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## **BIOPOLYOLS AS ECOLOGICAL LUBRICANT**

### **BIOPOLIOLE JAKO EKOLOGICZNE BAZY SUBSTANCJI SMAROWYCH**

#### **Key words:**

lubricants, vegetable oils, biopolyols, tribological properties

#### **Słowa kluczowe:**

substancje smarowe, oleje roślinne, biopoliole, właściwości tribologiczne

#### **Abstract**

Vegetable oils are characterized by high lubricity. Their applications are limited due to their low stability, particularly at high temperatures and in the presence of an oxidizing agent, e.g., atmospheric oxygen. A new approach has been proposed to obtain vegetable oil derivatives with higher stability. The approach consists in the epoxidation and then hydroxylation of the oils. These reactions resulted in obtaining a biopolyol in which double bonds were substituted by isopropyl alcohol.

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The biopolyol obtained was tested on a four-ball apparatus. The tests were carried out at a constant load, and the seizure tests were performed at a load increasing at a constant rate. The results obtained were compared with those for castor, sunflower, and rapeseed oils used in lubrication. It was found that biopolyol exhibited comparable or even better lubricating properties than the reference oils.

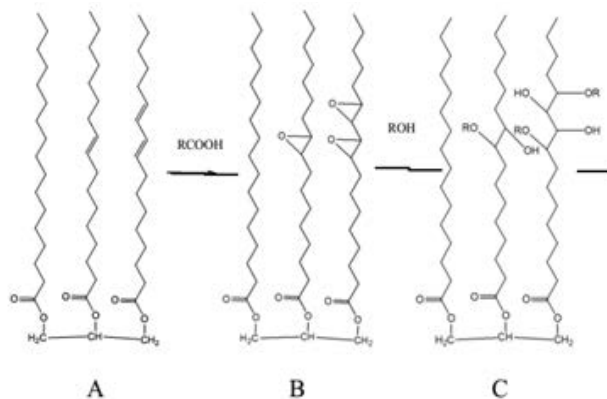
## INTRODUCTION

Vegetable oils were used as lubricants already in antiquity. During the Industrial Revolution their importance decreased due to high requirements concerning their stability. Modern lubricants are expected to be highly stable during long service life, even under extreme friction conditions, often at high temperatures and high unit pressures. Vegetable oils do not satisfy those requirements; therefore, lubricating substances are produced primarily from petroleum fractions.

In the last decade of the 20th century, following pro-ecological trends, there occurred a return to research on vegetable oils from the viewpoint of their applications as lubricants [L. 1]. Although the experimental research material is extensive, there has been only a small increase in the number of specific applications. Ecological lubricants comprise only about 5% of oils and greases produced, and they do not meet the demand even in the case of devices with open friction zones.

The main advantages of natural oils, compared to mineral oils, are their high level of biodegradation in the natural environment and their lubricity. The disadvantages of unmodified vegetable oils are their low resistance to oxidation and hydrolysis and an excessive increase in viscosity at negative temperatures. The main reason for a lack of stability of the oils under extreme friction conditions is the presence of double bonds and the ester bond in triglyceride molecules. They quite readily undergo hydrolysis at high temperatures and react with atmospheric oxygen in the process of autoxidation [L. 2, 3].

There are a number of methods that can be used to increase the stability of vegetable oils [L. 16, 17]. One of them is hydrogenation, but this process increases viscosity, which drastically limits the application range. Another approach is to introduce selected additives with targeted performance. However, the additives are usually toxic with low levels of biodegradation. Another interesting method is to obtain vegetable oil derivatives that do not have double bonds as a result of chemical reactions. This category includes the oxidation of oils and formation of oil derivatives as a result of epoxidation and hydroxylation. The courses of the two reactions are shown in Fig. 1.



