Depression of Pour Points of Vegetable Oils by Blending with Diluents Used for Biodegradable Lubricants

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ABSTRACT: Low-temperature properties need improvement before vegetable oils can receive wider recognition as biodegradable lubricants. Effects of dilution with major biodegradable fluids, namely poly alpha olefin (PAO 2), diisodecyl adipate (DIDA), and oleates, as well as impact of pour point depressant (PPD), were investigated. Since solidification of mixed unsaturated triacylglycerols is a complex thermodynamic process, the study was limited to pour point determinations. Vegetable oils demonstrated higher pour points with increased saturation and molecular weight. *Cis* unsaturation and hydroxy groups favored lower pour points. Dilution with oleates appeared less effective than dilution with PAO 2 and DIDA. Addition of 1% PPD (w/w) depressed pour points down to $-33°C$ for canola and $-24°C$ for high-oleic sunflower oils. However, neither higher amounts of PPD nor incorporation of diluent produced further depression. Depression of pour points was not proportional to the amount of diluent and ceased with further dilution. Low-temperature performance of vegetable oils limits their prospect as biodegradable lubricants, but well-balanced usage of PPD and diluents can deliver some improvements.

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Recently, there has been considerable interest in the applicability of vegetable oils (VO) as environmentally friendly lubricants. Biodegradable lubricants, hydraulic oils, and other functional fluids are particularly important for users of equipment exposed to the environment (1–4). When utilizing VO, biodegradable lubricant manufacturers face many problems such as insufficient oxidative stability (5–8), poor corrosion protection (9), or susceptibility to hydrolytic degradation (10). Low-temperature performance often presents a major problem as well (11,12). Petroleum-based hydraulic fluids function satisfactorily at $-25°C$. Synthetic esters or poly alpha olefin (PAO)-based fluids are considered an option at lower temperatures (13,14). For VO-based lubricants, reports have indicated cloudiness, precipitation, poor flowability, poor pumpability, and even solidification at $-15°C$ (12).

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Low-temperature behavior of triacylglycerols relates first of all to their crystallization kinetics. Major crystalline forms have been established for saturated triacylglycerols (15). Hagemann (16) has listed over a hundred reports on melting temperatures of mainly monoacid triacylglycerols. However, crystalline forms of unsaturated triacylglycerols have been established only for triacylglycerols with symmetrical distribution of monounsaturated fatty acids (17). Thus investigations of crystallization of unsaturated mixed acid triacylglycerols are mostly empirical (18), and solidification of such triacylglycerols is too complex to be studied using traditional techniques, such as X-ray diffraction. Nonetheless, it has been firmly established (15,16) that presence of *cis* unsaturation, lower molecular weights, and diverse chemical structures of triacylglycerols favor lower temperatures of solidification.

Crystallization kinetics generally is very sensitive to temperature fluctuations and related factors such as cooling rate or thermal history. As can be expected from nucleation theory and crystallization thermodynamics, presence of contaminants, foreign bodies, or other nucleation centers and even shaking may affect crystallization. Since solidification thermodynamics of VO is exceedingly complex, only indirect semiquantitative data are available from techniques such as cooling the liquid and measuring its viscosity increase, precipitation, or loss of fluidity.

In the industry one major characteristic of the low-temperature properties of lubricating fluids is pour point (PP). ASTM technique D 97 determines it by placing a test tube containing 50 mL of the sample into a metal cylinder, which is submerged into cooling media, and measuring the temperature at the top of the sample until it stops pouring (19). The temperature of cooling media is kept constant below the sample temperature. When the sample temperature reaches the specified range (e.g., three of the ranges are +9 to -6, -6 to -24 and -24 to $-42°C$), the temperature of cooling media is also reduced to the specified value (-18, -33 and $-51°C$, respectively). Statistically, the test shows satisfactory accuracy; as described in a precision statement (19), the difference between two test results from independent laboratories exceeds $6°C$ in only one case of 20, and repeatability is $2.87°C$ at 95% confidence.

