

Assessment of Plant and Microalgal Oil-Derived Nonisocyanate Polyurethane Products for Potential Commercialization

Tao Dong,* Ermias Dheressa, Matthew Wiatrowski, Andre Prates Pereira, Ashton Zeller, Lieve M. L. Laurens, and Philip T. Pienkos



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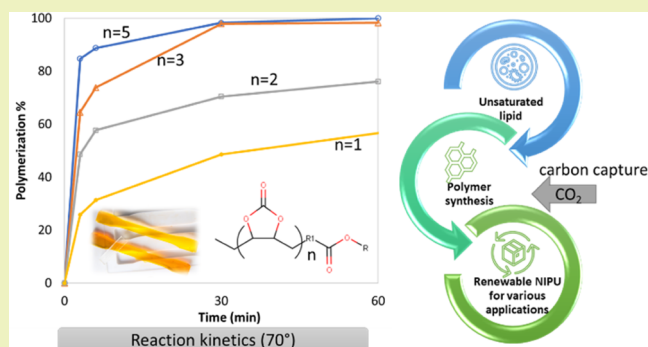
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ABSTRACT: Green pathways for nonisocyanate polyurethane (NIPU) production have attracted increasing levels of interest. The reaction between 5-membered cyclic carbonate and polyamines is one of the most promising pathways to produce NIPU polymers. Though promising, major technical hurdles such as slow polymerization rate and poor performance hinder the commercialization of NIPU. In this paper, we screened several commercially available triglyceride oil feedstocks for NIPU products, focusing on polymerization kinetics and product performance for industrial application. The impact of carbonated group density on polymerization rate and mechanical strength was determined. We have demonstrated a remarkably higher reactivity of carbonated oil derived from feedstocks with polyunsaturated fatty acid (PUFA). The NIPU derived from such feedstocks also showed improved performance for industrial application. Unlike traditional polyurethane foam production that uses isocyanate and water to generate CO₂ as a blowing reagent, there is no gas formation in NIPU polymerization. We have demonstrated a practical and cost-effective approach to produce NIPU foam material using bicarbonate as a blowing reagent. Furthermore, we conducted the first-ever technoeconomic analysis (TEA), revealing that profitable commercial NIPU production can be achieved when operating at sufficient production capacities.

KEYWORDS: nonisocyanate polyurethane, kinetics, bio-based polymer, vegetable oil, algae, technoeconomic analysis



INTRODUCTION

Polyurethane (PU) materials are widely used in our daily lives for various applications such as foams, coatings, sealants, elastomers, and adhesives.¹ Based on the annual global production, PU was the 6th most produced polymer in 2016.² Traditionally, PU has been produced via a step-growth reaction between polyols and hazardous isocyanates, which are produced by reacting corresponding amine compounds with extremely toxic phosgene. The use of isocyanates has been increasingly scrutinized by national regulatory agencies (e.g., U.S. Environmental Protection Agency and the European Union Registration, Evaluation, Authorisation and Restriction of Chemicals Program) across the world. In addition, petrochemical-derived isocyanates are sensitive to moisture, causing problems for stable storage.³ With a growing demand for green chemistry exploiting renewable resources, intensive efforts have been taken place to synthesize PU via nonisocyanate routes.

Production of PU via nonisocyanate routes has been comprehensively reviewed recently by Gomez-Lopez et al., Cornille et al., and Maisonneuve et al.^{4–6} The aminolysis reaction between 5-membered cyclic carbonates and amines is one of the most promising alternative pathways to produce

nonisocyanate polyurethane (NIPU). The 5-membered cyclic carbonates can be produced by reacting epoxy groups with CO₂ via a carbonation reaction, which is also a CO₂ sequestration approach. The produced carbonate monomers are nontoxic and do not require particular caution during storage.⁷ The ring-opening reaction of 5-membered cyclic carbonates with amines forms hydroxyl groups adjacent to the urethane linkages. Hence, the structure of this class of NIPU is also known as poly(hydroxyurethane) (PHU). The presence of these hydroxyl groups may improve the chemical resistance and mechanical performance of PHU due to the participation of intra- and intermolecular hydrogen bonds with carbamate and carbonyl groups.^{7,8} In addition, the extra hydroxyl groups in PHU have demonstrated increased adhesive capabilities, indicating that PHU can be a promising replacement for traditional PU adhesive.^{9,10} Finally, new research suggests that

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NIPUs have self-healing and vitrimer properties due to the internal transesterification exchange between the hydroxyl groups and carbamate groups,¹¹ providing a new route to recycle waste NIPU thermoset.

NIPUs have gained particular interest from academia and industry in recent years. There are four major pathways to produce NIPUs, and they are polycondensation, polyaddition, ring-opening polymerization, and rearrangement.⁵ Recently, it has also been reported that bio-based polyol (sugar, tannin, and lignin) could be used as precursors to produce NIPUs via a sequential conversion with dimethyl carbonate and diamines to produce novel adhesive and foam products.^{12–15} In addition, various feedstocks (both petroleum- and bio-based) have been tested as precursors in NIPU production.^{16–25} Among these feedstocks, commercially available and renewable plant-based oils represent attractive raw materials due to their low cost and availability. Triglyceride oils such as soybean, sunflower, and linseed oils have been converted into carbonated oils for NIPU production.^{26–28} The degree of cross-linking is a function of carbonate content, which is correlated with the number of double bonds in the fatty acid moieties of the oil. Feedstocks with a high degree of unsaturation are desired to produce NIPU products with enhanced mechanical strength due to their higher carbonation capacity. Microalgae have emerged as a promising feedstock for biofuel production because of high oil content and high productivity.^{29–31} Uniquely, microalgae are able to produce polyunsaturated fatty acids (PUFAs), such as eicosapentaenoic acid (EPA, C22:5) and docosahexaenoic acid (DHA, C22:6). These PUFAs can be considered as good candidates for highly cross-linked NIPU products with high tensile strength for commercial applications. For this research, a variety of triglyceride oils and PUFA feedstocks were selected to produce NIPU materials with a broad range of properties.

One of the major technical hurdles hindering the commercialization of NIPU technologies is the low reactivity of cyclic carbonates in polymerization to achieve quantitative conversion.^{2,3,9} The polymerization of carbonate monomers and diamines has been commonly studied in solvents at elevated temperatures, with curing times from hours to days.^{32–34} Although tremendous research efforts have been devoted to NIPU, there remains a significant technical hurdle to develop carbonate monomers with comparable reaction kinetics to conventional PU synthesis.⁹

In our preliminary experiments, we observed a high reactivity of carbonated PUFA oil in polymerization (unpublished data). This observation indicates that PUFA feedstock derivatives might have a higher reactivity in aminolysis due to the close proximity of the carbonate groups. For this work, to better understand applications of NIPU polymerization on future commercialization, a selection of triglyceride oil feedstocks containing various degrees of unsaturation were selected. We also demonstrated NIPU foam production in this research as well. Finally, the first-ever technoeconomic analysis (TEA) was conducted to provide more insights into NIPU commercialization.

