 software. The angle was measured after the needle was retracted and the droplet was in contact

with the substrate.

2.3.5. Peel strength

The peel strength of the polyurethane adhesive was quantified following ASTM D1876-08 Standard Test method for Peel Resistance of Adhesives on a Mark-10 EMS303 test stand equipped with a 22 N load cell (ASTM, 2015a). The test strips 2.54 cm (1 in.) wide x 30.48 cm (12 in.) in length consisted of a PET film adhered to PE as prepared above. All ten specimens from each sample formulation were tested at an angle of 180° with a crosshead speed of 0.253 mm/min (10 in./min.) The type of failure (cohesive vs adhesive) was also determined via confocal microscopy.

2.3.6. Confocal microscopy

The average arithmetic mean height (Sa) was used to determine the surface roughness values of the adhesive on the PET and PE substrate. After the peel-test, the PE and PET surfaces were analyzed to determine the type of failure. The adhesive surface was analyzed for surface roughness and microstructure via a 3D Laser Scanning Confocal Microscope (VK-x1000 series, Keyence, Japan). The measurements were collected at 20x magnification.

2.3.7. Statistical analysis

Differences between mean values were evaluated via one-way analysis of variance (ANOVA) at a 95% confidence interval via GraphPad Prism 8.4.3. Tukey's post hoc analysis was used to group mean values that were statistically the same (Ellison et al., 2009). Four different replicates were utilized for each formulation to validate reproducibility. For ATR-IR, Transmission IR, DSC, and TGA, three specimens were tested for each formulation-replicate pair (12 per formulation). Ten specimens were evaluated for peel-strength per formulation replicate (40 per formulation).

3. Results and discussion

3.1. Fourier-transform infrared spectroscopy (FT-IR)

Attenuated total reflectance and transmission sampling techniques were used to detect residual monomeric isocyanate on the surface and throughout the adhesive specimens as a method to understand extent of cure. Furthermore, maximum monomer reaction conversion is important to minimize small molecule migration through substrates into food products and to maximize adhesive performance. ATR and transmission infrared spectra of the five *Physaria* oil adhesive formulations (Fig. 2) possess a characteristic peak at 3349-3367 cm^{-1} corresponding to the urethane amide N-H stretching (Macalino et al., 2017). The absence of a signal at 2263-2264 cm^{-1} in both ATR and transmission spectra indicated no detectable residual isocyanate functional groups suggesting a complete cure. All adhesive spectra possess a characteristic band at 1520-1522 cm^{-1} corresponding to a (C-N-H) urethane linkage and a peak at 1722 cm^{-1} corresponding to the ester carbonyls of castor and *Physaria* oil and the urethane carbonyl (Islam et al., 2014). We

