The Study of Epoxidized Rapeseed Oil Used as a Potential Biodegradable Lubricant

Xuedong Wu[a],*, Xingang Zhang[a], Shengrong Yang[b], Haigang Chen[a], and Dapu Wang[a]

[a]School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai, 200240,
People's Republic of China, and [b]Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics,
Chinese Academy of Science, Lanzhou, 730000, People's Republic of China

ABSTRACT: The application of epoxidized rapeseed oil as a biodegradable lubricant is described. The epoxidation treatment has no adverse effect on the biodegradability of the base stock. Epoxidized rapeseed oil has superior oxidative stability compared to rapeseed oil based on the results of both oven tests and rotary oxygen bomb tests. Moreover, the oxidative stability can be dramatically promoted by the addition of a package of antioxidants. The epoxidized rapeseed oil has better friction-reducing and extreme pressure abilities according to tribological investigations. Formation of a tribopolymerization film is proposed as explanation of the tribological performance of epoxidized rapeseed oil.

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KEY WORDS: Biodegradable lubricant, epoxidation, oxidative stability, rapeseed oil, tribological behavior.

During the last few years, people have been paying more and more attention to environmentally friendly lubricants (1). Biodegradability is one of the most important features of environmentally friendly products. It has been estimated that, in Germany, for instance, the market share of biodegradable lubricating oil would grow from 2 to 3% in 1994 and up to 15% by the year of 2000 (2). Vegetable oils, such as rapeseed oil and high-oleic acid sunflower oil, are thought to be the best candidates to substitute for conventional petrol-based lubricating oils, as well as synthetic esters (3,4). Compared with the synthetic esters, vegetable oils are preferable because they are renewable resources and lower in cost. However, poor oxidative stability is one of the major disadvantages of vegetable oils in practice. Poor oxidative stability is substantially determined by the nature of the base oils. Rapeseed oils are chemically composed of saturated and unsaturated fatty acid triglycerides. The existence of unsaturated C=C bonds is responsible for their poor oxidative stability, especially such polyunsaturated compounds as linoleic and linolenic acids. Improving oxidative stability of vegetable oils is a major objective. Uosukainen *et al.* (5) improved oxidative stability by transesterification of trimethylolpropane and rapeseed oil methyl ester. Selective hydrogenation is another method to improve oil stability, by reducing polyunsaturated C=C bonds selectively (6). Epoxidized unsaturated fatty acids were employed as antirust additives in metalworking fluids (7). Tao *et al.* (8) applied epoxy plant oils as a lubricating additive to eliminate the corrosion caused by Cl-containing compounds. In this paper, epoxidation of rapeseed oils was used to improve oxidative stability. Epoxidized rapeseed oil showed superior oxidative stability and friction-reducing ability compared to the original oil.

EXPERIMENTAL PROCEDURES

A commercial grade refined, bleached, and deodorized low-erucic acid rapeseed oil was employed in this study. It consists mainly of triglycerides with the following fatty acid composition (mol%): palmitic, 5.1; palmitoleic, 0.3; stearic, 2.0; oleic 55.0; linoleic, 25.9; linolenic, 11.0; arachidic, 0.4; and erucic acid, 0.3. Antioxidants employed in this study were commercial products, which are 2,2′-methylene-bisphenol from Shanghai Solvent Factory (Shanghai, China), alkylated diphenylamine from Ciba Specialty Chemicals (Basel, Switzerland), benzenetriazole from Shanghai Chemical General Company (Shanghai, China), and methylene thiocarbamate from R.T. Vanderbilt Company (Bethel, CT), respectively. The epoxidized rapeseed oil was obtained *via* epoxidation with peracetic acid (9). The peracetic acid was *in situ* generated from acetic acid and hydrogen peroxide. The hydrogen peroxide, which was 40% stoichiometrically excess according to the iodine value of the rapeseed oils, was dropped into the mixture of rapeseed oil, benzene, and acetic acid. The temperature was maintained at 55–65°C for 7–8 h. After separation of water and solvents, a clear, pale yellow liquid was obtained, which was the final product.

Acid values and oxirane percentage values were determined according to American Oil Chemists' Society methods Te 2a-64 and Cd 9-57, respectively (10). The iodine values of samples were examined using Wijs Method. Flash point, pour point, and viscosity were tested according to ASTM D92, ASTM D97, and ASTM D445 standards, respectively (11). Biodegradability of base stocks was tested according to CEC-

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*To whom correspondence should be addressed.
E-mail: wuxd-c@online.sh.cn

L-33-A93 (12). The oxidative stability of oils was evaluated by both oven test and rotary oxygen bomb method. The oven tests were taken at 70°C, with air blowing. The hydroperoxide value of heated samples was monitored during the deterioration until a hydroperoxide value of 100 was reached. The rotary oxygen bomb test was conducted at 150°C, with O_2 at 826.8 kPa, Cu-spiral as catalyst, based on ASTM D 2272 Method (11). The lifetime was determined by the time of pressure dropping to 172.3 kPa. The tribological behaviors were measured by Four-Ball Machine method according to ASTM D 4172 (11). The tests were conducted at a load of 392 N and a rotating speed of 1450 ± 50 rpm, taking an average value of three parallel tests. The test balls were made of AISI standard steel No. E52100 with a diameter of 12.7 mm.