MATERIALS AND METHODS

Materials. Soybean oil (J61399-K2) and potassium iodide (KI) were purchased from Alfa Aesar (MA). Linseed oil, methyl oleate (C18:1), methyl linoleate (C18:2), methyl linolenate (C18:3), Amberlite IR-120, 30% hydrogen peroxide, tetrabutylammonium bromide (TBAB), Wijs solution, butane diamine (BDA), pentane

diamine (PDA), octane diamine (ODA), hexamethylene diamine (HMDA), and triazabicyclodecene (TBD) were purchased from Sigma-Aldrich (MO). Citric acid powder was obtained from Healthy Foods, and ammonium bicarbonate was obtained from pure ORGANIC Ingredients. Vorasurf DC 5951 was obtained from Dow Chemical. Thrive culinary algae oil (algae-mono) was produced by Corbion (Peoria, IL). High PUFA algal oil (alphamega³ 400, algae-PUFA) was purchased from Algaithm (Canada).

Epoxidation. Epoxidation procedures were conducted following procedures from Petrovic et al.³⁵ Oil sample, toluene, Amberlite IR-120, and acetic acid were sequentially fed into a 1 L three-neck flat-bottom flask (the weight ratio of oil sample/toluene/resin = 1:0.5:0.25) and placed in a water bath on a magnetic stirrer. Hydrogen peroxide was added dropwise (mole ratio of hydrogen peroxide/acetic acid/double bonds = 1.5:0.5:1.0). An ice bath was used to reduce reaction temperature and avoid overheating when hydrogen peroxide was added. The reaction was carried out at 60–70 °C for up to 12 h under strong stirring. Then, the mixture was dissolved in 200 mL of ethyl acetate and filtered to remove resin. The liquid mixture was transferred to a separatory funnel and washed with water at least five times until the pH was neutral. Anhydrous Na₂SO₄ was added to the organic phase to remove water. The solvent was removed using rotatory evaporation at 90 °C at a 5 mbar vacuum.

Carbonation. Carbonation of epoxidized oil was conducted following a reported procedure.²⁶ Epoxidized oil and TBAB (0.05 mol/mol of epoxy groups) were placed in a 600 mL Parr reactor, stirred, and heated under 500 psi of CO₂. The reaction was carried out at 110 °C for 1 h and then at 140 °C for 22 h. The CO₂ was continuously fed into the reactor using a CO₂ cylinder during the reaction. After the reaction, carbonated oil was transferred into a separatory funnel and ethyl acetate was added to dissolve the oil. Deionized (DI) water was used to wash the organic solution three times to remove TBAB. The solvent was removed by rotatory evaporation at 90 °C under a 5 mbar vacuum. The number of carbonate groups per triglyceride was calculated from the initial and final epoxy oxygen contents (EOCs), assuming no side reactions.^{20,26,27,36}

Kinetics Study. Carbonated oil samples were added to glass tubes and placed in an oil bath at 70 °C. The oil was constantly stirred using an overhead mechanical mixer. A stoichiometric amount of diamine was added to carry out the reaction. A small aliquot of the sample was taken from the tube and quenched in liquid nitrogen for attenuated total reflection-Fourier transform infrared (ATR-FTIR) analysis as the reaction proceeded.

Resin Preparation. Carbonated oil samples were weighed into flasks and stirred under vacuum for 30 min in an oil bath at 70 °C. Stoichiometric amounts of diamine were added to the carbonated oil, and the mixture was kept stirring for about 1–5 min until the mixture started to form a gel. The mixture was then poured into a preheated poly(tetrafluoroethylene) (PTFE) mold to cast “dog-bone”-shaped resins (ASTM D638 Type II). The resins were cured in an oven at 70 °C for 15 h and then at 100 °C for 15 h.

NIPU Foam Production. Carbonated linseed oil (CLO) and HMDA were used to produce the NIPU foam material. Citric acid and ammonium bicarbonate were used as blowing reagents. Two experiments were performed to produce NIPU foam samples. A silicone surfactant Vorasurf DC 5951 was used as a cell stabilizer in one batch. In preparation for the foaming reaction, CLO (79.3 g, 67 mmol) and HMDA (20.7 g, 175 mmol) were preheated to 60 °C in a convection oven. Dry ingredients including 2.67 g (14 mmol) of citric acid, 3.3 g (42 mmol) of ammonium bicarbonate, and 0.3 g (2 mmol) of TBD were weighed into separate weigh boats. Weighing out dry ingredients was done just before conducting the reaction to prevent excessive moisture uptake from the environment in the citric acid. Additionally, 3.3 mL (183 mmol) of DI water was measured out into a graduated cylinder. The CLO and TBD catalyst were added to a 400 mL beaker and mixed vigorously for a few seconds using a high shear mixing implement attached to a drill. Next, the preheated HMDA was quickly added to the CLO. The high shear mixing attachment was used to stir the HMDA into the CLO vigorously for 2 min. In this

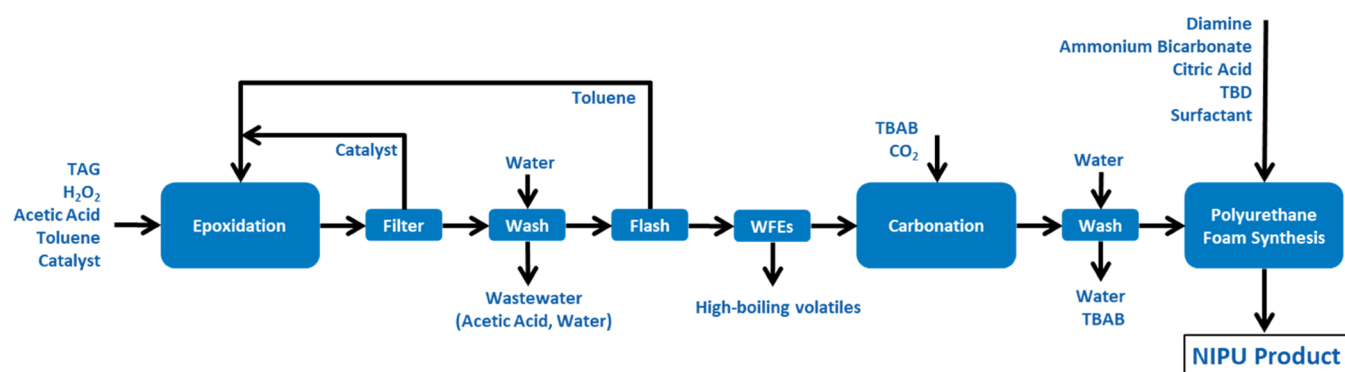


Figure 1. Block flow diagram of the modeled NIPU process for TEA. “Wash” steps represent washing with water and subsequent separation of the two liquid phases. “WFEs” represent wiped-film evaporators for the removal of high-boiling volatiles that may cause odors in the final product.

Table 1. Fatty Acid Profiles in Triglyceride and Model FAME Samples^a

fatty acid	triglyceride				model FAME		
	algae-mono (thrive)	soybean	linseed	algae-PUFA (alphamega3 400)	FAME 18:1	FAME 18:2	FAME 18:3
C12:0	0.4			0.9			
C14:0				8.6			
C16:0	1.5	10.8	5.5	20.1			
C16:1n7				3.8			
C18:0	1.5	3.9	4.0	0.7	0.8		
C18:1n9	93.4	23.4	20.7	1.5	98.2	0.5	0.6
C18:1n7		1.4	0.7	5.5			
C18:2n6	1.4	51.9	15.2	0.6	0.8	95.9	21.6
C18:3n3		7.0	52.8			0.8	77.8
C20:1	1.1						
C20:4				0.5			
C20:5n3				1.8			
C22:5				8.1			
C22:6n3				45.1			
iodine value	84	118	168	266	76	172	234
double bond per acyl chain	1.0	1.5	2.1	3.3	1.0	2.0	2.7
double bond per TAG	2.9	4.5	6.3	10.0			

^aNote: the unit of all fatty acid is %; the unit for iodine value is g of iodine per 100 g of oil.

step, the mixing attachment moved up and down in the beaker, scrapping the beaker's walls to ensure a good mix. The remaining dry ingredients, citric acid and ammonium bicarbonate, were added sequentially. If the Vorasurf DC 5951 was added, it was added immediately following the dry ingredients by pipette. Once the mixture was evenly mixed (30–60 s), the DI water was added to the mixture and stirred in for a few more seconds (<10 s). After adding the water, the mixture immediately produced bubbles as the acid and carbonate reacted. The mixture was swiftly poured into a silicon mold and then immediately placed into a preheated 80 °C convection oven. The mixture was left to cure for at least 15 min. After cooling to room temperature, the NIPU foam was removed from the silicon mold for characterization.