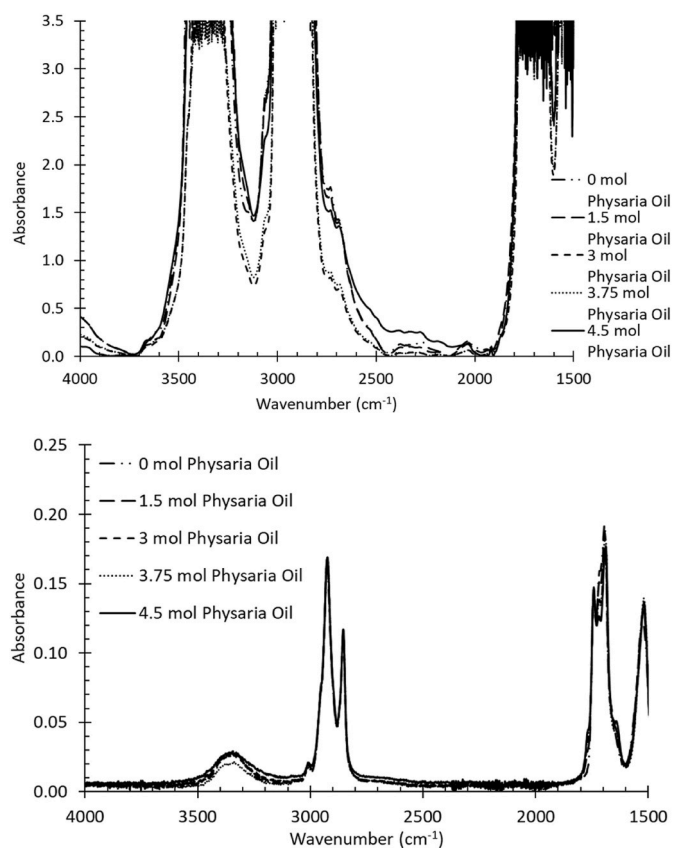


Fig. 2. (Left) Transmission IR spectra of each formulation post-cured indicating no residual isocyanate peak around 2300 cm^{-1} . (Right) ATR-IR spectra exhibiting a urethane peak 3500-3000 cm^{-1} and no isocyanate peak around 2300 cm^{-1} .

intentionally used thick specimens for the transmission FTIR experiments to increase sensitivity of the isocyanate functional group characteristic band for monitoring the polyurethane reactions; this resulted in sensor oversaturation in highly absorbing regions in Fig. 2 left ($\sim 3500 \text{ cm}^{-1}$, 2800 cm^{-1} , and 1600 cm^{-1}). Differences in each of the spectra within Fig. 2 were not anticipated because the formulations consist of the same chemical compounds, only varying in hydrocarbon side chain content from varying concentrations of *Physaria* oil.

3.2. Differential scanning calorimetry (DSC)

The measured glass transition temperature (T_g) of the adhesive formulations as a function of *Physaria* oil content was determined via DSC. The measured T_g is influenced by crosslink density, polymer chemical structure, and environmental parameters (e.g. humidity) (Curtzweiler et al., 2014a, b). The formulation with no *Physaria* oil has the highest T_g with a value of $-25 \text{ }^\circ\text{C}$, whereas formulations with 3.75 mol and 4.5 mol *Physaria* oil each have the lowest T_g of $-44 \text{ }^\circ\text{C}$ and were statistically the same; all other formulations possessed T_g s that were statistically different ($p < 0.05$).

The adhesive T_g influences the final adhesive properties and the stiffness of the chains will affect wetting of the adhesive on the surface of the desired substrate (Jovanovic and Dube, 2005). The hydrocarbon side chain of *Physaria* oil can increase free volume by creating more unoccupied space between polymer chains yielding a reduction in the measured T_g (Sun, 2005). The trend in Fig. 3 indicates that increasing the concentration of *Physaria* oil results in a lower T_g which would correspond to an increase in free volume. Since the crosslink density was designed to be as close as possible and with similar volatile loss (Fig. 4), the change in the T_g can logically be attributed to the hydrocarbon side chain of *Physaria* oil. According to the free volume theory, large nonpolar side chains, such as the side group on *Physaria* oil, tend to hold mutually attractive polymer chains apart and lower the T_g (Comyn, 2011). Therefore, an increased amount of *Physaria* oil leads to an increase of free volume and therefore a decreased T_g (Fox, 1956).

3.3. Thermogravimetric analysis (TGA)

The mass loss at 200 $^\circ\text{C}$ was measured via TGA of the adhesives to determine the amount of volatile content which can potentially migrate into food at elevated temperatures or artificially influence changes in the T_g (Fig. 4). Crosslinked polymers, such as the PU adhesive formulations here, have the potential to trap small molecules in the polymer structure upon curing due to reduced diffusion coefficients (Stansbury, 2012). From a safety perspective, it is essential to mitigate the small molecule migration and desorption of volatiles from packaging materials into food. Therefore, 200 $^\circ\text{C}$ was selected as an excessive abuse temperature as multilayer food packaging is commonly used in frozen-to-microwave applications (Comyn, 2011). Furthermore, PUs undergo severe degradation events when temperatures exceed 200 $^\circ\text{C}$, thus it is anticipated that volatiles below this temperature have potential to migrate (2015) and would be attributed to trapped solvent (Seo and Shin, 2010) or unreacted monomers (Feng et al., 2012).

