Study on synthesis of biodegradable polyurea grease using modified vegetable oil

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Received 30 Aug 2022; Revised 4 Nov 2022; Accepted 28 Nov 2022; Published 20 Dec 2022.
DOI: https://doi.org/10.54939/1859-1043.j.mst.FEE.2022.279-284

ABSTRACT

Lubricants have been applied in numerous industrial fields, as they help reduce friction and heat generated when operating machines and also protect metallic parts in corrosive environments. In some applications, especially in marine, these greases need to be biodegradable, or they get accumulated and can be harmful to aquatic life. To address this matter, modified vegetable oil was used instead of persistent mineral oil. Also, in submerged conditions, polyurea grease outperforms traditional lithium grease as the latter is more susceptible to water washout. So, in this paper, the polyurea thickener was synthesized in-situ in biodegradable modified vegetable oil by using methylene diphenyl diisocyanate and amines as precursors. The fabricated grease chemical properties were determined by FTIR, and its tribological characteristics were studied by dropping point, penetration, and four-ball test. Results showed that polyurea grease has high operational temperature (dropping point at 278 ^oC), excellent pumpability (penetration 275 mm^{-1}), and offers great wear resistance (wear load 233 kg).

Keywords: Polyurea grease; Biodegradable; Lubricant; Modified vegetable oil.

1. INTRODUCTION

Vegetable oil-based lubricants offer good anti-wear, anti-friction, and extreme pressure properties comparable to mineral oil-based lubricants, as well as possess biodegradability. Therefore, bio-lubricant has been studied extensively and gradually applied to replace the latter, as rapeseed oil [1] or other plant oils [2] were used instead of mineral oils.

However, along with superior lubricating properties, vegetable oils suffer from several drawbacks: poor thermal and oxidation stability, partly due to the presence of beta-hydrogen atom in the glycerol molecule, which is thermally unstable and prone to oxidation [3]. These disadvantages are major obstacles to the widespread application of vegetable oils, but can be addressed by replacing glycerol structure with a more resistant branched polyol such as trimethylolpropane (TMP). This method was proven to improve the stability of palm oil [4], rapeseed oil [5], palm kernel oil [6] and camelina oil [7]. The substitution of polyol groups in vegetable oils was carried out by transesterification, which usually requires two steps. In the first step, vegetable oils were methanolized with alkaline catalyst to obtain methyl ester carboxylic acid (MECA). In the second stage, the transesterification of MECA with TMP is a relatively slow reaction, requiring strong catalysts such CH_3ONa or K_2CO_3 at elevated temperatures to proceed. Among viable catalysts, sodium methoxide provides a higher product yield, but is caustic, toxic, flammable, and highly reactive toward the water. So in this paper, potassium carbonate was used instead because of its relatively low cost and easier of handling.

Besides base oil as the main component, grease also contains thickeners, an essential ingredient that can form a structural framework and regenerate bonds after mechanical processes. Among several candidates, polyurea which can be synthesized by a reaction between a diisocyanate and an amine, is one of the best choices for making grease thickener. Due to the popularity of soap grease, polyurea grease is still accounting for a relatively modest proportion, but in many areas, the use of this grease is irreplaceable [8]. Owing to a high dropping point,

around 270 °C, polyurea grease is capable of working over a wide temperature range. With its high specific load capacity, high resistance to hydrolysis, oxidation, chemical agents, and contains no metal ions which can catalyze oxidation reactions, polyurea is widely used as a thickener in many specialized greases [9].

The type of amine can greatly affect the characteristics of the grease, due to the compatibility of base oil with the hydrocarbon group attached to the nitrogen [10]. In this work, polyurea greases were prepared in-situ using methylene diphenyl diisocyanate (MDI) and various amines of different categories in the base oil medium. The final products were then tested for their lubricating properties.