Analytical Methods. The fatty acid composition in the oil samples was tested using the National Renewable Energy Laboratory (NREL) fatty acid methyl ester (FAME) protocol.³⁷ The unsaturated degree in the oil samples was measured as iodine value (IV), using the classic Wijs method.³⁸ Epoxy oxygen content (EOC) was obtained by following the AOCS standard test method Cd 9-57.³⁹ All oil and resin samples were characterized by a Nicolet iS50 Fourier transform infrared (FTIR) spectroscopy with attenuated total reflectance (ATR) from 4000 to 650 cm⁻¹. Thirty-two scans of each sample were taken with a resolution of 4 cm⁻¹. NMR tests were conducted using a Bruker Avance III HD 400 MHz NMR spectrometer with a 5 mm broad-band observe (BBO) probe. Samples were dissolved in deuterated chloroform. Viscosity measurements were done by a

Brookfield viscometer DV2T model with Cone type, CPE 40 for low viscosity oil and CPE 52 for high viscosity oil. The measurements were taken with a rotational speed of 5–0.1 rpm at 70 ± 3 °C. Samples of 5–15 mg were used in a temperature degradation study using TA's thermogravimetric analysis (TGA) Q500 model with a heating rate of 15 °C/min under a nitrogen gas atmosphere. Thermal glass-transition temperature (*T_g*) was measured using TA's dynamic scanning calorimetry (DSC) Q2000 model. Modulated DSC (MDSC) was run with a sample size of 10–20 mg, an amplitude of 1.3 °C, a 60 s cycle, and a 2 °C/min heating rate. Room-temperature tensile tests (ASTM D638) were done using an Instron 4465 Tension Frame. Samples were subjected to extension at a rate of 5 mm/min until breakage occurred. Tensile properties are reported as the average of three tests. Swelling tests in toluene and water were carried out at room temperature at a solvent-to-sample weight ratio of 50:1.⁴⁰

Technoeconomic Analysis. To assess the economic viability of building a full-scale NIPU processing facility, a technoeconomic analysis (TEA) was performed. The conceptual process design for the TEA is shown in Figure 1 and is described in more detail in the Supporting Information. This conceptual design was modeled in Aspen Plus⁴¹ to obtain a mass and energy balance, which was subsequently utilized to provide a full accounting of costs associated with building and operating a flexible NIPU facility at a commercial scale (sized at 2800 U.S. tons per year of NIPU product based on guidance furnished from an industry subcontractor). A discounted-cash flow analysis was performed over a 30 year plant life to determine

a minimum polyurethane selling price (MPSP). To avoid confounding effects of production and isolation of algal lipids (or other lipid feedstocks), a generic feedstock cost was applied reflecting the commercial price of linseed oil. A range of production capacities and feedstock costs were considered a sensitivity (Figure S3). More discussion on this, as well as a full description of the TEA and associated assumptions, can be found in the Supporting Information.

RESULTS AND DISCUSSION

Fatty Acid Profile in Triglyceride Oil Samples. As shown in Table 1, the dominant fatty acids in algae-mono, soybean, linseed, and algae-PUFA are C18:1, C18:2, C18:3, and C22:6, respectively. The four oil samples have a broad range in iodine value (IV) from 84 to 266. The average double bond numbers in each triglyceride molecule in algae-mono, soybean, linseed, and algae-PUFA oil are 2.9, 4.5, 6.3, and 10.0, respectively. These four oils were chosen for NIPU production, with the aim to illustrate the impact of the density of carbonated bonds on the polymerization rate and NIPU performance. To validate the results obtained from the TAG-derived carbonate, we used standard FAME compounds for the aminolysis reaction. The purity of both FAME 18:1 and FAME 18:2 is higher than 95%. The purity for FAME 18:3 is 78%, with 21% methyl linoleate in the sample. The IV in three model FAME feedstocks ranges from 76 to 234, and the average double bond number in these FAME compounds is from 1.0 to 2.7.

Epoxidation of Oil Samples. IV is an index that reflects the total number of double bonds, and EOC represents the epoxy content in the epoxidized oil.²⁶ Hydrolysis of epoxy groups is a major side reaction during the epoxidation. The epoxy groups can be hydrolyzed to form hydroxyl groups. This reaction is not desirable and needs to be minimized by limiting the epoxidation temperature and time. The IV and EOC of algae-PUFA during the epoxidation are shown in Figure 2.

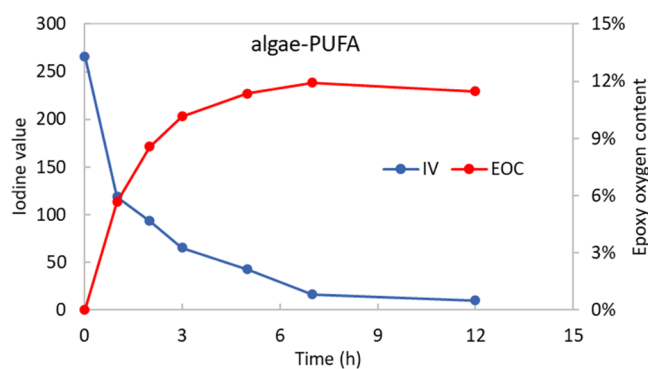


Figure 2. Epoxidation of algae-PUFA oil.

During the epoxidation, the IV decreased and EOC increased, indicating that double bonds were converted into epoxy groups. Based on our calculation, the double bonds were quantitatively converted into epoxy groups at the end of the epoxidation. In summary (Table 2), the final EOCs for algae-mono, soybean, linseed, and algae-PUFA oil were 4.2, 6.0, 8.5, and 11.5%, respectively.

The algae-PUFA oil contained the highest number of double bonds owing to the presence of C22:6 fatty acid. Due to the high reactivity and viscosity of the fully carbonated algal oil, it was very challenging to mix the carbonate monomer with diamine before casting the resin sample. Thus, we evaluated

Table 2. Epoxidized Triglyceride and FAME Samples

	EOC (%)	IV in epoxy	epoxy conversion (%)
algae-mono	4.2	3	96
soybean	6.5	4	97
linseed	8.5	21	87
algae-PUFA (27%) ^a	3.2	150	27
algae-PUFA (46%)	5.5	74	46
algae-PUFA (67%)	8.6	43	67
algae-PUFA (83%)	9.9	22	83
algae-PUFA (96%)	11.5	10	96
FAME 18:1	4.7	4	95
FAME 18:2	9	1	99
FAME 18:3	10.5	10	96

^aThe number in parentheses indicates the epoxy conversion; all values are the average of triplicates.

partial epoxidation and carbonation to produce monomers that are easier to process. Partial epoxidation of algal oil was conducted by terminating the epoxidation reaction at 0.5, 1.0, 2.5, 4.5, and 7.0 h (Figure S1). The results showed that 27–96% of double bonds were converted into epoxy groups under these conditions (Table 2). All of the epoxidized oil samples were used for carbonation to produce carbonate monomers.