The mass loss at 200 $^\circ\text{C}$ for all formulations was below 2 wt% and can be attributed to the presence of small, unreacted molecules such as residual monomer/solvent or absorbed water (Liu et al., 2019). Adhesive formulations with higher *Physaria* oil composition possessed higher volatile content which could be a result of increased free volume from the presence of the hydrocarbon side chain as suggested by the decrease in the T_g . However, there was higher variability in the results as the *Physaria* oil concentration increased and most formulations possessed mean values that were statistically the same. Tukey's post hoc analysis indicated that only formulations with 0 mol and 3.75 mol of *Physaria* oil were significantly different ($p < 0.05$).

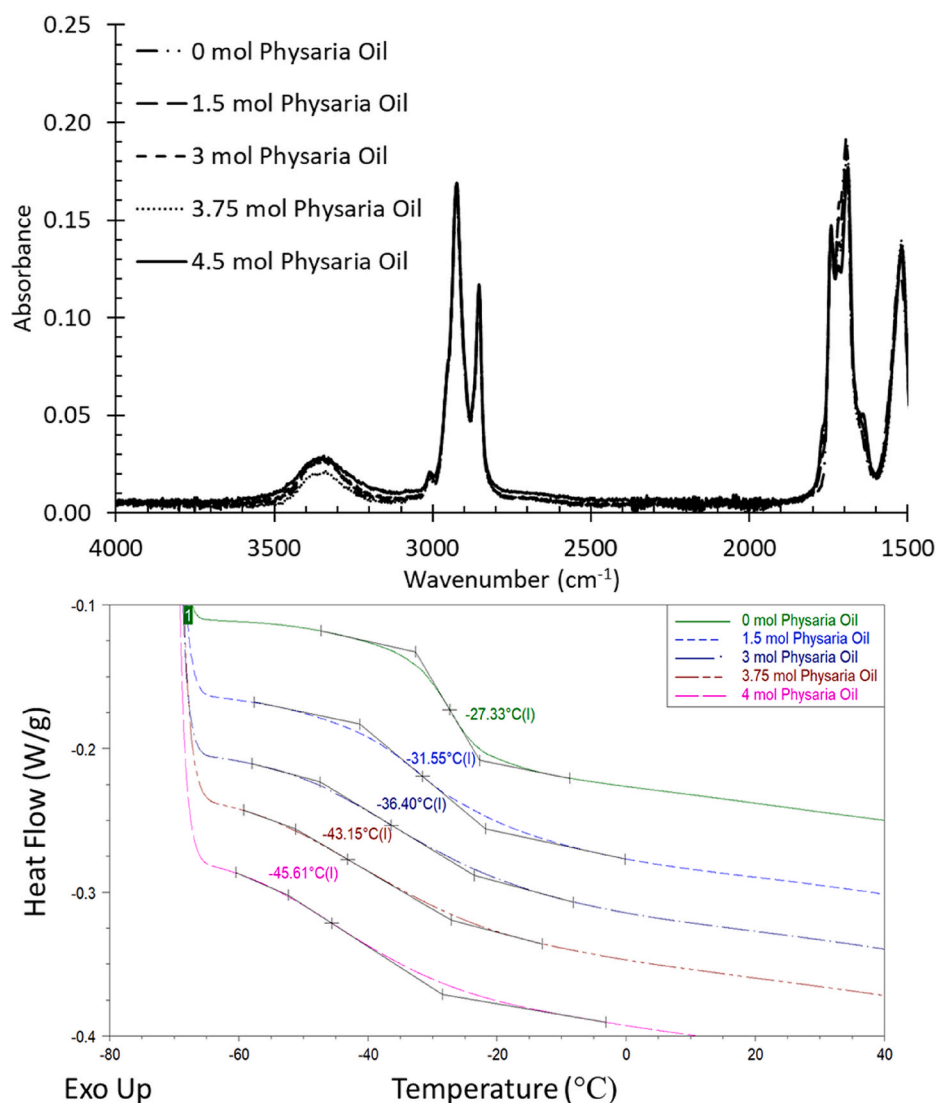


Fig. 3. Measured glass transition temperatures of adhesive formulations from DSC analysis and representative differential scanning calorimetry thermograms within the temperature region of interest.