2. EXPERIMENTAL

2.1. Materials

Canola oil, Sodium hydroxide NaOH 96%, Acetone CH_3CHO 99.5%, Ethanol C_2H_5OH 98%, Trimethylolpropane (TMP) $CH_3CH_2C(CH_2OH)_3$ 98%, Methylene diphenyl diisocyanate (MDI) $C_{15}H_{10}N_2O_2$ 98%, Dodecylamine $CH_3(CH_2)_{11}NH_2$ 99%, Cyclohexylamine $C_6H_{11}NH_2$ 99%, aniline $C_6H_5NH_2$ 99%. Methanol CH_3OH 98% and Potassium carbonate K_2CO_3.

2.2. Experiment preparation

2.2.1. Instrumentation

The modified canola oil was characterized by Fourier transform infrared (FT-IR) using Tensor II with a scan range of 400 - 4000 cm^{-1} to identify the functional groups. Proton nuclear magnetic resonance ^{1}H-NMR was used to learn the structure of the TMP-oil. The kinematic viscosity, density and flash point (open cup) were determined using ASTM D445, ASTM D1298 and ASTM D92, respectively.

The synthesized grease was dissolved in acetone to isolate the polyurea thickener, which was then analyzed by FT-IR. The dropping point, penetration and extreme-pressure properties of lubricating grease were determined by ASTM D566-20, cone penetration ASTM D217 and four-ball method ASTM D2596-02, respectively.

2.2.2. Synthesis of TMP-modified canola oil (TMP-CA)

In the first step, canola oil was treated with methanol in the presence of NaOH catalyst. In a typical procedure, 1 g NaOH was completely dissolved in 100 mL methanol, then 200 g canola oil was added. Due to the miscibility between the oil and the solvent, a clear, homogeneous solution was obtained. The mixture was then transferred to a double-layer flask, stirred under ultrasonication while maintaining the temperature at 40 ^oC for 1 hour. The reaction mixture was extracted by glycerol, washed several times using 5% NaCl solution at 75 ^oC until neutralized. Excess methanol was removed by vacuum distillation.

In the second stage, 200 g MECA from the previous step was put in a three-neck round bottom flask and was heated to 70 ^oC, then 28.2 g TMP was added under stirring to obtain a homogeneous solution. 2.27 g potassium carbonate was slowly added to the flask and the whole mixture was heated to 130 ^oC under a vacuum for 2 hours. The reacted solution was then diluted with acetone, catalyst and excess TMP was separated by centrifugation. The final product was obtained by removing acetone and MECA using vacuum distillation at 60 ^oC and 180 ^oC, respectively.

2.2.3. Synthesis of canola oil based polyurea grease

Vegetable oil based polyurea grease was synthesized in-situ by the following procedure. MDI and amines were first dissolved in the modified canola oil (20% wt). Then, oil solution of the diisocyanate and each amin was mixed at proportion so that MDI/amine ratio was 1:2 to form diurea. Because isocyanate and amine groups react vigorously with each other, the mixture

thickened immediately as amine was introduced to the MDI solution, so strong stirring was needed to avoid grease inhomogeneity. The reaction was kept at 60 ^oC for 30 minutes, then heated to 180 ^oC for 2 hours. Finally, a suitable amount of TMP-canola oil was added so that the thickener content was 10%.

3. RESULTS AND DISCUSSION

3.1. Synthesis of TMP-modified canola oil

^{1}H-NMR magnetic resonance spectroscopy was used to determine the presence of protons in modified canola oil (figure 1). It can clearly be seen that in the ^{1}H-NMR spectra, methyl (-CH_3) peak at 0.90 ppm and methylen (-CH_2-) peak at 1,35 ppm belong to both TMP and fatty acids from canola oil. Peak of -HC=CH- at 5.40 ppm and peak of -CH_2CH=$CHCH_2$- at 2.05 ppm are respectively from proton adjecent to the double bond and from methylen group near the double bond of the unsaturated fatty acids. Peak of methylen group attach with carboxylic group -CH_2C=O of TMP can be seen at 2.35 ppm. Finally, the peak at ~4,00 ppm with high intensity belongs to the proton of methylen group that bound to the oxygen of carboxylic acid group on TMP molecules (CH_2O), proving that the transesterification was nearly complete. The weak signal at 3,45 ppm from –CH_2-OH indicated the presence of a small amount of TMP diester as the hydroxyl group was not fully reacted. Also, a minor signal at 3,67 ppm of methoxyl group in MECA showed that the excess methanolized canola oil was not completely removed.