Carbonation of Epoxidized Oil Samples. The chemical structure of tested cyclic carbonate monomers is shown in Figure 3. More than 95% of the epoxide groups in most oils were converted to carbonates. Notably, the 27% partially epoxidized oil only achieved 65% carbonation. Foltran et al. have studied the solubility of various vegetable-based epoxidized oils (VBEOs) in CO₂ and concluded that all of these oils can be well solubilized and swell in CO₂ for the carbonation reaction.⁴² So, solubility of the oil is unlikely to be the reason for the low conversion. It is possible that the remaining cis double bonds caused the oil to take on a contorted shape that blocked access of CO₂ to epoxy groups due to steric hindrance.⁴³ It is unlikely to draw a solid conclusion with the limited data, and future analysis is worthy to illustrate the mechanism. From a carbon sequestration perspective, carbonation conversion is an effective approach to capture CO₂. As shown in Table 3, CO₂ sequestration is a function of epoxy content. The algae-PUFA96 oil can sequester up to 35.7 g of CO₂/100 g of triglyceride oil because of the high content of epoxy groups. This carbon sequestration during the production of renewable polyurethanes is advantageous to this method as it provides a significant contribution to the sustainability of the process, in addition to the carbon capture inherent in the photosynthetic production of the oil feedstocks.

The viscosity of carbonated oil samples was remarkably higher than their epoxy precursors. As shown in Table 3, the viscosity is a function of the content of carbonated groups, and a higher content of carbonated groups led to higher viscosity. The viscosity for the carbonated oil followed the order of algae-mono < soybean < linseed < algae-PUFA (96%). The viscosity of the carbonated algae-PUFA oil followed the same trend that algae-PUFA (27%) < algae-PUFA (46%) < algae-PUFA (67%) < algae-PUFA (83%). The algal-PUFA (83%) and algae-PUFA (96%) carbonated oil samples were still solid at 70 °C and could hardly flow at 90 °C. The log₁₀ value of viscosity (70 °C) has a linear relation with the carbonate content in the triglyceride oil (Figure S2). High viscosity may cause a problem for mixing with amine, as it may be difficult to

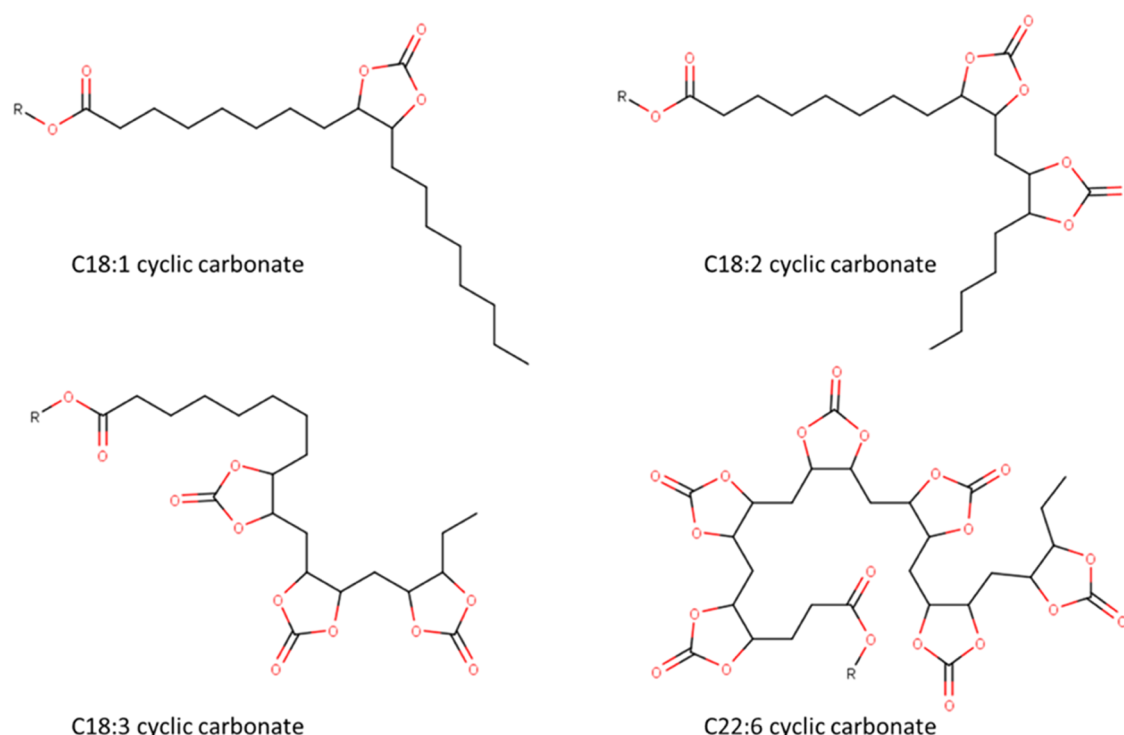


Figure 3. Chemical structure of tested cyclic carbonate monomers.

Table 3. Carbonation of Epoxidized Triglyceride and FAME Samples^a

	carbonation conversion (%)	viscosity @70 °C (cP)	CO ₂ sequestration (g/100 g oil)
algae-mono	95	120.9	10.9
soybean	97	674.9	19.4
linseed	98	4511.3	25.6
algae-PUFA (27%)	65	9.7	6.3
algae-PUFA (46%)	96	157.9	15.8
algae-PUFA (67%)	97	3906.6	23.2
algae-PUFA (83%)	99		29.7
algae-PUFA (96%)	96		35.7
FAME 18:1	95	10.7	
FAME 18:2	99	55.2	
FAME 18:3	96	274.9	

^aNote: the algae-PUFA (83%) and algae-PUFA (96%) samples were solid at 70 °C.

form a homogeneous mixture for use in the existing infrastructure to achieve quantitative polymerization. This problem may be a drawback for commercialization of NIPUs from highly epoxidized oils.

The NMR data for the epoxidized and carbonated monomers are shown in Figure 4. The peaks in 2.8–3.2 ppm indicate the epoxy groups (Figure 4A). After carbonation, the epoxy groups disappear in Figure 4B, and the cyclic carbonate groups give peaks at around 4.0–4.8 ppm.