3.4. Contact angle measurements

Adhesive wetting on a substrate is critical for strong bonding of two adherends. To measure the wettability of each adhesive formulation in the liquid state (as would be applied to substrates), the contact angle was measured on the PE and PET substrates used for lamination. The adhesive formulation without *Physaria* oil (0 mol) has contact angle values of 72° and 80° for PE and PET substrates, respectively (Fig. 5a). In comparison, the formulation with 4.5 mol of *Physaria* oil has contact angle values of 80° and 83° for PE and PET, respectively (Fig. 5b). All formulations were determined to have preference for substrate wetting of both the PE and PET substrates (i.e., angles below 90°).

Tukey's post hoc grouping identified a significant difference between formulation 0 mol and 4.5 mol ($p = 0.042$). There is no significant difference between the formulations determined by the one-way ANOVA for the contact angle of each formulation with the PET substrate. These data suggest that the hydrocarbon side chain of *Physaria* oil did not practically affect the wetting capabilities of the formulations for the PE and PET substrates. There was no clear trend on the wettability of the applied adhesive as a function of *Physaria* oil content, suggesting that changes in the peel strength will be more dependent upon other properties such as the molecular composition and cohesive strength

(Aliakbari et al., 2019).

3.5. Peel strength

After lamination and force-cure, the samples were tested for peel strength per ASTM D1876 to evaluate the force required to separate two substrates (representative force-extension curves can be found in Fig. S2). The maximum and minimum load plots of the adhesive formulations follow the same visible trend as the average load plot (Fig. 6) and can be found in the supplemental information (Figs. S3–S4).

The ANOVA results revealed no significant difference between formulations containing 3.0 mol, 3.75 mol, and 4.5 mol of *Physaria* oil. The average peel strengths of the adhesive samples were comparable except for formulation 1.5 mol with an average peel strength of 2 N which was repeatable across four replicate sample preparations. Tukey' posthoc analysis identified significant differences between formulation 0 mol value and formulations 1.5 mol, 3 mol, 3.75 mol, and 4.5 mol values ($p = < 0.05$). The significant differences between 0 mol and the rest of the formulations are a result of the increasing *Physaria* oil concentration which would have been anticipated by the reduced T_g . However, the similar peel strength for the three formulations suggests an additional mechanism needs to be accounted for beyond the T_g .

