Article

Solvent-Free Acid-Catalyzed Ring-Opening of Epoxidized Oleochemicals Using Stearates/Stearic Acid, and Its Applications

Byung-Jun Kollbe Ahn,[†] Stefan Kraft,[‡,§] and Xiuzhi Susan Sun*,[†]

[†]Bio-Materials and Technology Lab, Department of Grain Science and Industry, and [‡]Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, United States

ⓢ Supporting Information

ABSTRACT: Toxic solvent and strong acid catalysts causing environmental issues have been mainly used for ring-opening of epoxidized oleochemicals. Here, we demonstrated that magnesium stearate (Mg-stearate) was a high efficient catalyst for solvent-free ring-opening of epoxidized methyl oleate, a model compound of midchain epoxide. Mg-stearate resulted in the highest yield (95%) and conversion rate (99%) toward midchain alkoxyesters under the same conditions (160 °C, 12 h) superior to other fatty acid derivatives such as a Lewis acid (lithium and sodium stearate) and Brønsted acid (stearic acid). Based on this chemical study, we synthesized biogrease and thermoplastic using epoxidized soybean oil (ESO) and Mg-stearate via one-pot, solvent-free, and purification-free process. Mg-stearate played a significant role as a reactant for epoxide ring-opening and as a thickener when excess loading rate was used; viscosity increased from 1800 to 4500 Pa·s at 25 °C when ESO:Mg-stearate increased from 1:1 equiv to 1:2, then behaved like thermoplastics (T_g = −27 °C, T_m = 90 °C) with 1:4.

KEYWORDS: acid-catalyzed ring-opening, grease, epoxidized methyl oleate, epoxidized soybean oil

INTRODUCTION

New renewable materials derived from soybean oil and other oleochemicals are continuously increasing their market share over traditional petroleum-based products due to stricter government regulations, economic pressures, and international mandates.[1−8] Approximately 50% of most lubricants are ultimately released into the environment;[9] therefore, environmentally harmless lubricants such as oleochemicals[10] are needed. Unfortunately, plant oils often exhibit poor thermal and oxidative stability due to their propensity for E/Z isomerizations (cis/trans isomerizations) and allylic autoxidation.[11] To alleviate these problems, chemical modification of internal double bonds[12,13] is often undertaken to produce materials with more favorable characteristics; for example, the conversion of soybean oil into epoxidized soybean oil (ESO) dramatically improved oxidative stability as a high-temperature lubricant.[14,15] ESO is an attractive "green" oleochemical raw material[16−18] because of its low toxicity and inherent biodegrability.[19] Most importantly, subsequent chemical modifications of ESO can give rise to midchain branched oleochemicals that have desirable rheological properties (i.e., low pour points, good lubricity, and low volatility).[3,9,11,14,20−28] Fine-tuning of these modifications can be achieved through the size and morphology of the newly introduced branch. A particularly attractive midchain functionalization is the result of conversion of an internal epoxide into a vicinal hydroxy-carboxylate (Scheme 1); such a reaction provides an entry for superior lubricants with high oxidative stability as documented by Salimon and Salih, who showed that the introduction of midgroup branching points can alter low-temperature characteristics of plant oil-based lubricants by disrupting crystallization.[26]

Based on lifecycle assessments as well as toxicological and ecological data for various cases, products based on renewable

Scheme 1. Mid-Chain α-Hydroxy-Carboxylation of ESO or Other Epoxidized Oleochemicals
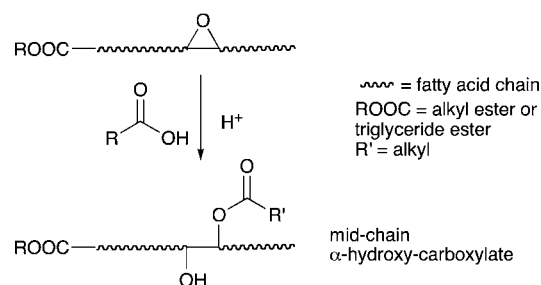
resources are commonly assumed to be more ecologically compatible when compared with petrochemical-based substances.[18,22,24] In the specific case of midchain esters in plant oils, good biodegradability was experimentally recorded,[23] which may be due in part to easily hydrolyzable ester moieties at the branching point; in contrast, simple alkyl branched fatty acids can be impervious to biological breakdown.[29]

A common problem in the synthesis of α-hydroxy-carboxylates from epoxidized oleochemicals is the need for strong Brønsted acids to activate the epoxide ring toward the attack of weakly nucleophilic carboxylic acids (Scheme 1). This can be accomplished through the addition of heterogeneous sulfonic acids and in the presence of a biphasic solvent mixture[30−33] or through the action of strong homogeneous acids such as H_2SO_4[25−27] or p-toluenesulfonic acid.[3,26,28] In all cases, the removal of acid and solvent requires a purification

step. Ring-opening esterification has been accomplished in the absence of catalysts and solvents simply by heating, but the extra carboxylic acid reaction component must be removed after the reaction.[34] Similar problems occur in the synthesis of estolides[35,36] (fatty acid polyesters) via a formal hydroxy-carboxylation of a fatty acid to internal double bonds; the latter require toxic and highly acidic $HClO_4$ as a catalyst for such reaction from oleic acid.[37]

In this research, we were encouraged by the fundamental work conducted by Chini et al., which demonstrated that attack of epoxides by weak *O*- and *N*-nucleophiles can be catalyzed by Lewis acidic alkaline and alkaline earth metals.[38−41] We reacted epoxidized methyl oleate (EMO) with Mg^{2+}, Li^+, and Na^+ salts (soaps), and stearic acids in the absence of solvents, and their nucleophilic competition in terms of atom economy and environmental factor was elucidated. Reaction products were identified by ^{1}H NMR and electrospray ionization mass spectrometry (ESI-MS). Cation-dependent conversions/yields in the case of EMO were also determined by ^{1}H NMR spectroscopy. Based on this fundamental chemistry, we synthesized soybean oil derivatives in the addition of alkaline and alkaline earth metal carboxylates (soaps) to internal epoxides of ESO. The role of the soap was conceived to be 3-fold in providing (a) a carboxylate nucleophile, (b) a cation acting as a Lewis acid catalyst,[41−43] and (c) miscibility with the product to act as a potential thickener additive. The reaction of ESO with magnesium stearate resulted in attractive thermal, mechanical, and rhelogical properties that can be modulated by the loading level of Mg soap. Thermal dynamic and mechanical properties of the resulting grease and thermoplastic-like materials were investigated by differential scanning calorimetry (DSC), thermogravity analysis (TGA), dynamic mechanical analysis (DMA), and dynamic rheometers.

■ EXPERIMENTAL SECTION

General. Methyl oleate was purchased from Fisher Scientific (Pittsburgh, PA). ESO was purchased from Scientific Polymer Products.

^{1}H NMR. ^{1}H NMR and [1]H−^{1}H COSY NMR spectra for our samples were recorded quantitatively using a Varian S spectrometer (Varian Inc., Palo Alto, CA) at observing frequencies of 500 MHz for ^{1}H on a 5 mm triple resonance probe. The sample solutions were prepared in $CDCl_3$. ^{1}H NMR spectra were obtained with 32 scans. [1]H−^{1}H COSY spectra were obtained with 128 increments and 4 scans for each increment. A sine bell function was used during processing for both dimensions. We used delay times of 10 s between scans in ^{1}H NMR acquisitions and used individually software (ACD)-optimized phasing parameters. This would minimize integration errors below the commonly assumed 5%. Furthermore, the protons compared to each other in Table 1 reside in chemically similar environments with an equal amount of vicinal coupling partners and presumably similar T_2-relaxation (spin−spin relaxation) times.