Polymerization Kinetics Study. To illustrate the effect of the carbonated group content on polymerization rate, we conducted a polymerization kinetics study using triglyceride and FAME-derived samples with various contents of

carbonated groups. We established a procedure to quantify polymerization degree using ATR-FTIR. The unreacted carbonated group content (1800 cm⁻¹) in the reaction mixture was normalized by the internal alkane group (2847 cm⁻¹) and used as an index to reflect the polymerization degree. As shown in Figure 5A, the polymerization reaction rate for the carbonated algae-PUFA (96%) was the highest for all of the triglyceride oils, while the reaction rate for the algae-mono had the slowest reaction rate. The reaction rate, especially in the early stage, follows the order of algae-PUFA (96%) > linseed > soybean > algae-mono, clearly indicating the positive effect of the carbonated group density on polymerization rate. The algae-PUFA and linseed oil fully cured after 30 min at 70 °C. For the algae-mono oil and soybean oil, full conversion was never achieved at 70 °C, even after 1000 min. The results of the kinetics study using carbonated FAME exhibited a similar trend, showing that a higher carbonated content can accelerate the reaction rate. As shown in Figure 5B, the reaction rate of carbonated FAME followed the order of C18:3 > C18:2 >> C18:1, indicating that the cascade effect of neighboring carbonated groups can accelerate the polymerization reaction. This result is consistent with the observation in Figure 5A where carbonated triglyceride oil was used. The higher reactivity of vicinal cyclic carbonate groups was predicted by Goldstein et al.⁴⁴ and demonstrated by Schmidt et al.⁴⁵ Maisonneuve et al. have also discussed that the inductive effect of the substituent of the 5-membered cyclic carbonate plays a role in its reactivity.^{6,46} Thus, we can tentatively conclude that the polymerization rate is related to the density of carbonated groups on fatty acid acyl chains. Also, it is possible that the high density of carbonated groups increases the hydrophilicity of the triglyceride molecule, therefore increasing the solubility of hydrophilic amine in the carbonated oil, leading to the high activity. Additionally, the newly formed hydroxyl groups on the α or β position may increase the hydrophilicity of the

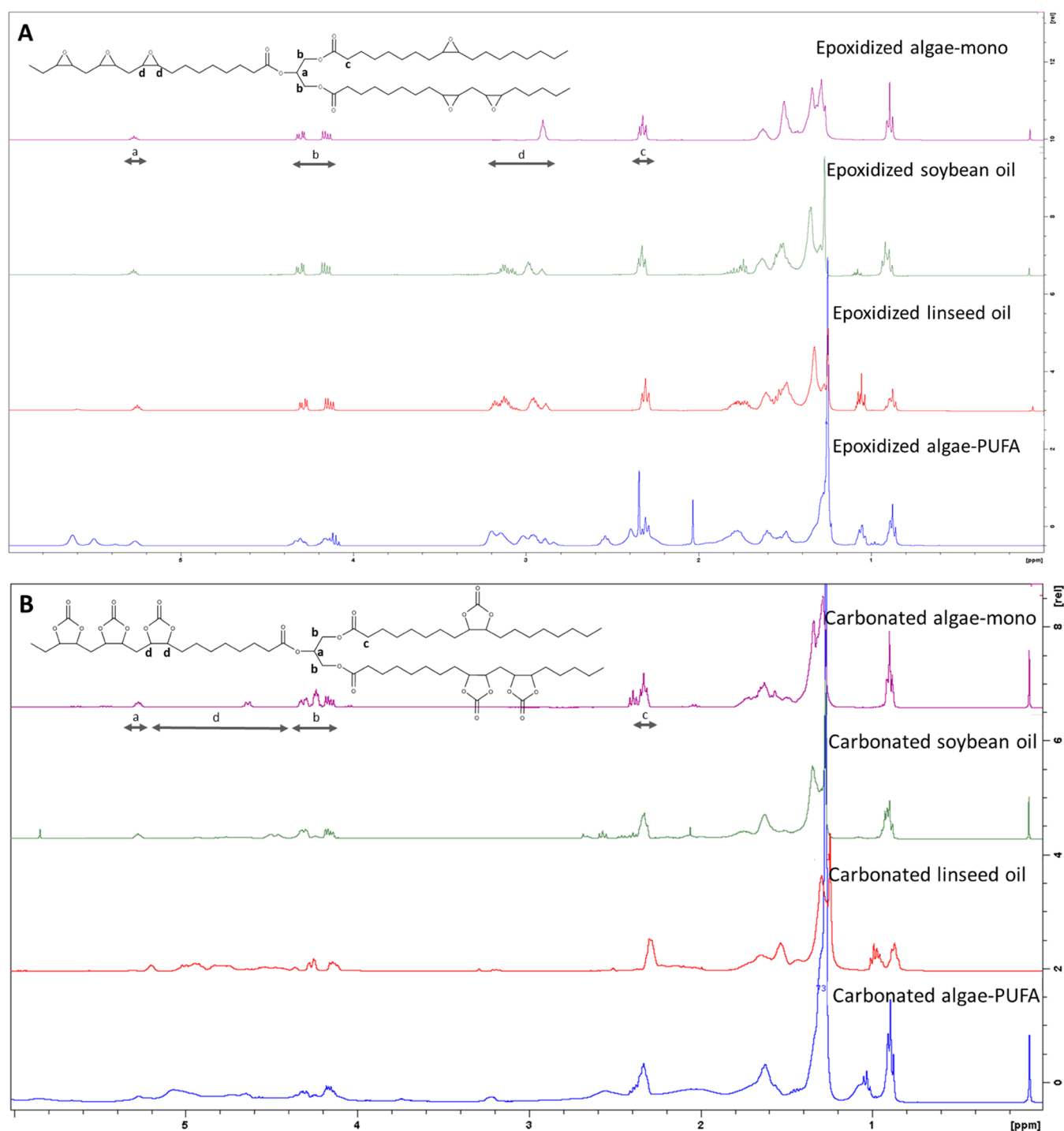


Figure 4. NMR of epoxidized (A) and carbonated (B) monomers.

microenvironment, making a favored site for hydrophilic amine to dissolve and attack the adjacent carbonate group. Further investigation is needed to determine the chemical mechanism of this phenomenon. Slow curing of NIPU has been a major technical hurdle for industrial application. Fast curing that is comparable to traditional polyurethane production is favored to be adopted in the existing infrastructure. Our results suggest that it is possible to use a precursor with high-density carbonated groups to shorten the curing time for a practical industrial application. Previously, it was reported that the reactivity of carbonate can be affected by ring size and different substituents that are located close to the carbonated

groups.^{32,33,47,48} Usually, the 6-membered, 7-membered, and 8-membered cyclic carbonated groups are more reactive than 5-membered cyclic carbonated groups; however, the production of these large cyclic carbonates requires harmful chemicals such as phosgene or its derivatives (ethylchloroformate).^{32,49,50} Although 5-membered cyclic carbonates are less reactive, they are still the most promising precursor for NIPU production due to their green chemical pathway and CO₂ sequestration benefit. Different substituents (aliphatic, ether, and ester) that are located close to the 5-membered cyclic carbonate can also significantly affect the reactivity in aminolysis.⁴⁷ However, it is technically challenging to produce such carbonate associated