Pour point depressants (PPD) have been created to suppress formation of large crystals during solidification, al-

TABLE 1
Fatty Acid Contents of Test Fluids

| | | Fatty acid contents (%) | | | | |
| | | Saturated | Monounsaturated | Polyunsaturated | | |
Fluid	Processing	Palmitic (16:0), stearic (18:0)	Oleic 18:1-Δ9	Linoleic 18:2-Δ9,12	Linolenic 18:3-Δ9,12,15	Other
Canola oil	Alkali refined	3	60	30	7	< 1
Castor oil	Alkali refined	3	4	4	0	89 of 18:1-12OH
Meadowfoam oil	Refined	1	80 of 20:1-Δ5 and 22:1-Δ5	1	0	18 of 22:2-Δ5,13 and other
Soybean oil	Alkali refined, winterized	16	23	53	8	< 1
High-oleic sunflower oil	Alkali refined	4	89	5	1	< 1
Oleates	Synthetic	10	76	13	1	< 1

though the mechanism of PPD action on triacylglycerol crystallization remains undisclosed (20). Typically, commercial PPD are known to contain a polymethacrylate backbone with a certain type of branching, which allows inclusion of the PPD molecule into the growing crystal. However, VO containing PPD have still shown unsatisfactory performance when exposed to low temperatures for durations significantly longer than those specified in D 97 test (12).

For purposes of producing biodegradable lubricants with improved low-temperature performance various diluents are often added to VO (11). Lack of fundamental knowledge on crystallization of mixed acid triacylglycerols does not permit more accurate prediction of the PP and other low-temperature properties. Dilution with petroleum products may reduce the PP (21) to a limited extent. It is still unclear whether other diluents can demonstrate this effect as well. Synthetic diesters and polyol esters (usually isodecyl or isotridecyl adipates) (3,4), PAO (usually PAO 2 and PAO 4) (22,23), and oleates (24) have typically been employed as diluents in biodegradable lubricants. The rules to predict how PP of VO change with dilution need to be established experimentally.

EXPERIMENTAL PROCEDURES

Alkali-refined canola (NutraClear™ oil) and soybean oils (refined, bleached, deodorized, winterized) were commercial products of Bunge Edible Oil Corporation (Kankakee, IL). Refined meadowfoam and castor oils were provided by Fanning Corporation (Chicago, IL). High-oleic (89%) sunflower oil was supplied by International Flora Technologies, Ltd. (Gilbert, AZ). All oils were stored below −5°C under nitrogen atmosphere. Poly alkyl methacrylate copolymer-based PPD EF-133V (molecular weight approx. 8,000 amu), containing ~50% (w/w) of canola oil carrier, was supplied by Rohm and Haas (Philadelphia, PA). Oleate esters were provided by Unichema (Chicago, IL). Their fatty acid contents and degree of processing are listed in Table 1 (see Table 2 for identification of alcohol fragments). Diisodecyl adipate (DIDA) was provided by Hatco (Fords, NJ). PAO 2 (the notation 2 indicates approximate kinematic viscosity in mm²/s at 100°C and differentiates it from PAO 4, PAO 6, PAO 10,

etc.), which essentially represents a 90:10 mixture of hydrogenated dimers and trimers of 1-decene, was provided by Amoco (Lisle, IL).

HPLC analyses of fatty acid contents were performed on a Thermo Separation Products instrument with a P2000 binary pump and an AS2000 autosampler/injector (Fremont, CA), coupled to a UV2000 detector set at 295 nm. It utilized the 25 cm nonpolar C_8 column "Onift Tube 5." Gradient elution at 1 mL/min with acetonitrile/acetone was programmed 50:50 at 0 min with linear propagation to 100% acetone at 12 min and reverse to 50:50 at 17 min. Triacylglycerols were converted to their fatty acid methyl esters by treatment of the oils (~10 mg) with 0.5 mL of 0.5 M KOH/MeOH for 1 h in a sealed vial at 100°C. The vial was cooled to room temperature and 1 mL of 1.0 M H_2SO_4/MeOH was added. The vial was resealed and placed at 100°C for 10 min. After cooling to room temperature the contents were extracted into hexane (2 mL). The hexane was washed with saturated brine and then dried over Na_2SO_4. The resultant ester mixture was analyzed by HPLC and identified using standards supplied by Alltech Associates (Deerfield, IL).