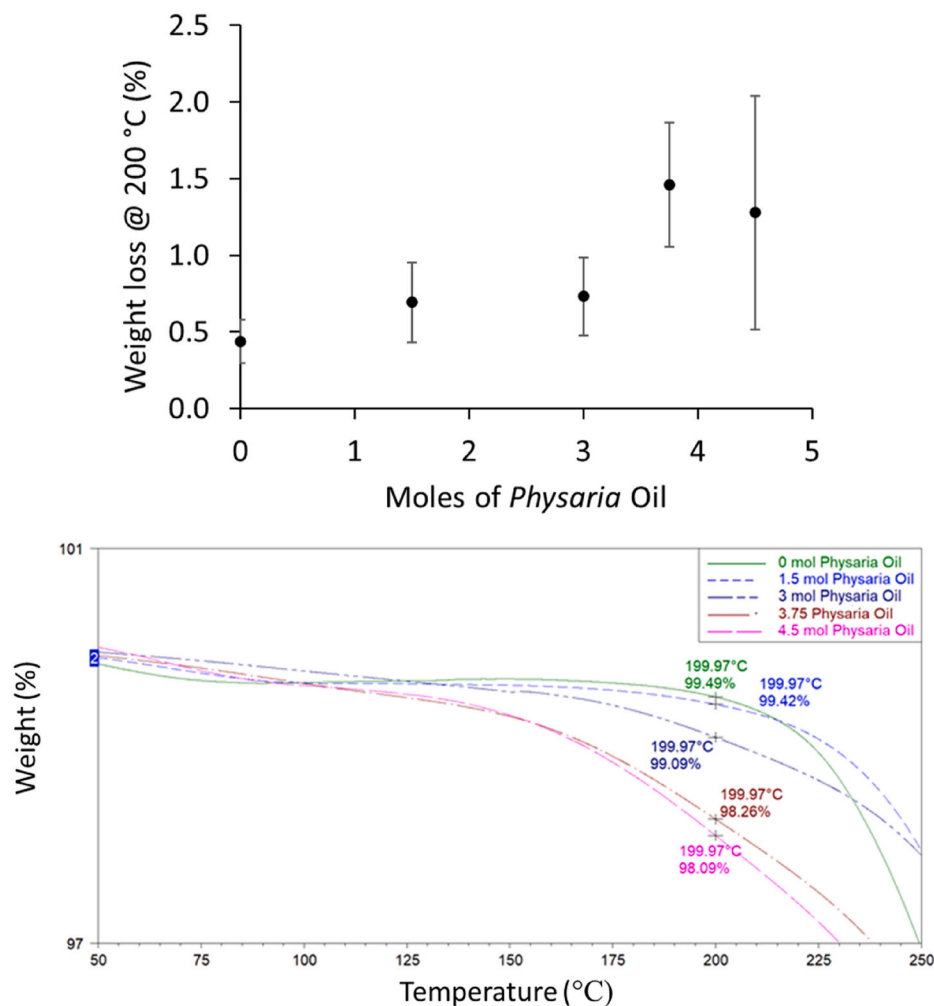


Fig. 4. Weight loss at 200 °C for volatiles within cured adhesive system and representative thermogravimetric analysis thermograms within the temperature region of interest.

The minimum peel strength between the formulations was comparable except for the formulation with 1.5 mol of *Physaria* oil which was similar to the average peel strength values (Fig. S3). The formulation with no *Physaria* oil had the highest maximum peel strength of 11 N (N), but upon addition of more *Physaria* oil, the peel strength lowered similarly to the average values (Fig. S3).

Other researched bio-based resins had lower peel strength values than the adhesive formulations containing 0 mol, 3 mol, 3.75 mol, and 4.5 mol of *Physaria* oil. In comparison, Karami et al. reported bio-based adhesives possessing a peel strength of 5.78 N (Karami et al., 2019) and Kaiser et al. demonstrated a reversible crosslinked adhesive with a peel strength of ~3N which is nearly half of what we demonstrate here (Kaiser et al., 2020). However, more research is needed to understand the seemingly anomalous peel strength of formulation containing 1.5 mol of *Physaria* oil. There is statistical evidence that the hydrocarbon side chain of *Physaria* oil influences peel strength by decreasing the strength of the adhesive formulations. With increased concentration of *Physaria* oil, there is a decrease in T_g values. Lower T_g values cause a decrease in the adhesive systems' peel strength and can result in an increase of cohesive failure (Cassidy et al., 1972). The addition of higher T_g components such as isosorbide to the formulations could be used to improve cohesive strength and is the subject of ongoing research. No statistical correlation was observed between other physical property changes (i.e., glass transition temperature). This was an unexpected finding and identified as an area of future research. We hypothesize that the peel strength does not follow the other properties due to the

relatively low difference in the glass transition temperature relative to the testing temperature and similar molecular structures between formulations.