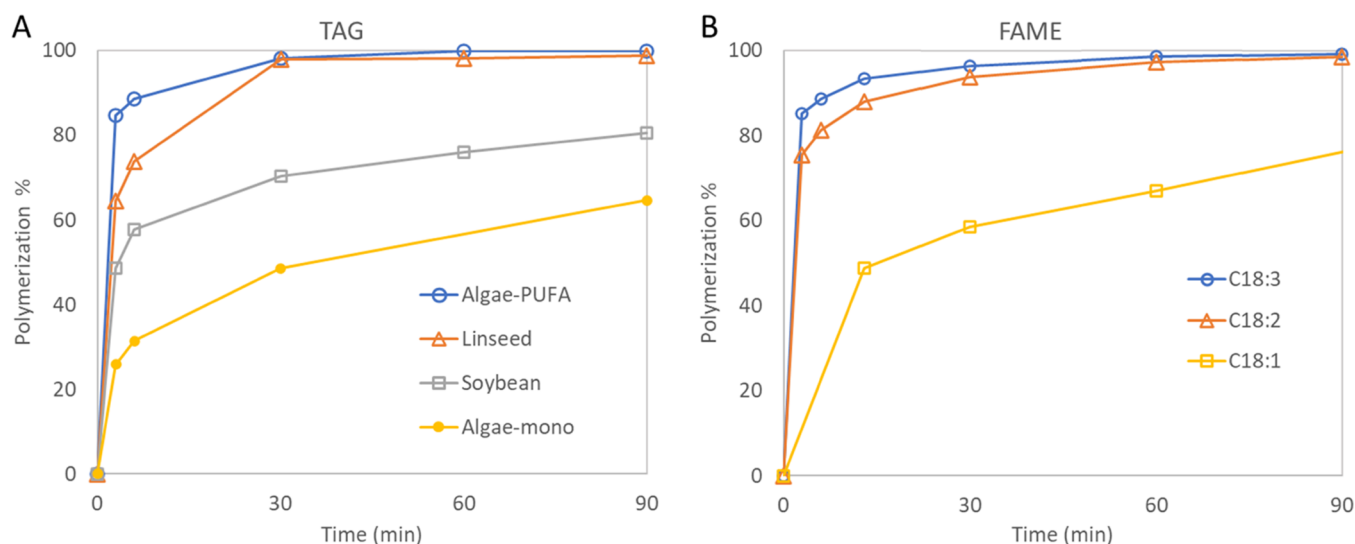


Figure 5. Kinetics of carbonated triglyceride oil: (a) algae-mono, soybean, linseed, algal-PUFA (96%); and (b) kinetics of carbonated FAME.

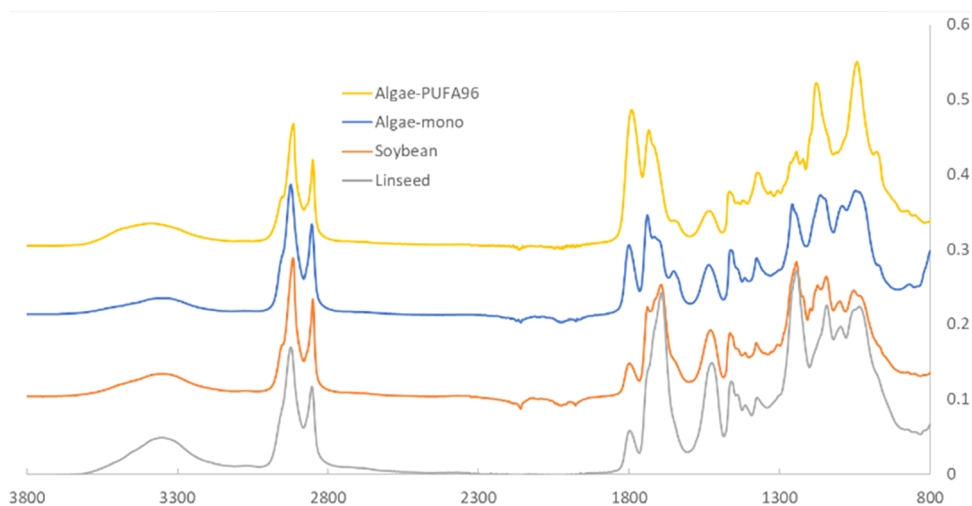


Figure 6. FTIR of algae-mono, soybean, linseed, and algae-PUFA (96%) resin.

with ether or ester groups. In this work, we have demonstrated a new approach to remarkably increase the reactivity of 5-membered cyclic carbonate using the natural PUFA-derived 5-membered cyclic carbonate. This new finding opens a new path to utilize bio-based PFAs as highly reactive precursors for NIPU production. Since the PUFA is abundant in many natural resources, such as linseed, hemp, and algal oil, it can help provide a stable feedstock supply for NIPU production. In addition, the high reactivity of carbonate derived from PUFA allows quantitative cure at a lower temperature (70 °C), preventing the formation of amide groups. The ester groups can be preserved in the NIPU to endow more flexibility of the product.

We envisage that plant-based PFAs will provide a bio-based, renewable, and sustainable resource to produce highly reactive monomers for NIPU production. This can be critical in advancing the commercialization of NIPU.

Production and Characterization of NIPU Resins.

Carbonated triglyceride precursors were used for NIPU resin production. Diamines, such as BDA, PDA, and ODA, were used as cross-linkers, with the aim to illustrate the impact of amine chain length on tensile strength. The carbonated oil and

a diamine cross-linker were mixed at 70 °C for 0.5–5 min before being poured into ASTM D638 Type II dog bone molds (Figure S3). The carbonated algae-mono and soybean oil gelled after about 5 min of mixing, while linseed oil reacted with diamines very quickly and gelled within 1.5 min. The mixtures of algae-PUFA96 and algae-PUFA83 oils and diamines were very viscous at 70 °C, and the reaction proceeded extremely quickly, gelling in less than 1 min, making it impossible to obtain a homogeneous mixture under our laboratory conditions. As shown in Figure 6, the resin produced from algae-PUFA (96%) had a major peak at 1800 cm⁻¹, indicating large amounts of unreacted carbonated groups, likely due to the poor mixing. Thus, the algae-PUFA (96%) was not a good precursor for NIPU production using our existing experimental setup; therefore, we did not test the tensile strength of the resin derived from these samples. We did, however, successfully use the partially carbonated algal oil (algae-PUFA 43% and algae-PUFA 67%) to produce resin samples (Figure S4). Notably, there are peaks around 1639 cm⁻¹, indicating the formation of the amide group. This is a typical side reaction for monomers with ester groups during aminolysis, and the reaction's mechanism has been well studied

Table 4. Mechanical and Thermal Properties of NIPU Products^a

carbonated oil	diamine	T_g (°C)	Young's modulus (MPa)	tensile strength (MPa)	elongation at break (%)
soybean	BDA	1	2.7 ± 0.2	1.1 ± 0.1	46.7 ± 3.8
	PDA	11	2.1 ± 0.0	1.0 ± 0.1	53.7 ± 3.7
	ODA	15	2.5 ± 0.1	1.2 ± 0.0	54.4 ± 2.2
linseed	BDA	40	590.1 ± 99.2	16.1 ± 2.1	26.0 ± 6.5
	PDA	42	335.3 ± 23.3	18.8 ± 1.3	53.2 ± 2.0
	ODA	50	103.2 ± 10.8	11.9 ± 1.5	57.1 ± 0.5
algae 46%	BDA	3	1.3 ± 0.0	0.5 ± 0.0	50.9 ± 6.6
	PDA	-15	0.8 ± 0.1	0.3 ± 0.0	46.5 ± 4.2
algae 67%	BDA	52	570.4 ± 41.2	16.0 ± 2.0	7.3 ± 1.0
	PDA	46	464.3 ± 9.5	13.3 ± 0.4	15.6 ± 1.3

^aBDA, butane diamine; PDA, pentane diamine; ODA, octane diamine.