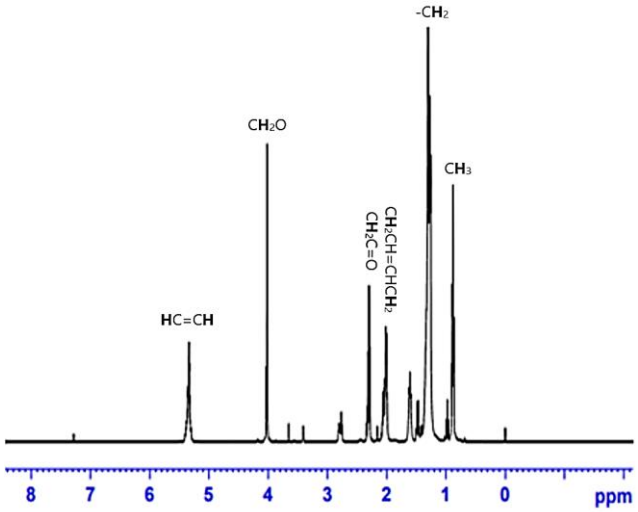

Figure 1. *^{1}H-NMR spectrum of TMP-canola oil.*

FT-IR spectrum of modified canola oil was shown in figure 2. The peak at 3006.92 cm^{-1} and at 2924.28 cm^{-1} belonged to the stretching of the C-H bonds attached to single bond and double bond, respectively. The C=O stretching peak of ester can be seen at 1742.95 cm^{-1}. The weak peak at 1654.42 was from the stretching of disubstituted C=C bond having cis-configuration, which was belonged to the double bond in oleic acid, the main composition of canola oil. The peak at 3535.10 cm^{-1} was attributed to the vibration of –OH group on unreacted TMP molecule. The existence of this peak indicate that glycerol was succesfully substituted by TMP. The peak intensity was low showed that the transesterification reaction was almost completed. This result agree with ^{1}H-NMR analysis.

The TMP-modified oil samples after synthesis have been determined some properties such as density, viscosity, freezing point and flash point, the results are shown in table 1. These characteristics are similar to the respective properties of mineral oil, especially the viscosity value; so it can be used to make grease at equivalent quality.