ESI-MS. Electrospray ionization spectra were acquired on a LCT Premier (Waters Corp., Milford, MA) time-of-flight mass spectrometer. The instrument was operated at 10,000 resolution (W mode) with dynamic range enhancement that attenuates large intensity signals. The cone voltage was 60 eV. Spectra were acquired at 16666 Hz pusher frequency covering the mass range 100−1200 u and accumulating data for 2 s per cycle. Mass correction for exact mass determinations was made automatically with the lock mass feature in the MassLynx data system. A reference compound in an auxiliary sprayer was sampled every third cycle by toggling a shutter between the analysis and reference needles. The reference mass was used for a linear mass correction of the analytical cycles. Samples were presented in acetonitrile as a 20 μL loop injection using an autoinjector (LC PAL, CTC Analytics AG, Zwingen, Switzerland).

Table 1. Yields and Conversion of the Reaction of 1 with a Stearate Source To Form 2

entry	stearate source[a]	conversion of 1	yield[b,c] % 2 (% 3)	ratio 2:3
1	stearic acid	96%	47% (20%)	2.4:1
2	Li-stearate	24%	15% (8%)	1.9:1
3	Na-stearate	67%	27% (5%)	5.4:1
4	Mg-stearate	99%	95% (4%)	24:1

[a]Mixed with **1** in a 1:1 ratio and heated at 160 °C for 12 h. [b]Determined by ^{1}H NMR integration using the CO_2CH_3 singlet at δ 3.65 (composite signal from **1** and all ring-opened products derived from **1**). [c]Initially formed 2^{Li}, 2^{Na}, and 2^{Mg} were hydrolyzed to **2** under conditions of NMR sample preparation. Equally, 3^{Li}, 3^{Na}, and 3^{Mg} were hydrolyzed to **3** (see Scheme 2).

FTIR. FT-IR spectra were recorded using a PerkinElmer Spectrum 400 FT-IR/FT-NIR spectrometer (PerkinElmer, Waltham, MA). All spectra were recorded in the wave range of 400−4000 cm^{-1} with a detection resolution of 4 cm^{-1} and 32 scans per sample.

X-ray Diffraction (XRD). Powder X-ray diffraction was used to characterize the composition of the thermoplastic-like material. Cu $K\alpha$ radiation was used with a curved crystal graphite monochromator. The operating range for X-ray target was 35 kV and 25 mA. The X-ray scans were in range of $2° < 2\theta < 75°$.

DSC. Thermal transitions (T_g and T_m) were obtained with a TA DSC Q200 instrument. About 5.8 mg of the developed thermoplastic sample was sealed in a hermetic pan. The sample was heated from −70 to 250 °C at a rate of 10 °C/min, then cooled to −70 °C and reheated to 250 °C at the same rate, and isothermally conditioned at −70 and 250 °C for 10 min. A second scan was collected.

TGA. Decomposition characteristics were determined with a PerkinElmer Pyris1 TGA (Norwalk, CT). About 5 mg of each sample was placed in the pan and heated from 40 to 800 °C at a heating rate of 20 °C/min under nitrogen atmosphere.

DMA. Dynamic mechanical analysis was carried out using a DMA-7e dynamic mechanical analyzer (PerkinElmer, Norwalk, CT) with the compressive method following ASTM D5024. The rate was 3 °C/min.

Rheology. Apparent viscosity measurements of blends were performed using a Bohlin CVOR 150 rheometer (Malvern Instruments, Southborough, MA) with a PP 20 parallel plate. Shear rate dependence was measured from 1 to 50 rpm, and time dependence was collected at a fixed speed of 1 rpm. Temperature dependence was measured from 25 to 150 °C with 20 °C increment at fixed speed of 1 rpm.

Synthesis and Reaction Monitoring. *9,10-Epoxidized Methyl Oleate (1).* Methyl oleate was epoxidized with *m*-chloroperoxybenzoic acid (mCPBA) using the method of Holland et al.[44] Briefly, methyl oleate (4.5 g, 15 mmol) in 100 mL of dichloromethane was stirred at 0 °C, and a solution of mCPBA (7.9 g, 46 mmol) in 50 mL of dichloromethane was added gently. After completion, the temperature was raised to room temperature, and the mixture was stirred for another 18 h. After purification, **1** was obtained as clear oil in 87% yield after drying under high vacuum.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.61 (s, 3H), 2.84 (m, 2H), 2.25 (t, J = 7.5 Hz, 2H), 1.57 (m, 2H), 1.50−1.17 (m, 24H), 0.83 (t, J = 7.6 Hz, 3H) (Figure S3 in the Supporting Information).

*9(or 10)-Stearic Ester-10(or 9)-ol Methyl Stearate (2^{Mg}, **2**, 2^{Li}, 2^{Na}).* **1** (0.450 g, 1.44 mmol) was mixed with magnesium stearate (0.425 g, 0.72 mmol), stearic acid (0.409 g, 1.44 mmol), lithium stearate (0.418 g, 1.44 mmol), or sodium stearate (0.441 g, 1.44 mmol), respectively, at 160 °C for 12 h. Aliquots were taken after 10 min and 12 h and dissolved in $CDCl_3$, and ^{1}H NMR and 2D [1]H−^{1}H NMR spectra were acquired without separation of the product. Since the singlet of epoxide at δ 2.84 is not prone to overlapping with any other signals, we can conveniently monitor the conversion rate without separation.

Semisolid Biolubricant (Grease). A 1:1 mixture of ESO (20 g, 20 mmol) and magnesium stearate (11.8 g, 20.0 mmol) was heated at 160

°C as a neat mixture for 12 h to produce a semisolid biolubricant (grease). Under identical conditions a 1:2 mixture of ESO (20 g, 20 mmol) and magnesium stearate (23.6 g, 40 mmol) also produced a semisolid biolubricant.

Thermoplastic. A 1:4 mixture of ESO (1.8 g, 1.8 mmol) and magnesium stearate (4.2 g, 7.2 mmol) was heated at 160 °C as a neat mixture for 12 h to produce a yellow transparent thermoplastic-like material. NMR analysis was conducted from a small aliquot suspended in CDCl₃. Prior to data acquisition the sample was filtered over Celite to remove insoluble magnesium stearate.

■ RESULTS AND DISCUSSION

Chemical Pathways of EMO with Stearates/Stearic Acid. In studying the reactions of internal epoxides of fatty acids with carboxylic acids and carboxylates, we initially used epoxidized methyl oleate (**1**-EMO) as a model compound representing epoxidized oleochemicals including ESO. Although the functional groups (internal epoxide and terminal ester) are identical in both ESO and model **1**, the use of the latter has two key advantages in data analysis. First, **1** is a discrete compound with a distinct molecular weight whereas ESO consists of a mixture of triglycerides, so **1** allows for a more straightforward mass spectroscopy analysis. Second, the ¹H NMR analysis of ESO and its derivatives is complex above δ 4.0 due to three multiplets from one internal and two terminal diastereotopic ester hydrogens that would obscure the formation of new esters from an epoxide attack. Furthermore, **1** displays a single epoxide multiplet at δ 2.84 (Figure S1 in the Supporting Information) whereas ESO has a set of at least six multiplets (in the range of δ 3.21−2.85) whose disappearance can be difficult to quantify in its reaction over time.