**Fig. 1. Sequences of reactions of triglycerides (A) resulting in formation of bioepoxides (B) and biopolyols (C)**

Rys. 1. Sekwencje reakcji triglicerydów prowadzące do powstania bioepoksydów i biopolioli

It is possible to present the first results of studies on tribological properties of bioepoxides and biopolyols [L. 4–7]. The results obtained can be a starting point for further research and for the application of bioepoxides and biopolyols as lubricant bases. The aim of the study is to select a group of compounds having required tribological properties determining future applications. The studies on biopolyols were inspired by an analysis of the properties and applications of the natural polyol, i.e. a ricinoleic acid ester present in castor oil. It is used primarily in pharmaceuticals and cosmetics, as well as in engineering as a lubricant in machines and aircraft engines.

Polyols prepared according to the scheme presented in **Fig. 1** retain the biodegradability and lubricity of vegetable oils, and their stability is substantially higher. Due to the multitude of various substituents, the biopolyols obtained can have various physicochemical and tribological properties. The biopolyols with the most beneficial characteristics will be successively used in field tests. The subject of the study presented here is a biopolyol obtained in a two-stage reaction (**Fig. 1**) as a result of the addition of isopropyl alcohol to an epoxide. The reactions were carried out according to the methodology described in the literature [L. 8–11].

## MATERIALS AND METHODS

### Materials

The basic lubricating substance tested will be a *biopolyol* prepared according to the scheme shown in **Fig. 1**. Its tribological properties will be compared with the properties of castor, sunflower, and rapeseed oils.

### ***Biopolyol***

Biopolyol will be treated as a base of ecological lubricating substances. It was obtained in a two-stage synthesis (**Fig. 1**). In the first stage, a bioepoxide was obtained as a result of a reaction of sunflower oil and a carboxylic acid (acetic acid) and hydrogen peroxide in the presence of a catalyst (sulphuric acid). The reaction was carried out for 6 hours at 60°C [**L. 12**]. The second stage of the synthesis of biopolyols (**Fig. 1**) was the opening of oxirane rings using isopropyl alcohol according to the procedures described in the literature [**L. 8–11**]. The reaction was carried out at 82–100°C in the presence of a catalyst (tetrafluoroboric acid).

Castor oil (*Oleum Ricini*) obtained by cold pressing of the seeds of the castor oil plant was used in this study. Additionally, refined sunflower and rapeseed oils were used in this study.

### **Test methods**

The tribological properties (antiwear and antiseizure) were determined on a T02 four-ball tester according to the methods presented in the literature [**L. 13, 14**]. Two kinds of tests were carried out: at a constant load (2 kN, 3 kN, 4 kN) and at a linearly increasing load.

#### ***Tests at a constant load***

The tests were carried out for 15 minutes at 3 constant loads: 2 kN, 3 kN, and 4 kN at the rotational speed of the spindle of 200 rpm. The coefficient of friction ( $\mu$ ) determined based on the values of the moment of friction force obtained ( $M_f$ ) was a measure of resistance to motion. A measure of wear was a mean value of wear scar diameters parallel and perpendicular to the direction of sliding (d).

#### ***Tests with a linearly increasing load***

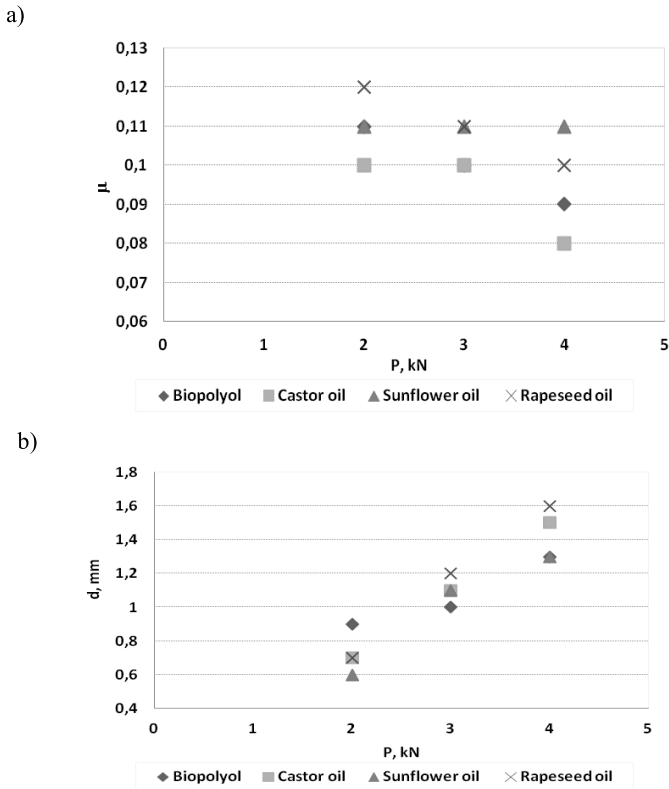
The tests were performed at a constant rotational speed of 500 rpm. The load increment rate was 409 N/s. On the basis of the course of variations in the moment of friction forces as a function of load ( $M_f(P)$ ), seizing load  $P_t$  and seizure load  $P_{oz}$  were directly determined and limiting pressure of seizure  $p_{oz}$  was calculated [**L. 13–15**].