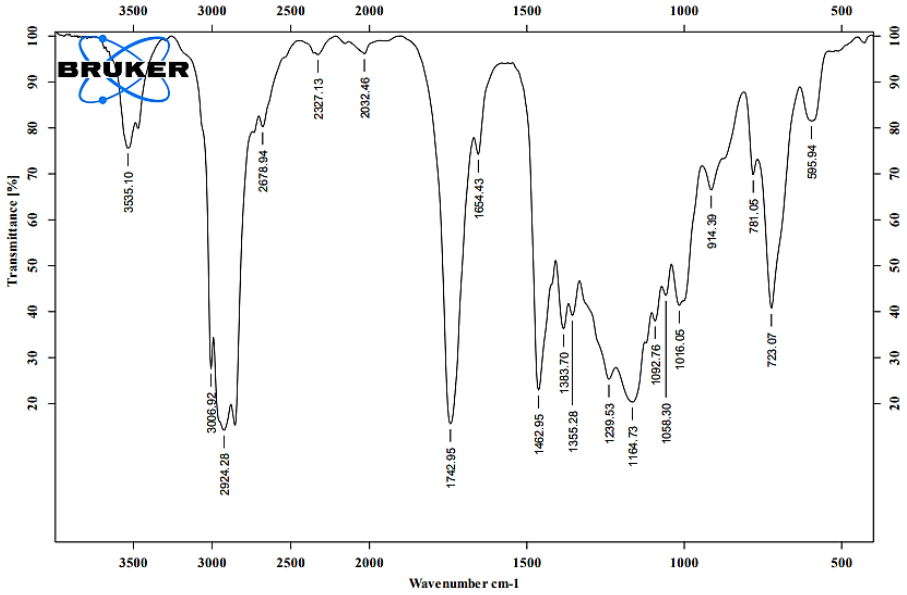

Figure 2. *FT-IR spectra of TMP-canola oil.*

Table 1. *Physical properties of TMP-modified canola oil.*

Density, g/mL at 15 °C, ASTM 1298		0.9188
Kinematic viscosity, mm^2/s, ASTM D445	40 °C	41.35
	100 °C	8.89
Freezing point, °C, ASTM D97		-16
Flash point (open cup), °C, ASTM D92		251

3.2. Synthesis of polyurea grease

Polyurea thickener was separated after dissolving the oil with acetone. From FT-IR result, the vibration at 3328.9 cm^{-1} is attributed to the –NH- group, and the signal at 1631 cm^{-1} from oscillation of –CO- in urea bond. It can also be seen that the stretching vibration of isocyanate group –N=C=O at 2275-2250 cm^{-1} does not appear, indicating that MDI was completely reacted.

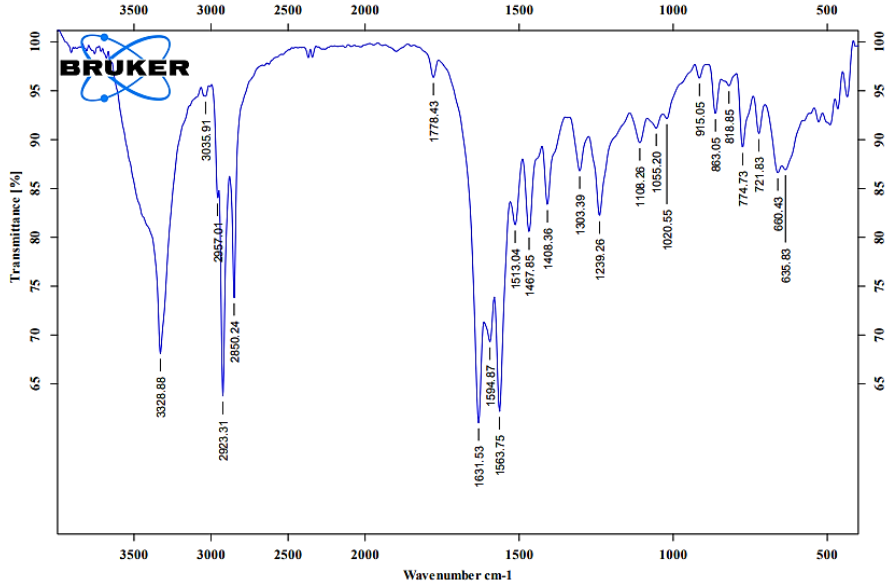

Figure 3. *FT-IR spectra of polyurea thickener.*

As mentioned above, monoamine plays a crucial role in the fabrication of polyurea grease. Depending on whether the amine is aromatic, aliphatic or cyclic, the functional group on the polyurea surface will be that corresponding type. These groups directly affect the compatibility of the thickener with the oil medium. The physical properties of polyurea grease at 10 % thickener from different monoamine were shown in table 2.