3.6. Surface roughness

Surface roughness is a direct measurement of the surface's topography. Surface roughness measurement analysis was also used to determine the type of failure of the peel tested adhesive samples. Scanning confocal laser microscopy confirmed cohesive failure over adhesive failure during the peel tests. The surface morphology of each adherend after testing was noticeably different with increased roughness compared to the as-received film (0.307 μm and 0.444 μm for as-received PE and polyester films, respectively) indicating the presence of residual adhesive (Figs. S5–S16). As for the PET samples, there were no significant differences among the sample means as determined by one-way ANOVA ($p > 0.05$) (Fig. 7). All the adhesive formulations failed cohesively rather than adhesively. This is expected due to the lower T_g values leading to a decrease in strength of the system, which causes an increase in cohesive failure (Cassidy et al., 1972).

4. Conclusions

Plant extract oils are excellent renewable resources to replace petroleum-based components in coatings and adhesives due to their abundant, cost-effective, sustainable, and inherent chemical functional

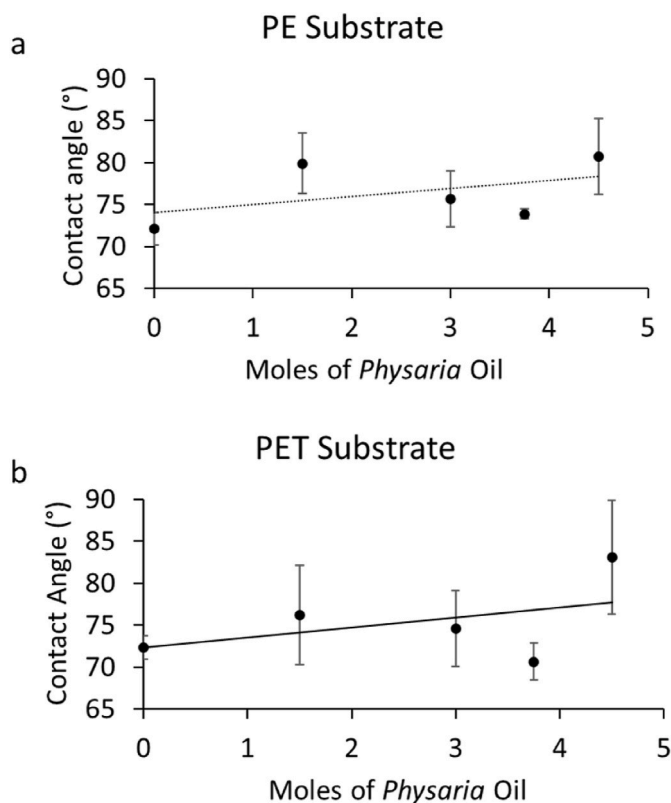


Fig. 5. Contact angle measurements of uncured adhesive on PE (a) and PET (b) substrates to determine wettability of the formulations.

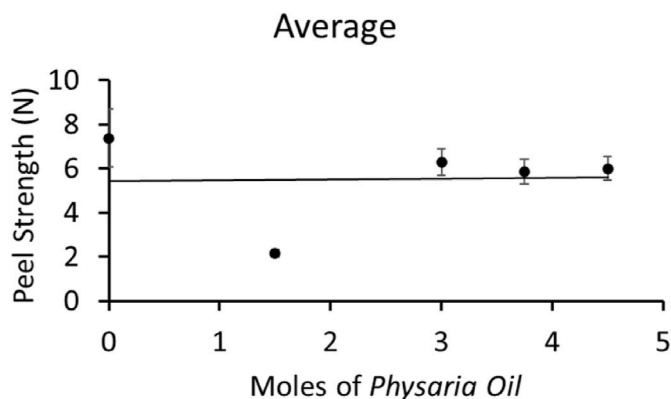


Fig. 6. Average peel strength for the five different adhesive formulations between polyethylene and polyester films. Maximum and minimum load plots followed the same trend as the average load strength plot (Figs. S3–4).