Heating mixtures of **1** and stearic acid (1 equiv) or magnesium stearate (1 equiv) for 12 h at 160 °C in the absence of solvents resulted in a 96% disappearance of the ¹H NMR (CDCl₃) epoxide signal of **1**[45] relative to the methyl ester signal at δ 3.65 (CO₂CH₃) that we used as an internal standard (Figure 1a from stearic acid and Figure 2a from magnesium stearate).[46] In both cases, multiplets at δ 4.83 revealed the formation of an ester of a secondary alcohol (R¹R²C(H)-OOCR³). In support of the ring-opening event, a new signal at δ 3.57 was consistent with the CH-proton of an alcohol functionality [R⁴R⁵C(H)OH] next to the ester. Both signals have integrals that are approximately 1/3 the intensity of the methyl ester signal. Two-dimensional ¹H−¹H COSY NMR (Figure 1b and Figure 2b) of the products presented a cross peak between R¹R²C(H)OOCR³ and R⁴R⁵C(H)OH signals that unequivocally established their vicinal relationship within one product. Mass spectroscopy for both products further confirmed the covalent connection of the two fatty acid fragments of 9(10)-hydroxy-10(9)-octadecanoyloxy stearic acid methyl ester (**2**) (ESI-MS, m/z = 635.5 [M + K⁺]) (Figure S2 in the Supporting Information).

Under identical reaction conditions (160 °C, neat 1:1 mixture of reactants), in the reaction between **1** and stearic acid, the conversion rate of **1** was 96% after 12 h (Table 1, entry 1) with a yield of 47% for **2**. As a byproduct, a second ester of a secondary alcohol was formed in 20% yield with a signal for R¹R²C(H)OOCR³ at δ 5.00 (Figure 1a and Figure 3). The ¹H−¹H COSY NMR spectrum (Figure 1b) revealed a cross peak with a signal at δ 3.41 well within the range of a vicinal ether proton [R⁴R⁵C(H)OCR⁶]. This is complemented by another set of signals at δ 3.33 and δ 3.27 that can be attributed to the presence of alcohols and/or ethers. The mass spectrum (ESI-MS) revealed a peak of **3** at m/z = 948.8 for [**3**
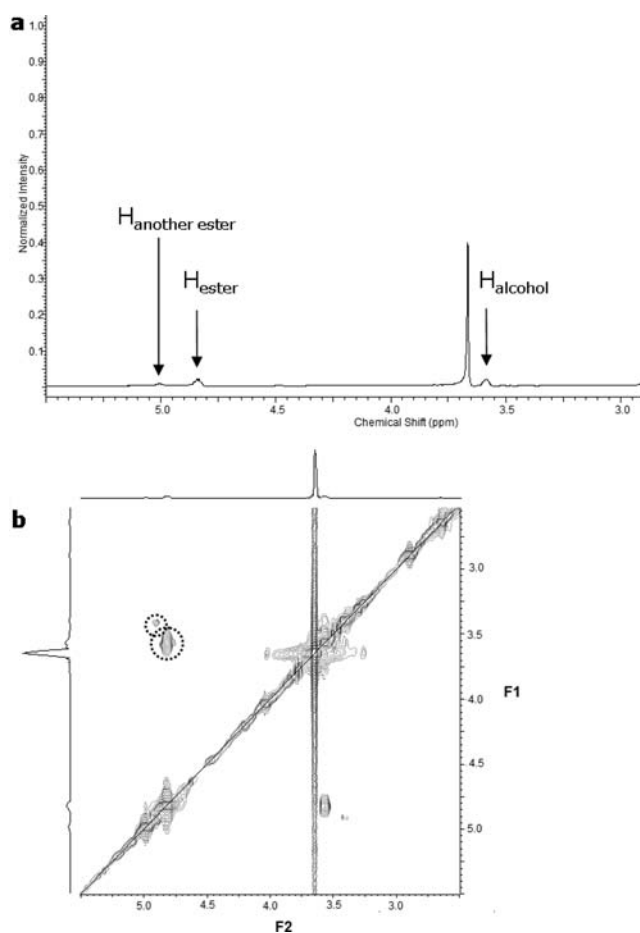

Figure 1. (a) ¹H NMR of 9(10)-hydroxy-10(9)-octadecanoyloxy stearic acid methyl ester (**2**) from ring-opening of epoxidized methyl oleate (**1**) with stearic acid. (b) ¹H−¹H COSY of the identical **2** sample from panel a. In circles are a cross peak between ester protons R¹R²C(H)OOCR³ at δ 4.83 and the C−H proton of a secondary alcohol [R¹R²C(H)OOCR³] at δ 3.57 of **2** as well as a another cross peak between the ester proton of **3** at δ 5.00 and an ether C−H proton [R⁴R⁵C(H)OCR⁶] at δ 3.41.

+ K⁺] (Figure S2 in the Supporting Information). In combination, both ¹H NMR and MS spectroscopic results point out the formation of ether adduct (**3**) (in the form of 9,10- and 9′,10′-regioisomers). We proposed that **3** (ESI-MS, m/z = 635.5 [M + K⁺]) was formed from the acid-catalyzed alcoholysis of epoxide in **1** with alcohol in **2**.[41,42,47−53] Although these reactions typically require stronger acids, we have recently discovered that the relatively weak acid H₃PO₄ can catalyze alcoholyses of epoxidized methyl oleate.[54]

The use of lithium and sodium stearate (1 equiv) produced lower conversions of **1** (24% and 67%) (Table 1, entries 2, 3) under otherwise identical reaction conditions. The two stearate salts not only exhibited lower reactivity but also were unable to improve selectivities for **2** over **3**, and the product ratios **2**:**3** of 1.9:1 and 5.4:1 (entries 2, 3 in Table 1) were not significantly different from the 2.4:1 value for stearic acid (entry 1).[55] On the other hand, magnesium stearate opened the epoxide ring of **1** efficiently (99% conversion after 12 h at 160 °C) (entry 4); moreover, the product selectivity **2**:**3** was improved to 24:1 (presumably both adducts were initially formed as magnesium alkoxides **2**^Mg and **3**^Mg).[56] We attributed the higher conversion primarily to the relatively low melting point of magnesium
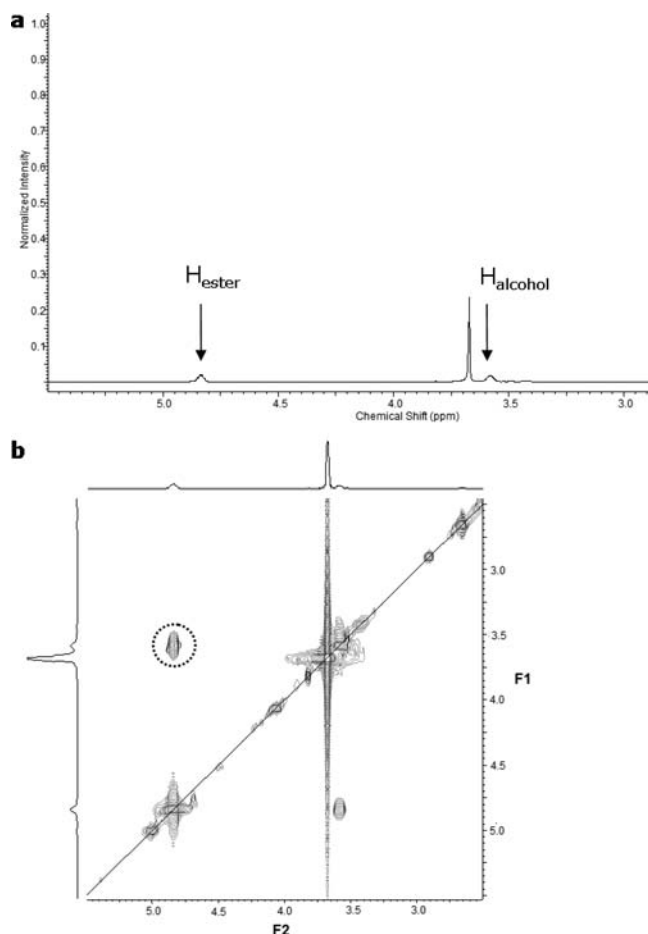
Figure 2. (a) ^{1}H NMR of **2** from ring-opening of **1** with magnesium stearate; product signals are identical with those in Figure 1a as initially formed **2**[Mg] that is hydrolyzed to **2** during NMR sample preparation. (b) [1]H−^{1}H COSY of the sample in panel a. In circles are a cross peak between ester protons R[1]R[2]C(H)OOCR[3] at δ 4.83 and the C−H proton of a secondary alcohol [R[1]R[2]C(H)OOCR[3]] at δ 3.57 of **2**.