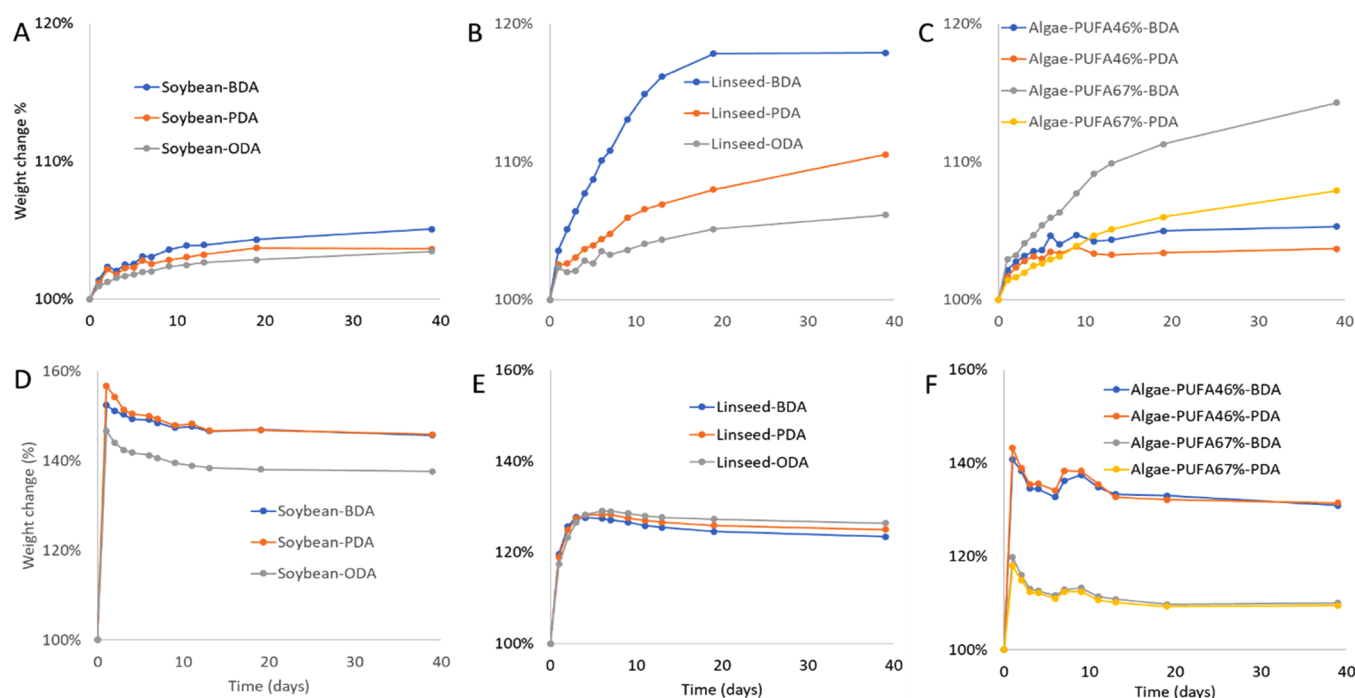


Figure 7. Swelling tests of NIPU resins: (A) soybean oil in water, (B) linseed oil in water, (C) partially carbonated algal NIPU in water, (D) soybean oil in toluene, (E) linseed oil in toluene, and (F) partially carbonated algal NIPU in toluene.

in previous publications.^{5,6,51} Though it is not a big issue in this case, it is worthy to mention that this side reaction might change the nature of networks. To avoid the side reaction, an extra amount of diamine should not be used. Also, using a selective catalyst might be helpful to improve polymerization without increasing the amidation side reaction.²¹

The performance of triglyceride-derived NIPU was tested, and the results are summarized in Table 4. The NIPU samples with more cross-linking generally have higher glass-transition temperature and higher Young's modulus. The soybean-derived NIPU samples have low Young's modulus, and the FTIR result showed that the soybean oil was not fully cross-linked and might be a mixture of oligomers, causing poor tensile performance. The linseed-derived NIPU exhibited higher glass-transition temperature and remarkably higher tensile strength. This is consistent with its high cross-linking degree and quantitative polymerization. Notably, algae-PUFA (46%)-derived NIPU displayed similar results to soybean NIPU, and the algae-PUFA (67%) showed similar results to linseed NIPU. This result indicates that algal oil containing PUFA is a versatile precursor that can be used to produce

NIPU for a wide range of applications by changing the epoxidation and thus carbonation degree. It is also worth noting that increasing the chain length of the diamine cross-linker from C4 (BDA) to C8 (OCA) reduced Young's modulus by a factor of 6, suggesting that short-chain diamines like ethylene diamine could further increase the structural strength of the polymers.

The NIPU resin samples were cut into small cubes and immersed in water or toluene for the swelling test. The results are shown in Figure 7. All of the resin samples absorbed water and toluene. The hydroxyl groups formed at α or β positions of the urethane linkages endow the hydrophilicity to the NIPU resin. The linseed oil resin produced by BDA absorbed the most water, which might be related to the highest hydroxyl density in the linseed NIPU (Figure 7B). As shown in Figure 7, NIPUs produced from shorter-chain diamines generally have high hydrophilicity, while the resins produced with longer-chain diamines are more hydrophobic.

In the toluene swelling test, all resins first absorbed toluene to increase weight and then lost weight due to the dissolving of unreacted monomers and oligomers. The toluene absorption

data are better separated into different categories. Soybean absorbed the most toluene due to its incomplete cross-linking (Figure 7D). The linseed resin slowly absorbed toluene and saturated with 30% of toluene, probably because of its complete polymerization and dense cross-linking structure (Figure 7E). Algae-PUFA (46%) resins behaved similarly to soybean resins, while the algae-PUFA (67%) resins exhibited the same trend as linseed resins on the first day and started to lose weight due to the unreacted monomers. Again, results indicate that by changing the carbonation degree of algal oil with PUFA, the property of the final products can be tuned.

Foam Production. The NIPU foam samples (Figure 8) were initially very soft and springy to the touch with a very



Figure 8. NIPU foam produced by carbonated linseed oil.

slow rebound characteristic. However, after 24 h, the foam became much stiffer and after several weeks developed into a very stiff polymer with a significant resistance to compression or deformation. It is hypothesized that the cyclic carbonate groups might not fully cross-link at the curing condition (80 °C, 15 min), and this partially cross-linked foam gave an apparent property similar to memorial foam. Overtime, the unreacted cyclic carbonate groups continued to react with diamine to form more cross-links and eventually produced a rigid foam. After several weeks, the T_g of the foam was tested as 42 °C, which is very similar to the linseed-derived resin samples (Table 4). The higher T_g might also partially explain the rigidity of the foam at room temperature. Based on these results, we believe that the rigidity of foam can be adjusted by partially cross-linking the cyclic carbonates in the linseed monomers (6.3 cyclic carbonates per triglyceride; Table 2). This might affect the tensile strength of the foam product, but the flexibility of the foam can be improved for certain applications.

We notice that the morphology of the foam can be improved and therefore applied the cell stabilizer Vorasurf, which is a surfactant that has been widely used in polyurethane foam production to improve the morphology of cells. However, it had no discernible impact on the cell stability or size and consistency, probably because of the very high viscosity of the monomer mixture. Since the mixture was quite thick while mixing and pouring into the mold, chemical interactions (modified by Vorasurf) probably had a lower effect on bubble morphology, size, and distribution than material viscosity. The CLO was largely composed of triglyceride constituents with high viscosity, which likely affected reaction kinetics (reduce mass transfer) and distribution of bubbles or cells in the developing foam. Testing with free fatty acid oils, which would have lowered viscosity, would likely yield a faster foaming reaction and better cell formation in the developing foam and would make cell stabilizers like Vorasurf more likely to have a noticeable effect in the finished foam. In addition, mixing such

free fatty acid-derived carbonates can also reduce the cross-linking degree, improving the flexibility of the foam. In this paper, we have demonstrated a practical method to produce NIPU foam via a cost-effective approach. More work will be conducted to improve the mechanical performance and morphology of the NIPU foam for commercial applications, such as soft foam for footwear and rigid foam for insulation.