### **Experimental**

The results obtained in tests at a constant load are given in **Fig. 2** and at an increasing load in **Fig. 3**.

### Results tests at constant loads

The dependence of the coefficient of friction ( $\mu$ ) and wear scar diameter ( $d_{oz}$ ) as a function of load and kind of lubricant are presented in **Fig. 2a** and **Fig. 2b**, respectively.



**Fig. 2. Dependence of a) friction coefficient ( $\mu$ ) and b) wear scar diameter ( $d$ ) on load and kind of lubricant. Test at constant load, rotational speed 200 rpm, test duration 15 min**

Rys. 2. Zależność a) współczynnika tarcia ( $\mu$ ) oraz b) średnicy śladu zużycia ( $d$ ) od obciążenia i rodzaju substancji smarowej. Test przy stałym obciążeniu, prędkość obrotowa 200 rpm, czas trwania testu 15 min

The coefficient of friction for sunflower oil does not change. However, the value of the coefficient for the other oils decreases with an increase in load.

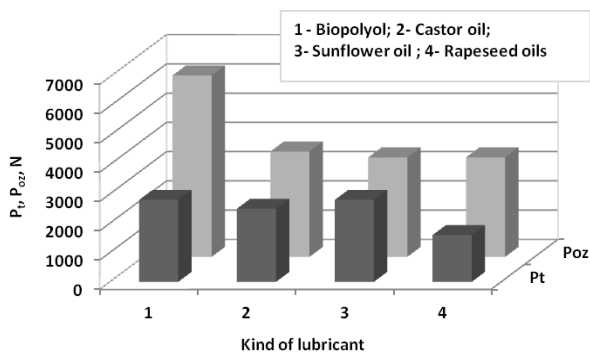
As expected, wear ( $d$ ) increases with an increase in load ( $P$ ). It has been found that biopolyol shows the relatively largest wear scar diameter at the lowest load. However, at higher loads (3 kN, 4 kN) the values of  $d$  are lower compared with those for sunflower and rapeseed oils and comparable with those for castor oil.

Resistances to motion and wear for biopolyol at constant loads (2 kN, 3 kN, 4 kN) are lower than or comparable to those for the other vegetable oils. However, due to a different structure (no double bonds), biopolyols are more stable at higher temperatures and in the presence of an oxidizing agent.

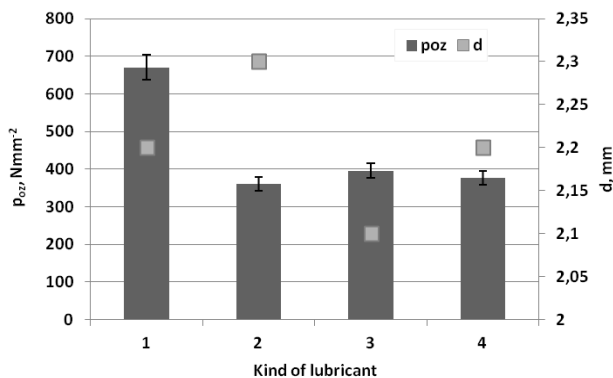
### Results of tests at an increasing load

Figures 3a and 3b show, respectively, the dependence of seizing load ( $P_t$ ), seizure load ( $P_{oz}$ ), limiting pressure of seizure ( $p_{oz}$ ) and wear scar diameter ( $d_{oz}$ ) on the variety of lubricant.