Figure 3. ^{1}H NMR of reaction products of **1** and magnesium, sodium, and lithium stearate and stearic acid (bottom to top) (a) product mixture obtained from the reaction of **1** and stearic acid, (b) product mixture obtained from the reaction of **1** and lithium stearate (the initially formed **2**[Li] and **3**[Li] were hydrolyzed to **2** and **3** during sample preparation), (c) product mixture obtained from the reaction of **1** and sodium stearate (the initially formed **2**[Na] and **3**[Na] were hydrolyzed to **2** and **3** during sample preparation), and (d) product mixture obtained from the reaction of **1** and magnesium stearate (the initially formed **2**[Mg] and **3**[Mg] were hydrolyzed to **2** and **3** during sample preparation).

stearate (∼90 °C) allowing complete miscibility of liquid **1** and the liquid Mg salt at 160 °C. In contrast, lithium stearate (mp 220 °C) and sodium stearate (mp 245−255 °C) are solids at 160 °C, and form only heterogeneous mixtures with **1** during the reaction despite constant stirring of the suspension. Low efficient mass transfer due to low solubility of the Li soaps and Na soaps may therefore be partially responsible for the sluggish conversion. Furthermore, the relatively mild Lewis acidity of alkaline metals (in conjunction with relatively strongly coordinating carboxylates) may provide only limited electrophilic activation through oxygen coordination prior to nucleophilic attack, whereas the dicationic and more electrophilic magnesium ion is likely to interact with the oxirane ring more strongly.

The reaction of **1** and metal stearates produced metal alkoxides **2**[Li], **2**[Na], and **2**[Mg] (Scheme 2). The formation of **3**[Li], **3**[Na], and **3**[Mg] from **2**[Li], **2**[Na], and **2**[Mg] is likely to occur through similar mechanisms involving Lewis acid activation (Scheme 2).[38,41−43]

Data in Table 1 showed excellent atom economy (predominant selectivity) of magnesium stearate. Only entry 4 presented that the conversion rate matched to product (**2** and **3**) yields while stearic acid and other salts resulted in unidentified multiple byproducts. In entries 2−4 (Table 1),
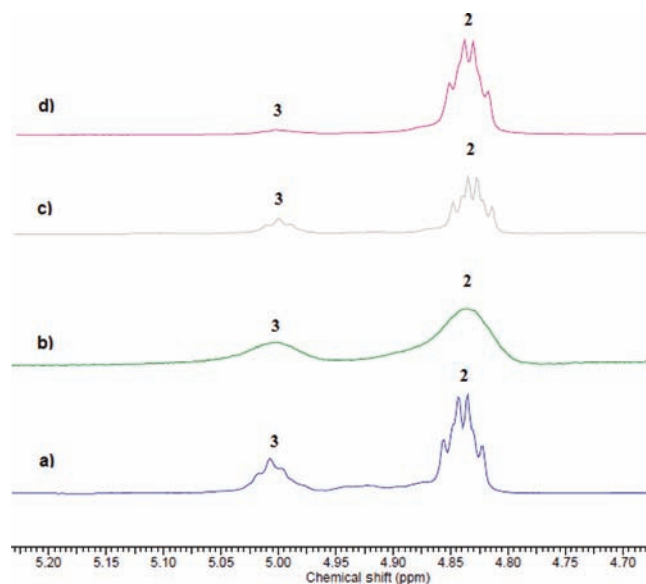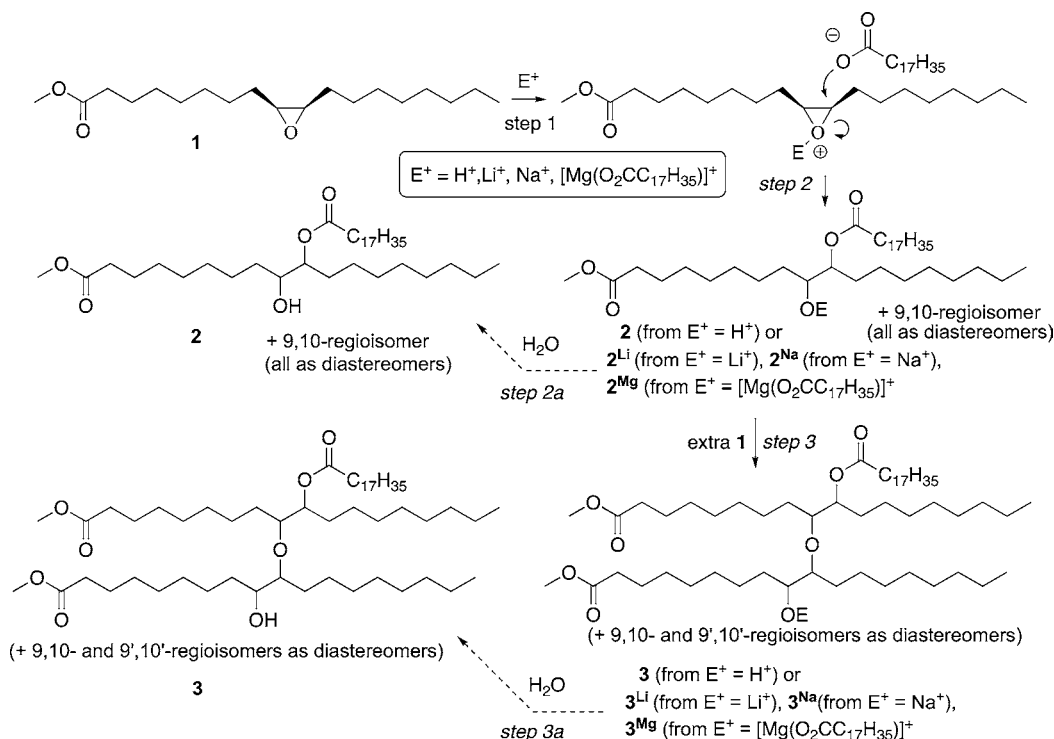
the formed products are metal alkoxides that in turn acted as reagents and attacked a second epoxide molecule. In fact, sodium alkoxides previously have been found to attack secondary epoxide centers.[57−59] At the beginning of reaction, the stearate anion concentrations in entries 2−4 are higher than the concentrations of **2**[Li], **2**[Na], and **2**[Mg]; at this point, the conversion rates in step 2 are statistically advantageous over conversion rates in step 3 (Scheme 2). This contributed to the reaction's yield of more product **2** than **3** (the neutral species **2** and **3** were formed during hydrolyses in steps 2a and 3a during NMR sample preparation); in the case of magnesium stearate, a 99% conversion (of both **1** and stearate anions) was found (entry 4). As conversions approached 50%, the alkoxide nucleophiles of **2**[Li], **2**[Na], **2**[Mg] are more abundant than stearate anions, which would make step 3 a statistical advantage over step 2; in this case, the reaction would yield more product **3** than **2**, effectively nullifying the initial statistical bias favoring the formation of **2**. In the presence of magnesium salts in entry 4, however, with an experimentally determined **2**:**3** ratio of 24:1, we concluded that the ether-forming step 3 must be intrinsically slower than the epoxide-opening step 2. Therefore, magnesium alkoxide **2**[Mg] must be less reactive toward epoxide **1** than magnesium stearate despite the fact that alkoxides are generally stronger nucleophiles than carboxylates.[60,61] We proposed that a tight ion pair association in **2**[Mg] is strong enough to mutually attenuate Lewis acidity of the metal and Lewis basicity of the oxy-anion of the alkoxide. A related course of action was previously found in the reaction of MgI$_2$ with secondary benzylic and secondary aliphatic epoxides in which in situ formed alkoxides (of iodohydrins) did not engage in further attacks on epoxide starting materials.[62−65]