PP apparatus and procedure accurately followed ASTM D 97. The automated low-temperature bath manufactured by

TABLE 2
Pour Points of Test Fluids

Fluid	Pour point (°C)
Canola oil	−18
Soybean oil	−9
High-oleic sunflower oil	−12
Meadowfoam oil	+3
Castor oil	−24
Diisodecyl adipate	−60
PAO 2[a]	−72

Fluid (oleates)	Pour point (°C)
2-Ethyl hexyl oleate	−36
Neopentyl glycol dioleate	−27
Trimethylol propane trioleate	−24
Pentaerythritol tetraoleate	−15
Isobutyl oleate	−27
Isopropyl oleate	−9

[a]Poly alpha olefin (PAO) with viscosity of 2 cSt at 100°C (hydrogenated dimers/trimers of α-decene).

Cannon Instruments (State College, PA) capable of maintaining temperatures down to −50 ± 0.1°C and cooling rate of −3°C/min in the ethylene glycol bath was employed. Test jars, thermometers, corks, and rubber rings fully met D 97 specifications. In addition, the corks were wrapped with a laboratory film to prevent possible entrainment of humid air into the jar. In this study all the runs were carried out at least in duplicate. The D 97 test calls for determining PP at segments of 3°C, and no attempt was made to differentiate them into smaller segments. All samples were stored at 50°C for at least 1 h prior to the test to minimize possible effects of thermal history. The cooling scheme specified in the test was followed to maximum capability of the cooling bath to ensure consistent cooling rates.

RESULTS AND DISCUSSION

In this investigation the vegetable oils and diluents were blended to observe changes in PP. The original components demonstrated PP as listed in Table 2. It must be noted that some of the fluids may actually still pour after quite significant durations at slightly lower temperatures than their determined PP. A good example is castor oil, which pours after more than 24 h when stored at −25°C, although its PP appeared as −24°C in triplicate runs. There may be several arguments to explain this observation. First, the D 97 calls for determining the PP at either −24 or −27°C, i.e., the actual loss of fluidity may occur at the temperature which is closer to −27 than −24°C, but it still qualifies as a PP of −24°C, rather than −27°C. Second, the D 97 requires lowering the bath temperature from −33 to −51°C when the sample thermometer reaches −24°C. This produces pronounced changes in the cooling rate and temperature profile within the sample, which may have implications on the solidification kinetics. Despite the complexities of interpreting the data, it can be observed that increasing molecular weight of fatty acids and full saturation contribute to the increase in PP, whereas *cis* unsaturation favors the decrease. Castor oil demonstrates PP notably lower than those of soybean, high-oleic sunflower, and canola oils, suggesting that interaction between the hydroxy groups (hydrogen bonding) of ricinoleic acid interferes with the crystal growth.
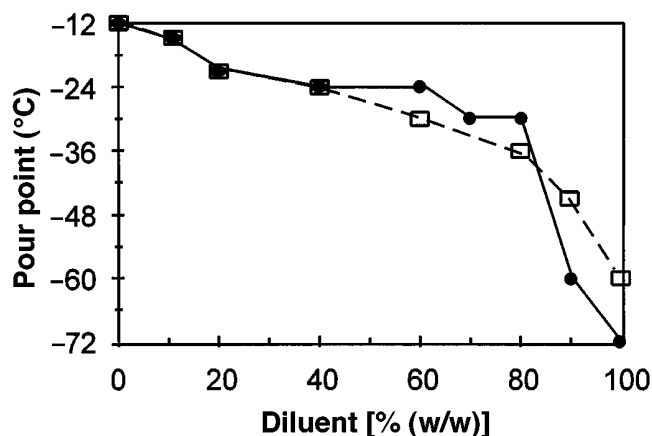

FIG. 1. Depression of pour points in high-oleic sunflower oil diluted with poly alpha olefin (–●–) and diisodecyl adipate (–□–).