groups. Two oils containing different equivalents of hydroxyl functional fatty acids ($f \sim 2$ *Physaria fendleri* oil; $f \sim 3$ castor oil) were systematically varied in PU adhesive formulations to understand the influence of a hydrocarbon side chain on physical properties of adhesives designed for multilayer food packaging applications. DSC results revealed that the hydrocarbon side chain of *Physaria* oil decreases the measured T_g . This can likely be attributed to increasing free volume within the polymer structure. TGA results indicated that less than 2% of volatiles are given off before 200 °C, providing support that changes in the T_g are attributed to the hydrocarbon side chain and not residual small molecule plasticization. Contact angle analysis of each adhesive formulation on each substrate determined that all formulations preferentially wet each substrate (PE and PET) independent of composition. The measured peel strength was nearly twice that of other reported biobased adhesive

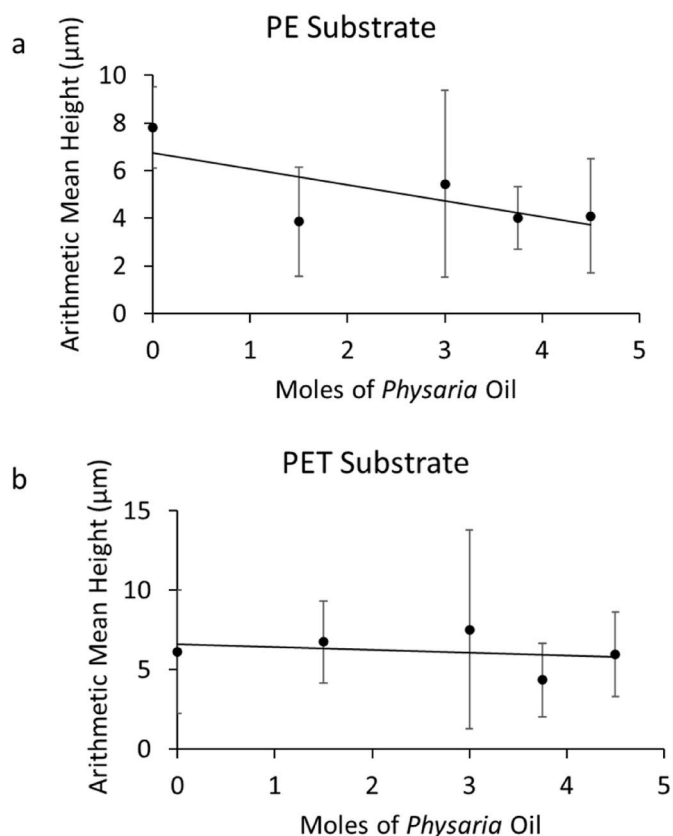


Fig. 7. Surface roughness measurements of PE (a) and PET (b) substrates after peel strength analysis.

formulations and was independent of *Physaria* oil concentration when present. The addition of *Physaria* oil to polyurethane adhesives provides an opportunity to enter the market for bio-based adhesives for sustainable packaging within the food industry. Future work on these formulations seek to eliminate the need for active isocyanate chemistry upon application, such as amine-carbonate reactions (non-isocyanate PU) and eliminating the need for solvents for application.

Declaration of competing interest

A provisional patent application was filed in 2019 on the research outlined in this manuscript. The authors Greg Curtzwiler, Alexandra Ivey, and Keith Vorst are listed as inventors and Iowa State University Research Foundation is listed as the assignee.

Acknowledgements

The authors would like to thank the Iowa Regents Innovation Fund and the Agricultural and Home Economics Experiment Station, Ames, Iowa, and Project No. IOW04202 by the Hatch Act, State of Iowa. This research was supported in part by the U.S. Department of Agriculture National Institute of Food and Agriculture and Agricultural Research Service. USDA is an equal opportunity provider and employer. The authors would like to acknowledge Sharan Raman and Henry Thurber for their help and contribution from sample preparation to advice.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.clet.2021.100216>.

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