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Scheme 2. Proposed Reaction Pathways for the Reaction of 1 with Magnesium, Sodium, and Lithium Stearate and Stearic Acid[a]

$E^+ = H^+, Li^+, Na^+, [Mg(O_2CC_{17}H_{35})]^+$

2 (from $E^+ = H^+$) or
2^{Li} (from $E^+ = Li^+$), 2^{Na} (from $E^+ = Na^+$),
2^{Mg} (from $E^+ = [Mg(O_2CC_{17}H_{35})]^+$)

3 (from $E^+ = H^+$) or
3^{Li} (from $E^+ = Li^+$), 3^{Na} (from $E^+ = Na^+$),
3^{Mg} (from $E^+ = [Mg(O_2CC_{17}H_{35})]^+$)

[a]Diastereomer: the products can be 9 ester (ether) 10 alcohol (ether) or 9 alcohol (ether) 10 ester (ether).

Chemical Properties of Products Derived from ESO and Magnesium Stearate.

The clean conversions and high yields in the reaction of **1** and magnesium stearate prompted us to investigate reactions of the Mg soap with epoxidized soybean oil (ESO, 3.9 epoxides per triglyceride). Heating a 1:1 mixture of magnesium stearate and ESO (stearate anions per epoxide = 0.51:1) at 160 °C for 12 h caused partial epoxide ring-opening (conversion 51% relative to ESO) and formation of alkoxyesters (yield of hydroxyesters after hydrolysis: 51% relative to ESO) (Figure 4a). Although no distinct ^{1}H NMR
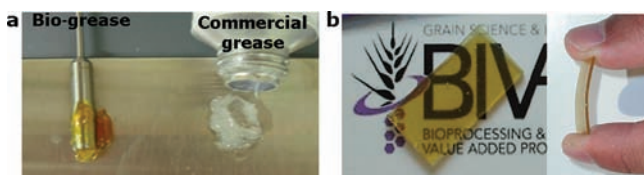

Figure 4. (a) Semisolid biolubricant (grease I) compared to commercial silicon-based grease (Dow Corning high-vacuum grease). (b) Transparent thermoplastic-like material.

signals (Figure 5b) are suitable for tracking the fate of magnesium stearate directly, the yield and conversion of ESO indicate the quantitative uptake of the soap. The obtained material has grease-like properties (grease I). Heating a 1:2 mixture of ESO with magnesium stearate (ratio of carboxylate anions to epoxide = 1.1:1) at 160 °C for 12 h also produced a grease (grease II). The ^{1}H NMR spectra of the hydrolyzed materials (Figure 5b−d) underscore the virtual consumption of epoxides (δ 3.21−2.84) of the starting material ESO (Figure 5a). New signals in the range δ 5.37−4.80 (secondary esters, R′R″HCO$_2$CR) and δ 4.25−3.35 (CH and OH alcohol signals, R′R″HCOH and R′R″HCOH) were consistent with the

formation of midchain hydroxyesters. The ratio of ester and alcohol integrals in grease II (Figure 5c) was 1:2 as expected for the presence of CH and OH signals (integral 2H) in the range δ 4.25−3.35. Relative to the terminal glyceride ester signals at δ 4.25 (integral 2H), the integral for newly formed esters was 3.7 H and the integral for newly formed alcohols (CH and OH) was 7.4 H, which is consistent with a quantitative product yield. Then, we further increased the content of the soap in the starting mixture and heated a 1:4 mixture of ESO and magnesium stearate (ratio of carboxylate anions to epoxide: 2.2:1) for 12 h at 160 °C (Figure 5d). This reaction produced a transparent thermoplastic-like material after cooling (Figure 4b). For the product analysis, the composite was subsequently extracted via Celite filtration with chloroform in which the excess magnesium stearate was poorly soluble. The Mg soap was identified by FT-IR through its antisymmetrical and symmetrical C=O stretches at 1549.2 cm^{-1} and 1455.4 cm^{-1}, which is an important characteristic of a RCOO$^-$ moiety (Figure 6a), while glyceride ester C=O bands (ν = 1732.9 cm^{-1}) were absent; on the other hand, the filtrate (Figure 6b) did not contain these carboxylate anion bands. In combination, these FT-IR results confirm the presence of a blend that contains an excess of nonbranched magnesium stearate acting as a thickener.

The ^{1}H NMR spectrum of the CDCl$_3$ extract of the thermoplastic-like material (Figure 4b) is shown in Figure 5d. Although a slightly lower spectral quality, a good match with Figure 5c ("grease") is apparent, which suggests that the basic organic constituents in greases I and II are identical with the thermoplastic-like material. The main difference between both materials is due to the presence of excess magnesium stearate within the thermoplastic-like material (about 4.3 equiv of unreacted carboxylate anions per triglyceride after complete epoxide conversion). The magnesium stearate is apparently
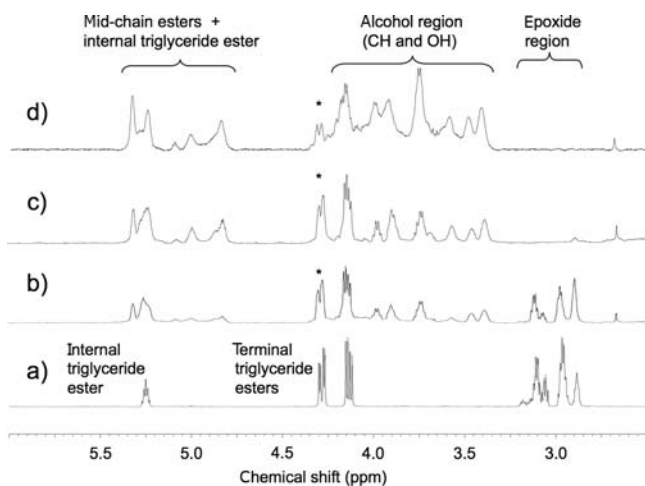
Figure 5. Expansions of ^{1}H NMR spectra of the region δ 6.00–2.50. (a) Spectrum of starting material ESO featuring signals for triglyceride esters and with an average ratio of 3.9 epoxides per triglyceride. (b) Spectrum of grease I obtained from the reaction of ESO with magnesium stearate (1 equiv) (ratio of stearate anions per epoxide = 0.51:1) for 12 h at 160 °C. The ratio of integrals of terminal trigycerides (asterisk) to the epoxide region amounted to an average of 1.9 residual (unreacted) epoxide units per triglyceride. New signals for midchain esters (R′R″HCO$_2$CR) appeared in the range δ 5.37–4.80, and peaks for newly formed secondary alcohols (R′R″HCOH and R′R″HCO*H*) emerge at δ 4.25–3.35. (c) Spectrum of grease II obtained from the reaction of ESO with magnesium stearate (2 equiv) for 12 h at 160 °C (ratio of stearate anions per epoxide = 1.1:1). Virtually complete disappearance of ESO epoxide signals was accompanied by the appearance of ester and alcohol signals similar to those in experiment b. (d) Spectrum of the thermoplastic material from the reaction of ESO with 4 equiv magnesium stearate (ratio of stearate anions per epoxide = 2.2:1) for 12 h at 160 °C. The spectral expansion is virtually identical to that in experiment c.