a)



b)



**Fig. 3. Dependence of a) scuffing load  $P_t$ , seizure load  $P_{oz}$  and b) limiting pressure of seizure  $p_{oz}$  and wear scar diameter  $d_{oz}$  on kind of lubricant. Tests during increasing loads, rotational speed 500 rpm, and load increment rate 409 N/s**

Rys. 3. Zależność a) obciążenia zacierającego  $P_t$ , granicznego obciążenia zatarcia  $P_{oz}$  oraz b) granicznego nacisku zatarcia  $p_{oz}$ , średnicy śladu zużycia  $d_{oz}$  od rodzaju substancji smarowej. Test przy narastającym obciążeniu, prędkość obrotowa 500 rpm, szybkość narastania obciążenia 409 N/s

Tests at increasing loads verify the tribological properties of a system under start-up conditions. Seizing load ( $P_t$ ) indicates the stability of a lubricant film under dynamic friction conditions. It can be seen in **Fig. 3a** that the highest values were obtained for biopolyol and sunflower oil. The values are 12% higher than are those for castor oil, and 75% higher than are those for rapeseed oil. A high value of seizure load was obtained for biopolyol compared with the other reference oils. The determined value of limiting pressure of seizure  $p_{oz}$  confirms the ability of the system with biopolyol as a lubricant to carry higher loads.

## SUMMARY

Biopolyol was obtained in the reactions of epoxidation and hydroxylation of vegetable oils. Its stability is higher due to a lack of double bonds in alkyl chains. Its beneficial tribological properties were substantiated in our studies.

In tests at a constant load ( $P$ ), the coefficient of friction ( $\mu$ ) takes the value of about 0.1 and decreases with an increase in load (2, 3, 4 kN), whereas wear scar diameter ( $d$ ) increases from 0.9 mm at 2 kN to 1.3 mm at 4 kN. The values of resistances to motion and wear are comparable with those obtained for the vegetable oils tested (castor, sunflower, and rapeseed). Biopolyol showed surprisingly good results in seizure tests. The high values of seizing load ( $P_t$ ) can be interpreted as a result of the formation of a lubricant film that separates friction pair elements. A stable adsorption layer may result from the interaction of functional groups formed as a result of the addition of isopropyl alcohol with the surface. Hydration of those groups and the formation of surface associates may be important in this case. This thesis may be confirmed by the high values of seizure load  $P_{oz}$  (6200 N), indicating the ability to reconstruct the adsorption layer under mixed friction conditions. It is particularly important to refer the results obtained for the biopolyol to castor oil that is a natural polyol. The results from the tests at a constant load are comparable, whereas the ability to form an adsorption layer under conditions close to seizing and seizure is significantly higher for biopolyol. The reasons for this may be found in the presence of functional groups in the alkyl chain of biopolyols.

Preliminary studies on potential applications of biopolyols presented here cannot form a basis for generalizations. However, it is possible at this stage of research to say that biopolyols can be a new group of lubricants of plant origin.

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## Streszczenie

**Oleje roślinne charakteryzują się wysoką smarnością. Ich szerokie stosowanie jest ograniczone ze względu na niską trwałość, szczególnie w wysokich temperaturach i w obecności czynnika utleniającego, na przykład tlenu atmosferycznego. W celu otrzymania pochodnych olejów roślinnych o wyższej trwałości zaproponowano nowe podejście, które polega na reakcji epoksydowania, a następnie hydroksylowania tych olejów. W wyniku tych reakcji otrzymano biopoliol, w którym wiązania podwójne podstawiono alkoholem izopropylowym.**

**Otrzymany biopoliol poddano badaniom na aparacie czterokulowym. Wykonano testy przy stałym obciążeniu oraz testy zatarcia przy wzrastającym ze stałą szybkością obciążeniu węzła tarcia. Uzyskane rezultaty odniesiono do stosowanych w technice smarowniczej olejów: rycynowego, słonecznikowego i rzepakowego. Stwierdzono, że biopoliol charakteryzował się porównywalnymi, a nawet korzystniejszymi właściwościami smarowymi w porównaniu z olejami referencyjnymi.**