Oleates, DIDA, and PAO 2 (20%) were blended with high-oleic sunflower and soybean oils to observe their effect on PP as listed in Table 3. Oleates depressed PP somewhat; however, DIDA and PAO 2 showed greater effects. As it appears from Figure 1, significantly larger fractions of the diluent do not deliver proportionate depressions of PP. Although the difference is not statistically significant for the dilution range from 0 to 80%, DIDA, being more branched than PAO 2 and not uniform structurally, appears to slow down solidification more efficiently. PAO 2 does not produce nearly as much of an effect as could be anticipated from its own PP of −72°C. Notably, during the determination of PP, solidification of the whole bulk liquid was observed rather than precipitation of solid particulates. No particulates were precipitating even at 80% dilutions. At such high dilutions the solidification mechanism may change resulting in drop of PP, as demonstrated by dilution with 90% of PAO 2.

PPD appears to exert a more pronounced effect as suggested by the PP of canola, high-oleic sunflower, and soybean oils with various amounts of PPD shown in Table 4. An amount of 0.4% by weight of PPD significantly reduces rates of solidification. PPD appears somewhat more efficient on canola oil. Increased amounts of PPD may still slow down solidification; however, the further depression ceases quite rapidly.

Compared to diluents, PPD provides a somewhat stronger effect on reducing the rates of solidification. Since the two mechanisms of PP depression may be different, the impact of combination of both diluent and PPD was investigated, as

TABLE 3
Effect of 20% Dilution (w/w) on Pour Points of High-Oleic Sunflower and Soybean Oils

	Pour point (°C)	
Diluent	In high-oleic sunflower oil	In soybean oil
2-Ethylhexyl oleate	−18	−12
Isobutyl oleate	−15	−12
Trimethylol propane trioleate	−18	−12
Pentaerythritol tetraoleate	−15	−12
Diisodecyl adipate	−21	−18
PAO 2[a]	−21	−21

[a]See Table 2 for abbreviation.

TABLE 4
Effect of Pour Point Depressant (PPD[a]) on Pour Points (°C) of Vegetable Oils

	Amount of PPD[a] [% (w/w)]			
Vegetable oil	0	0.4	1	2
Soybean oil	−9	−18	−18	−18
High-oleic sunflower oil	−12	−21	−24	−24
Canola oil	−18	−30	−33	−33

[a]Poly(alkyl methacrylate) copolymer of ~8,000 amu, canola oil carrier 1:1.

TABLE 5
Effect of PAO 2[a] and PPD on Pour Points of High Oleic Sunflower Oil

Blend ratios (wt/wt)		PPD	Pour point
High-oleic sunflower oil	PAO 2	[% (w/w)]	(°C)
0	100	0	−72
100	0	0	−12
90	10	0	−15
80	20	0	−21
60	40	0	−24
90	10	0.66	−24
80	20	0.66	−24
60	40	0.66	−27
100	0	1	−24
90	10	1	−24
80	20	1	−27
60	40	1	−27

[a]See Tables 1 and 2 for abbreviations.

shown in Table 5. However, no synergism between the two mechanisms of depressing PP can be observed. It appears that even 40% of PAO 2 does not depress PP of high-oleic sunflower oil more significantly than does 1% of PPD, and the blends still demonstrate PP closer to those of high-oleic sunflower oil than those of the diluents. Thus the diluents and PPD provide only limited improvement in the low-temperature performance.

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