capable of thickening the organic base material to the extent of becoming a solid. We tested this hypothesis by melting a sample of grease II with 2 equiv of additional magnesium stearate (4 equiv of stearate anions) until complete mixing was achieved (within 5 min); subsequent cooling of the mixture did, in fact, produce a thermoplastic material similar to that in Figure 4b. Previously, in situ generated magnesium soaps were used as thickeners in petrochemical-based magnesium greases.[66] In addition, X-ray diffraction (XRD) was performed to determine whether the thermoplastic-like material is totally amorphous or partially crystalline. XRD (Figure 7) provided a typical XRD pattern of magnesium stearate (wide peak around 22°)[67] which explained that it was partially crystalline. This XRD result also supported our hypothesis that magnesium stearate can be a thickener at extra high concentration.

In a separate experiment, we found that the chemical conversion of epoxides in ESO to alkoxyesters was crucial for the establishment of both grease and thermoplastic properties as simple (physical) melting of ESO and magnesium stearate for 5 min (with very few epoxides chemically converting during that time) created only opaque and soft puttylike materials upon cooling.

Thermal and Mechanical Properties of ESO with Magnesium Stearate. Thermal properties of the biogrease (Figure 4a) and thermoplastic-like material (Figure 4b) were investigated with the aid of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Dynamic mechanical thermal analysis (DMTA) was used to study the
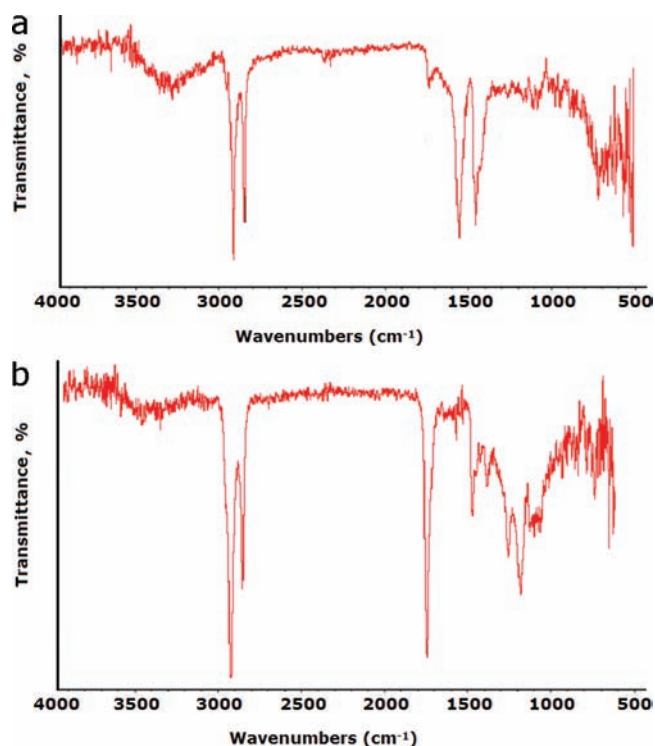

Figure 6. FT-IR spectra of the thermoplastic-like material derived from ESO and magnesium stearate after adding CHCl$_3$ and separating a soluble and an insoluble component. (a) FT-IR of the insoluble material (magnesium stearate, ν = 1549.2 cm^{-1} and 1455.4 cm^{-1}). (b) The filtrate containing hydroxy esters of **2** (ester ν = 1732.9 cm^{-1}; alcohol $\nu \approx 3500$ cm^{-1}).
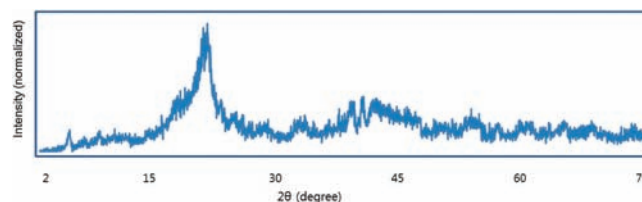

Figure 7. XRD of the magnesium stearate-rich theromplastic-like material.

viscoelastic behavior of the thermoplastic-like material. DSC results showed that the magnesium stearate had two discrete endotherms at around 90 °C (T_m)[67] and 110 °C (Figure 8, top); the latter is possibly due to the loss of Mg^{2+}-hydrated or entrapped water. A scan of thermoplastic-like material displayed the same "double endotherm," (albeit less pronounced) due to the presence of magnesium stearate in the blend (Figure 8, bottom); this is expected due to the presence of unreacted magnesium stearate in the blended material. The glass transition temperature was found at T_g = −27 °C.[68,69]

In contrast, grease I did not show the double endotherm at higher temperatures due to the absence of excess magnesium stearate. Its glass transition temperature $(T_g = -25$ °C) was slightly different from that of the thermoplastic-like material.