Table 2. *Characteristics of polyurea grease from different amines.*

Amine	Dropping point, ^oC, ASTM D566-20	Penetration, mm^{-1}, ASTM D217	Wear load, kg, ASTM D2596-02
Dodecyl amine	278	275	233
Aniline	260	244	194
Cyclohexyl amine	270	262	224
Dodecyl amine + Cyclohexyl amine (1:1)	262	254	205

Visually, samples made of aliphatic and cyclic amine give the product a high degree of homogeneity, which is reflected in the absence of turbidity in the product. This is because the dodecyl and cyclohexyl chains are well compatible with the oleates in vegetable oils. In contrast, because there are no aromatic hydrocarbons in the vegetable oil, the phenyl moiety of aniline is not compatible. As a result, the aniline sample is cloudy and separates the oil after a while. Sample from mixed amines has similar properties but due to different reaction rates of amines with isocyanate groups (cyclohexylamine reacts faster than dodecylamine due to less bulkiness), the control of the composition and structure of polyurea is very difficult, which causes the resulting product to be cloudy.

The results showed that all samples had high dropping point values, above 260 °C. A relationship between thickener-oil compatibility and grease properties was also revealed: turbid (low compatibility) samples have lower dropping point values. For the other two samples, dodecylamine-derived thickener with a longer carbon chain has better oil holding capacity and thus has the highest dropping temperature value.

The penetration value allows a relative assessment of the thickener's thickening ability. The results showed that the aniline-based grease had the lowest penetration value, followed by cyclohexylamine and dodecylamine, respectively.

From the four-ball machine experiment, it can be seen that the anti-wear property of polyurea grease follows the same pattern as the dropping point value. Inhomogeneous samples have a rather low weight load while dodecylamine with the best compatibility provides the highest wear resistance. Considering no anti-wear additive was used, the value of 233 kg can still be improved.

4. CONCLUSIONS

The canola oil was successfully modified using TMP through two steps procedure. The FTIR and NMR showed that the glycerol was almost completely replaced by TMP. The modified oil has technical parameters comparable to commercial oil. Results showed that the grease made from synthesized oil and dodecylamine-based polyurea thickener has better properties than grease using different types of amines. At a very high dropping point of 278 ^oC, the grease can work at a much higher temperature range than traditional lithium grease. The high penetration of 275 mm^{-1} indicated that the grease has good pumpability. Also, four-ball test showed that non-additives sample having good anti-wear property at 233 kg wear load.

Acknowledgement: *This research was funded by Academy of Military Science and Technology according to Science and Technology Agreement 51/2020/HDKHCN. We thank the Academy for the financial support, which this work would not have been possible without.*

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TÓM TẮT

Nghiên cứu chế tạo mỡ bôi trơn polyurea phân hủy sinh học từ dầu thực vật biến tính

Các chất bôi trơn hiện tại đang được sử dụng phổ biến trong rất nhiều ngành công nghiệp do khả năng làm giảm ma sát cũng như nhiệt sinh ra khi vận hành thiết bị, đồng thời bảo vệ các chi tiết kim loại khỏi môi trường có tính ăn mòn. Trong một số ứng dụng, đặc biệt là trong hàng hải, các loại mỡ bôi trơn cần phải có khả năng phân hủy sinh học, nếu không chúng sẽ tích tụ và gây hại cho môi trường nước. Để giải quyết vấn đề này, dầu thực vật biến tính được sử dụng thay thế dầu khoáng trong thành phần chế tạo mỡ. Hơn nữa, trong điều kiện bị ngâm dưới nước, mỡ poliurea hoạt động tốt hơn mỡ liti truyền thống do mỡ liti dễ bị rửa trôi. Do đó, trong nghiên cứu này, chất làm đặc poliurea được chế tạo trực tiếp trong dầu thực vật biến tính có khả năng phân hủy sinh học, sử dụng tiền chất là methylene diphenyl diisocyanat và các amin. Tính chất hóa học của mỡ tạo thành được xác định bằng FTIR, khả năng bôi trơn được đánh giá qua nhiệt độ nhỏ giọt, độ lún kim và phương pháp bốn bi. Kết quả cho thấy mỡ poliurea có nhiệt độ làm việc cao, khả năng bơm và khả năng chống mài mòn tốt.

Từ khoá: Mỡ poliurea; Phân hủy sinh học; Chất bôi trơn; Dầu thực vật biến tính.