Technoeconomic Analysis Results. Technoeconomic analysis revealed that commercially produced NIPU could be sold at prices comparable to the market price of conventional polyurethane. Given that this technology has not been demonstrated beyond the bench scale, the TEA modeling conducted here is intended to serve as an engineering feasibility assessment to quantify the economic potential of the process, make reasonable assumptions, and perform a sensitivity analysis on parameters that are not well understood. Future iterations and experimental progress may shed additional light on the process, including areas of lower clarity such as reactor design and costing. In addition to the NIPU process, a conventional (isocyanate-based) flexible foam polyurethane plant was analyzed for comparison. TEA modeling and financial assumptions were approached consistently with methodologies described in prior studies, including 330 days per year process uptime, 2016 year dollars, 40% equity/60% debt financing, and 10% internal rate of return (IRR) reflective of *n*th-plant technology maturity.⁵² More details can be found in the [Supporting Information](#).

This feasibility TEA study found the NIPU minimum polyurethane selling price (MPSP) to be \$2.17/lb, using linseed oil as a representative feedstock and 2800 TPY as the base scale. This can be compared to an estimated polyurethane market price of \$2.04/lb (5 year average of industry database prices),⁵² therefore showing a potential for competitive NIPU economics from a renewable feedstock approximately on par with traditional polyurethane prices. With minimal cost reductions, NIPU production could achieve cost parity with conventional polyurethane technologies, garner a value premium as could be attributed to market drivers associated with renewable sourcing, or improve product properties if those are realized experimentally. For the purpose of comparison and validation, a similar TEA assessment on a conventional polyurethane production facility found an MPSP of \$2.07/lb for isocyanate-based polyurethane produced from the same linseed oil feedstock basis. The similarity in MPSP between the conventional and NIPU analyses shows that replacing the assumed conventional PU process (one-step epoxidation and ring-opening reaction) with the NIPU process (two-step epoxidation and carbonation reactions) is not deemed to add significant cost to the process.

To determine the major cost drivers of the process and identify areas with room for improvement, a sensitivity analysis was performed on key process parameters. A more complete discussion on the sensitivity analysis can be found in the [Supporting Information](#). From the sensitivity analysis, we conclude that NIPU economics can change drastically based on the economy of scale. The plant scale was set at 2800 tons per year (TPY) of NIPU product for the base case, in line with typical polyurethane manufacturing facility scales available in industry databases. However, guidance from the industry suggests that larger polyurethane production facilities can generally reach capacities on the order of 100 000 TPY. Accordingly, scales in this range were considered as a sensitivity (Figure S7). Significant benefits were demonstrated

for increased capacities (Figure 9); the MPSP of linseed oil-based NIPU was shown to be <\$1.30/lb for scales exceeding

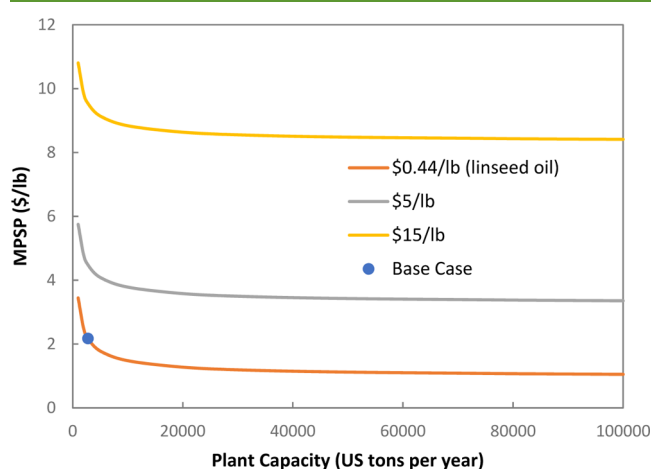


Figure 9. MPSP as a function of production capacity for a range of feedstock costs. Linseed oil at a cost of \$0.44/lb is assumed for the base case. Gray and yellow lines represent the MPSP of NIPU products that are generated from feedstocks at \$5/lb and \$15/lb, respectively.

20 000 TPY, with the MPSP approaching \$1/lb for capacities on the order of 100 000 TPY. It should be noted that the upper ranges of these scales could exceed the current U.S. production of linseed oil (ranging from 88 000 to 120 000 TPY from 2014 to 2018). This limitation could be addressed by utilizing a mixed feedstock of linseed oil and alternative oils such as algae or soybean oil.

In addition to the importance of plant scale, we demonstrated that significant cost savings can be realized when considering the retrofitting of existing foam production equipment. If an existing foam production facility was retrofitted for NIPUs (assuming a 75% reduction in installed equipment cost for foam production and a 100% reduction of cost for the polyurethane warehouse), an MPSP of \$1.90/lb could be achieved. For a conventional polyurethane producer looking to transition to NIPUs, retrofitting their equipment for NIPUs could lead to profitable NIPU production. Other risk factors examined in the sensitivity analysis—diamine price, catalyst recycle capability, and the use of alternate diamine cross-linkers were found to have a relatively low effect on MPSP within reasonable bounds of consideration. Incomplete conversion during epoxidation and carbonation was also found to have a low impact, though any influence this might have on product quality and saleability is not captured here.

CONCLUSIONS

Four kinds of commercially available triglyceride oil samples were successfully used as precursors for NIPU production. The density of the carbonated group on the fatty acid chain had a positive impact on polymerization rate, which is critical for industrial production. The linseed oil and algal oil with PUFA content showed much higher reactivity than other precursors, indicating that the application of PUFA can be a practical approach to shorten curing time. However, the viscosity increases with the content of the carbonated group and high viscosity can be problematic for mixing to achieve a homogeneous mixture for quantitative conversion. The identification of carbonated precursors with high reactivity

and low viscosity holds great promise for industrial applications. Finally, technoeconomic analysis revealed that the profitable commercial NIPU production from renewable feedstocks could be achieved at cost parity with traditional isocyanate polyurethanes when operating in a retrofit foam facility at sufficient production capacities.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.1c03653>.

FTIR spectra; monomer and resin photos; and foam formulation and detailed technoeconomic analysis (PDF)

AUTHOR INFORMATION

Corresponding Author

Tao Dong — Renewable Resources and Enabling Sciences Center, National Renewable Energy Laboratory, Golden, Colorado 80401, United States; orcid.org/0000-0002-4961-7576; Email: tao.dong@nrel.gov

Authors

Ermias Dheressa — Intel Corporation, Phoenix, Arizona 85226, United States

Matthew Wiatrowski — Renewable Resources and Enabling Sciences Center, National Renewable Energy Laboratory, Golden, Colorado 80401, United States

Andre Prates Pereira — Department of Chemical Engineering, University of Bath, Bath BA2 7AY, United Kingdom

Ashton Zeller — Algix, Meridian, Mississippi 39301, United States

Lieve M. L. Laurens — Renewable Resources and Enabling Sciences Center, National Renewable Energy Laboratory, Golden, Colorado 80401, United States; orcid.org/0000-0003-4930-3267

Philip T. Pienkos — Renewable Resources and Enabling Sciences Center, National Renewable Energy Laboratory, Golden, Colorado 80401, United States; Polaris Renewables, Lakewood, Colorado 80228, United States

Complete contact information is available at: <https://pubs.acs.org/10.1021/acssuschemeng.1c03653>

Notes

The authors declare no competing financial interest.

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