The TGA plot of the thermoplastic-like material indicated a small weight loss at around 160 °C followed by a major weight loss (thermal degradation) at around 420 °C with an onset at around 260 °C that was completed at 530 °C (Figure 9). The TGA curve of grease I presented a similar thermal degradation
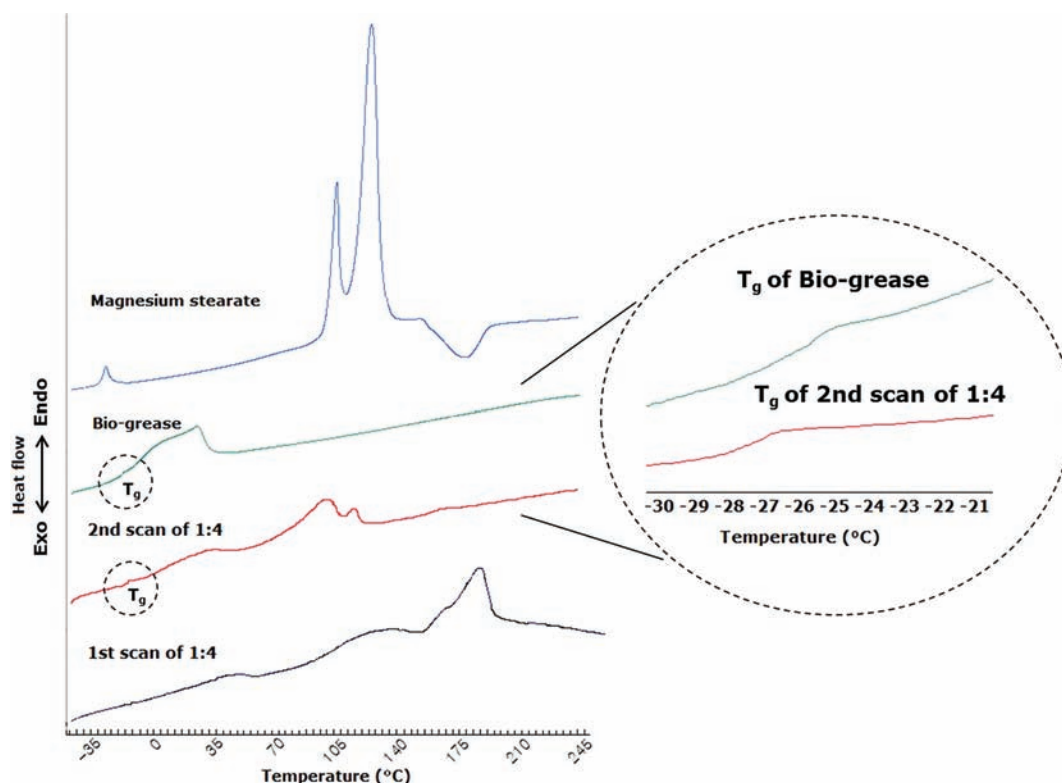
Figure 8. (Bottom to top) DSC of the first and second scans of the thermoplastic-like material from ESO/magnesium stearate (1:4 equiv), biogrease [grease I from ESO/magnesium stearate (1:1 equiv)], and magnesium stearate.
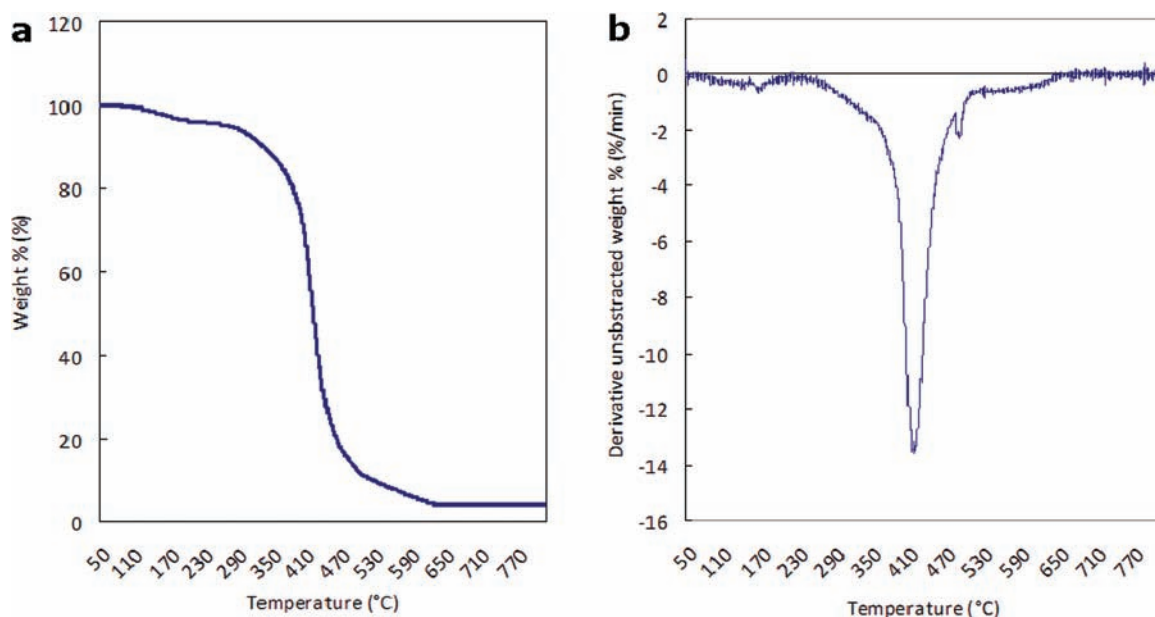

Figure 9. TGA of the thermoplastic-like material derived from ESO/magnesium stearate (1:4 equiv): weight % (a) and derivative weight % (b).

profile with major weight loss at around 390 °C (Figure S4 in the Supporting Information).

DMTA results of the thermoplastic-like material showed that storage modulus (E') and loss modulus (E'') were independent of frequency (Figure 10) but decreased as temperature increased (Figure 11). This transparent thermoplastic-like material has unique thermal and mechanical properties; it is sensitive to temperature changes with a long rubbery region. The excess of magnesium stearate is believed to generate the

long rubbery region due to physical blending with Mg soap instead of chemical incorporation between the two ingredients.

In rheological studies, greases I and II were compared to commercial silicone grease (Dow Corning high-vacuum grease, Midland, MI) as a function of shear rate, time, and temperature (Bohlin CVOR 150 rheometer). Grease I displayed a shear thinning behavior similar to that of commercial silicone grease (Figure 12) whereas grease II had continuously higher viscosities at the same shear rates. The decrease in viscosity
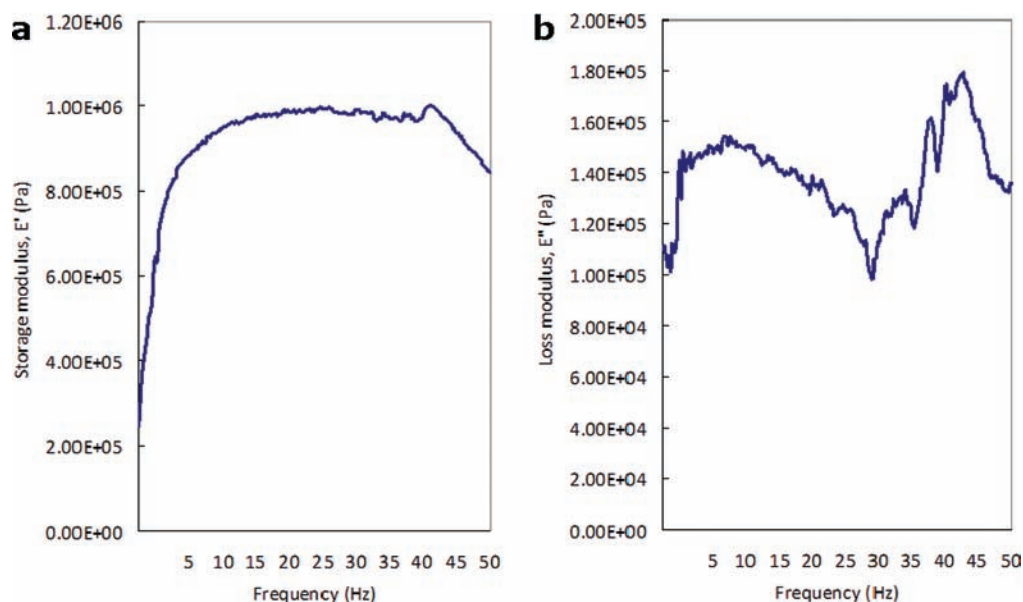
Figure 10. Dynamic mechanical properties of the thermoplastic-like material from ESO/magnesium stearate (1:4 equiv) by frequency: storage modulus E' (a) and loss modulus E'' (b).
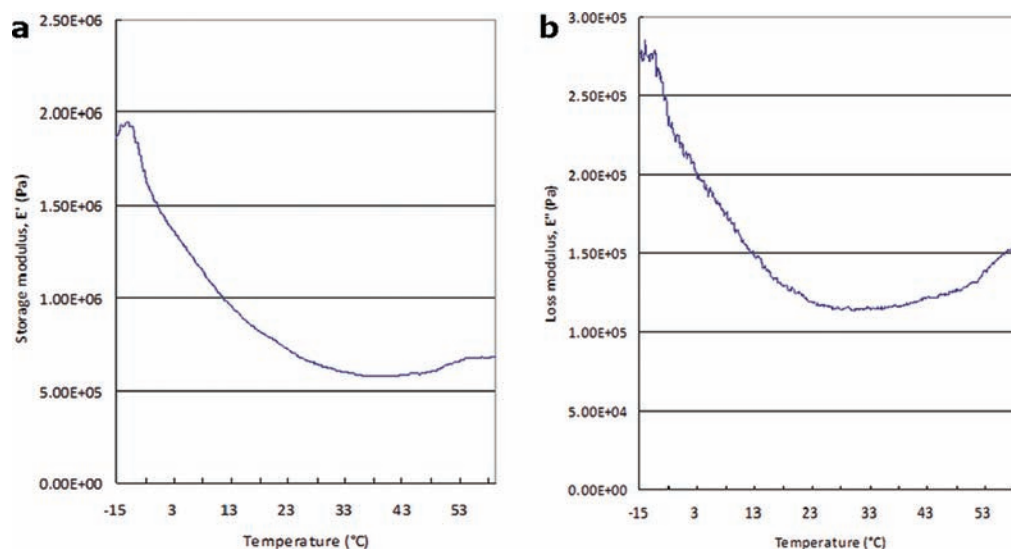