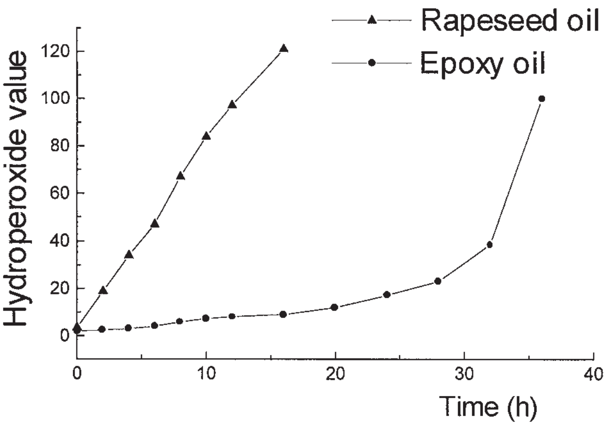

FIG. 1. Hydroperoxide development at 70°C.

RESULTS AND DISCUSSION

The properties of rapeseed and epoxidized rapeseed oils are listed in Table 1. Both density and viscosity of epoxidized rapeseed oil are more than the original rapeseed oil. This can result from molecular weight, polarity, and intermolecular forces. The epoxidized oils have high molecular weight and more polar structure than the original oil; consequently, the interactions between molecules would be stronger. Epoxidation by *in situ* peracetic acid generation is almost complete as indicated from the iodine value, which was controlled under 6 mg I_2/g after epoxidation. It was predicted that the elimination of unsaturated bonds would improve the oxidative stability of base stock greatly. The epoxidation treatment did not reduce the biodegradability of rapeseed oil based on CEC–L33–A93 tests, which makes it possible to apply epoxidized rapeseed oil as a biodegradable lubricant.

The hydroperoxide value of rapeseed oil increased gradually up to 100 within 16 h, as shown in Figure 1. As for the epoxidized rapeseed oil, the hydroperoxide value increased very slowly in the first 30 h, and then rose to 100 by 37 h. Allyl radicals could be formed very easily in the rapeseed oil due to the existence of C=C bonds, which would be converted to peroxide causing the oxidative deterioration. Undoubtedly, the elimination of unsaturated C=C bonds greatly improves the thermal stability. Rotary oxygen bomb tests were employed to further evaluate the oxidation performance. In order to evaluate the performance of formulated oils, a package of antioxidants (AO) was added into the base oils. The AO contains 0.5 wt% 2,2′-methylene-bisphenol, 0.1 wt% alkylated diphenylamine, 0.5 wt% benzenetriazole, and 0.5 wt% methylene thiocarbamate. Becker and Knorr (13) found that a mixture of polyphenol, diamine, and thiocarbamate exhibited synergistic antioxidative effect. From Figure 2, it can be seen that the oxidative stability of epoxidized oil was better than the rapeseed oil and was dramatically promoted by the addition of the above AO.

The antiwear properties of lubricants were evaluated by measuring the mean wear scar diameters (WSD) of three lower balls after 30 min rubbing in Four-Ball Machine method. From Table 1, the corresponding WSD of rapeseed oil and epoxy rapeseed oil were 0.63 and 0.72 mm, respectively. Vegetable oils, such as rapeseed oil, have good lubricity under moderate load owing to their strong tendency to form a chemico-absorption film on the metal surface (14). The frictional coefficients were monitored on-line by recording the shaft torque continuously, as shown in Figure 3. The epoxy rapeseed oil showed better friction-reducing and extreme pressure ability than the rapeseed oil. During the initial

TABLE 1
The Properties of the Two Base Stocks Without Additive

Properties	Rapeseed oil	Epoy rapeseed oil
Appearance	Yellow liquid	Pale yellow liquid
Density (kg/m^3)	917.1	961.5
Flash point (°C)	323	239
Pour point (°C)	–15	–12
Viscosity at 40°C (mm^2/s)	34.75	86.73
Viscosity at 100°C (mm^2/s)	8.096	12.72
Viscosity index	218	145
Acid value (mg KOH/g)	0.296	0.653
Iodine value (mg I_2/g)	121	4.1
Oxirane percentage (O%)	—	4.9
Biodegradability (%)	>95	>95
WSD (wear scar diameter, mm)	0.63	0.71
Extreme pressure (kg)	45	70

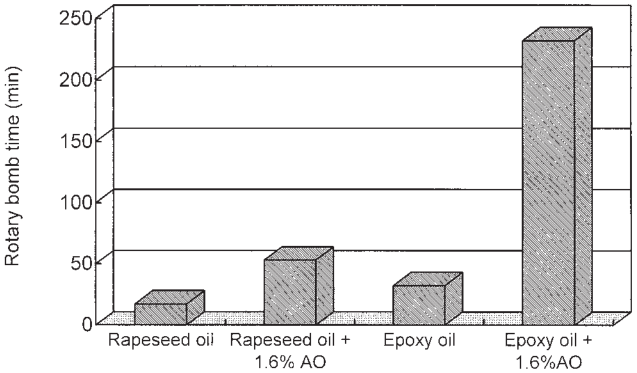

FIG. 2. Rotary bomb tests of rapeseed oil and epoxy rapeseed oil. AO = package of antioxidants. See text.