Figure 11. Dynamic mechanical properties of the thermoplastic-like material by temperature: storage modulus E' (a) and loss modulus E'' (b).

with increasing shear rates is typical of greases in general. All samples showed fairly time-independent flow (Figure 13).

When temperature increased, grease I experienced a gradual decline of viscosity from 1800 Pa·s at 25 °C to about 1000 Pa·s at 120 °C, which closely matched the behavior of the commercial silicone grease (Figure 14). In contrast, grease II, which is more viscous at 25 °C (4500 Pa·s compared to 1800 Pa·s for grease I), rapidly declines in viscosity when temperature increases, measuring <100 Pa·s at 120 °C. Clearly, the viscosity in greases derived from ESO and magnesium stearate depends on various factors. At lower temperatures, the higher viscosity of grease II compared to grease I can be correlated with the higher average molecular weight of its components due to exhaustive conversion of epoxides to alkoxyesters (Figure 5) or the effect of partial crystallization (Figure 7) in the magnesium stearate rich domains in grease II. At elevated temperatures a separate factor must come into play

to lower the viscosity of the "heavier" grease II below the values of the "lighter" grease I.

In conclusion, the acid-catlyzed ring-opening of epoxidized methyl oleate (**1-EMO**) with magnesium stearates produced a midchain alkoxyester in near quantitative conversion and yield in 12 h at 160 °C with traces of ether formation (oligomerization) detected as a result from alcoholysis of the product alkoxide with **1**. This reaction was significantly cleaner as measured by ether-forming oligomerizations than analogous reactions with stearic acid, lithium, and sodium stearate. Based on this chemistry, we obtained grease I by reacting epoxidized soybean oil (ESO) with magnesium stearate via a green process (solvent free, one pot, purification free). Grease I has great potential for industrial uses in the temperature tested in this work. We were able to manipulate the properties of the reacted materials by controlling the ratio of ESO and magnesium stearate. Greases, for example, were obtained at ratios of 1:1 to 1:2 equiv of ESO:Mg-stearate, and a transparent thermoplastic-
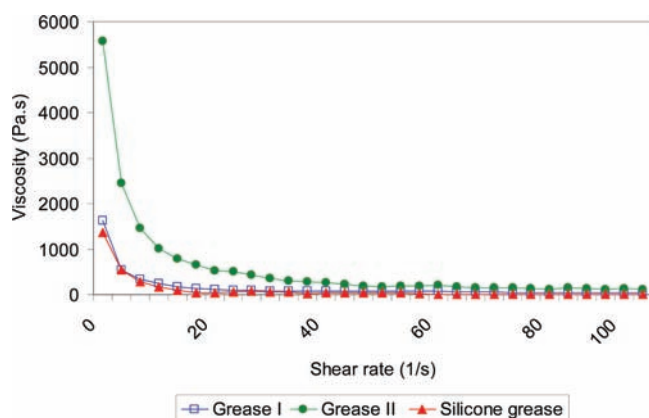
Figure 12. Viscosity vs shear rate of grease I (derived from ESO/magnesium stearate, 1:1 ratio) and grease II (derived from ESO/magnesium stearate, 1:2 ratio); commercial silicon grease was measured as a reference.
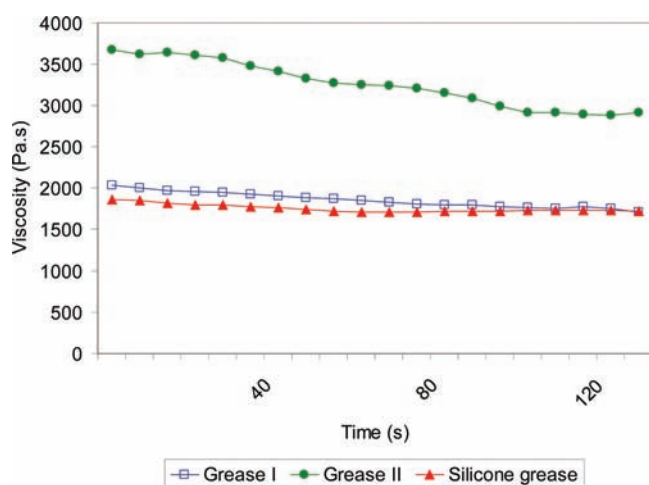

Figure 13. Viscosity vs time of grease I (from ESO/magnesium stearate, 1:1 ratio), grease II (from ESO/magnesium stearate, 1:2 ratio), and commercial silicone grease.
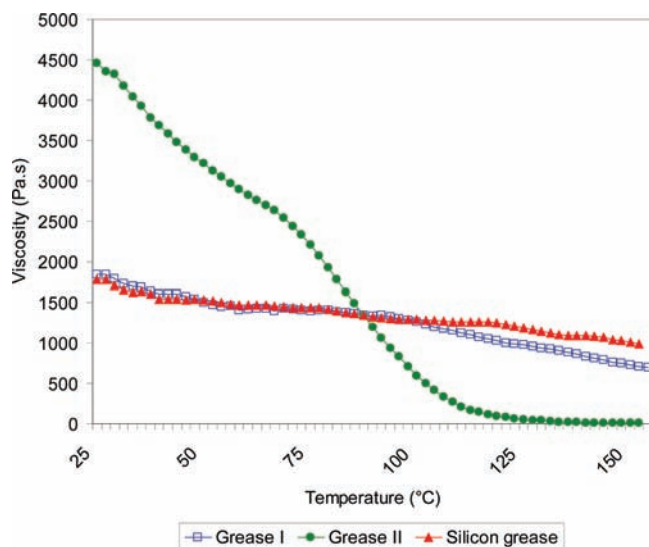

Figure 14. Viscosity vs temperature plot for grease I (from ESO/magnesium stearate, 1:1 ratio), grease II (from ESO/magnesium stearate, 1:2 ratio), and commercial silicone grease.

like material was the result of higher loading of Mg soap (i.e., 1:4 of ESO:Mg-stearate). Magnesium stearate played two roles depending on its loading level: it functionalized either partially or completely the epoxides in ESO, and it also acted as a thickener in excess loading. These biobased materials were formed in solvent-free processes that did not require further workup or purification steps. In the absence of waste generation, these reactions attain 100% atom economy and environmental factor.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures depicting ^{1}H NMR spectrum of EMO and ESO, ESI-MS of EMO/stearic acid and EMO/magnesium stearate, and TGA of the biogrease of ESO/magnesium stearate. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*Tel: 785-532-4077. Fax: 785-532-7193. E-mail: xss@ksu.edu.

Present Address
§S.K.: 7840 Sunset Ln, Indianapolis, Indiana 46260, United States.

Notes
The authors declare no competing financial interest.

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