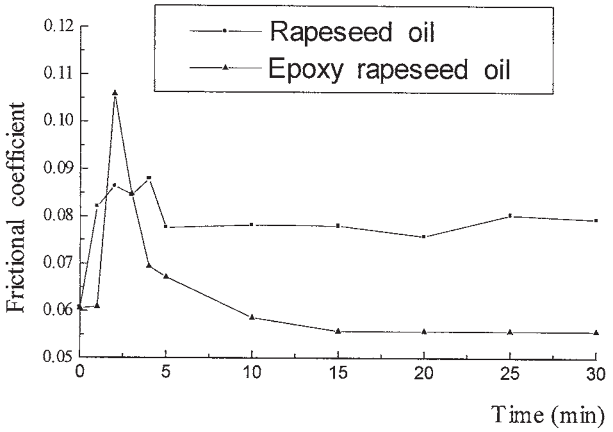

FIG. 3. The frictional coefficient curve vs. time of the two base stocks.

time of friction, the frictional coefficient was determined by the viscosity of the base oil. Because epoxy oil has higher viscosity at room or low temperature, the frictional coefficient was higher. After a period of running-in, a tribochemical reaction film could be formed on the frictional surface. The three-member ring of oxirane could form polyester or polyether material due to tribo-polymerization, which is tribologically effective to reduce friction (15).

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REFERENCES

1. Rhee, I., Evaluation of Environmentally Acceptable Hydraulic Fluids, *NLGI Spokesman 60(5)*:28–35 (1996).
2. Mang, T., Environmentally Harmless Lubricants—Current Status and Relevant German Environmental Legislation, *Ibid. 57(6)*:233–239 (1993).
3. Randles, S.J., Environmentally Considerate Ester Lubrication for the Automotive and Engineering Industries, *J. Syn. Lubri. 9*:145–161 (1992).
4. Asadauskas, S., J.M. Perez, and J.L. Duda, Oxidative Stability and Antiwear Properties of High-Oleic Vegetable Oils, *Lubri. Eng. 52*:877–882 (1996).
5. Uosukainen, E., Y.Y. Linko, M. Lämsä, T. Tervakangas, and P. Linko, Transesterification of Trimethylolpropane and Rapeseed Oil Methyl Ester to Environmentally Acceptable Lubricants, *J. Am. Oil Chem. Soc. 75*:1557–1563 (1998).
6. Johansson, L.E., and S.T. Lundin, Copper Catalysts in the Selective Hydrogenation of Soybean and Rapeseed Oils: I. The Activity of the Copper Chromite Catalyst, *Ibid. 56*:974–980 (1979).
7. Watanabe, S., T. Fujita, and M. Sakamoto, Epoxides of Unsaturated Fatty Acid as Anti-rust Additives in Water-Based Cutting Fluids, *Ibid. 65*:1311–1312 (1988).
8. Tao, D., H.L. Zhu, and Z.M. Hu, Free Chlorine Fixation and the Protective Film in Boundary Lubrication, *Lubri. Sci. 8*:397–407 (1996).
9. Lutz, J.T., in *Encyclopedia of Chemical Technology,* 3rd edn., edited by J.G. Wallace, John Wiley & Sons, New York, Vol. 9, 1978, pp. 251–266.
10. *Official Methods and Recommended Practices of the American Oil Chemists' Society,* edited by R.C. Walker, American Oil Chemists' Society, Champaign, 1984, Method Te 2a-64and Method Cd 9-57.
11. *Annual Book of ASTM Standards, Petroleum Products, Lubricants and Fossil Fuels,* American Society for Testing and Materials, Philadelphia, 1995, Section 5, Vol. 05:1 ASTM D92, ASTM D97, ASTM D445, ASTM D2272, and ASTM D4172.
12. Co-ordinating European Council for the Development of Performance Tests for Lubricants and Engine Fuels, *Biodegradability of Two-Stroke Cycle Outboard Engine Oil in Water,* CEC-L33-A-93, London, 1993.
13. Becker, R., and A. Knorr, An Evaluation of Antioxidants for Vegetable Oils at Elevated Temperatures, *Lubri. Sci. 8*:95–117 (1996).
14. Steren, O.O., Tribological Properties of Some Vegetable Oils and Fats, *Lubri. Eng. 45*:685–690 (1989).
15. Furey, M., The Formation of Polymeric Films Directly on Rubbing Surface to Reduce Wear, *Wear 26*:369–392 (1973).

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