Drying Properties of Metathesized Soybean Oil

Sevim Z. Erhan*, Marvin O. Bagby, and T.C. Nelsen[1]
Oil Chemical Research, USDA, ARS, NCAUR, Peoria, Illinois 61604

ABSTRACT: Soybean oil was metathesized with the standard homogenous metathesis catalyst, which consisted of tungsten hexachloride (WCl_6) and tetramethyl tin (Me_4Sn) in chlorobenzene as solvent. The reactions were terminated at different time intervals. Soybean oil was mixed with metathesized soybean oil in the presence of cobalt-drier to evaluate drying properties. Five weight percentage (% w) of metathesized oil was found to be all that was needed to decrease the drying time of soybean oil from 312 to 182 min. Drying times for heat-polymerized soybean oil with Gardner-Holdt viscosity of Z_1–Z_2 and Z_3–Z_4 were 71 and 75 min, respectively. In both cases, 5% weight metathesized soybean oil in the blend gave the best results for reducing drying time to 67 and 69 min, respectively.

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KEY WORDS: Coating, drier, drying, heat polymerized oil, ink, linseed oil, metathesis, paint, soybean oil, viscosity.

Catalytic metathesis of alkenes was first described by Banks and Bailey (1). Homogenous metathesis of alkenes and of alkenes carrying functional groups, represented by

$$2R_1CH{=}CHR_2 \rightleftharpoons R_1CH{=}CHR_1 + R_2C{=}CHR_2 \qquad [1]$$

has been fostered by the discovery of several catalyst systems. The metathesis of fatty esters by means of the $WCl_6(CH_3)_4Sn$ catalytic system was first described in 1972 (2). Since then, numerous publications have appeared that deal with the metathesis of esters, such as methyl oleate (3), methyl linoleate (4), and methyl linolenate (5), as well as the metathesis of fatty oils (6).

Printing inks consist of fluid ingredients (vehicles), solids (pigments), and additives. Fluid ingredients for sheet-fed and heat-set inks are composed of resin, drying oil (or drying alkyd), and solvent. Generally, vegetable oils (mainly linseed oil) are used as drying oils.

Metathesis of unsaturated oils (olive, soybean, linseed, etc.) leads to the formation of high-molecular dicarboxylic acid glyceryl esters with improved drying properties (7,8). In this study, our objective was to improve the drying time of soybean oil with a minimal increase in viscosity and to eliminate or reduce volatile solvent content in inks, paints, and coatings.

MATERIALS AND METHODS

Metathesis reaction. Alkali-refined soybean and linseed oils were obtained from Archer Daniels Midland Co. (Decatur, IL). Cobalt drier was obtained from Huls America Inc. (Piscataway, NJ). WCl_6 (99.9+% pure) and $(CH_3)_4Sn$ were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. The experiments were carried out in a conventional three-necked flask (250 or 500 mL), fitted with a thermometer, rubber septum and a condenser, on top of which a T-piece was placed to allow for continuous flow of nitrogen. Appropriate mixing of reactants was assured with a magnetic stirrer placed in the flask. The reactions were carried out under dry nitrogen atmosphere by using air-tight syringes. The ratio of the reactant to cocatalyst was 12:1 by weight, and in all experiments, the mol ratio of $(CH_3)_4Sn$ to WCl_6 was 2:1. The great sensitivity of WCl_6 toward moisture makes working under dry nitrogen necessary to obtain good reproducibility of the reaction. Materials were transferred into the reaction flask under nitrogen atmosphere in a glove box. Chlorobenzene was used as a solvent. This solvent favorably influences selectivity of the homogenous metathesis reaction (3). The reactions were allowed to proceed for 2, 4, 6, and 8 h, and were then terminated by exposure to air. The reaction product was filtered under vacuum through a sintered funnel to separate the catalyst (100%) from the oil.

Performance characteristics. The drying test was done by ASTM-1640 (9). The film was considered dry when it no longer adhered to the finger and did not rub up when the finger was lightly rubbed across the surface. Experiments were done in duplicate, and average values are reported.

Viscosities of all samples were determined with a Gardner-Holdt Bubble Viscometer by following ASTM D-1545-63 (9).

Gel permeation chromatography analysis. Polystyrene standards from Polymer Laboratories Ltd. (Amherst, MA) had the following specifications [peak average molecular weight (Mp) and molecular weight distribution (MWD), respectively]: 580, 1.14; 1320, 1.09; 3250, 1.04; 9200, 1.03; 28500, 1.03; 66000, 1.03; 156000, 1.03; 435500, 1.04; 1030000, 1.05; 2250000, 1.04; and 2880000, 1.04.

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*To whom correspondence should be addressed at USDA, ARS, NCAUR, 1815 N. University St., Peoria, IL 61604.
E-mail: erhansz@mail.ncaur.usda.gov.

[1] Statistician.

The samples were dissolved in tetrahydrofuran (THF) (0.4% wt/vol), filtered through 0.5-μm Teflon filters and then injected into the high-performance liquid chromatography (Model 8100; Spectra Physics, Fremont, CA). Chromatograph operating conditions were: solvent flow rate, 1 mL/min; oven temperature, 40°C; column, 30 cm, 7.5 mm, PL-Gel 5 μm mix; detector, differential refractive index (Model 6040; Spectra Physics); and injection volume, 50 μL. Each sample was chromatographed twice, and their average values are reported (10).

RESULTS AND DISCUSSION

Linseed oil, classified as a drying oil, takes much less time (216 min) to dry than does soybean oil (312 min) in the presence of 2% cobalt dryer (typical ink and paint formulations would contain about 2% Co-Drier). The improved drying times (min) of metathesized soybean oil after 2, 4, 6, and 8 h were 210, 218, 222, 213, respectively. Drying time did not improve with increased reaction time and was done by ASTM-1640 (9) cobalt drier was added (2% by weight). However, the drying time of soybean oil was significantly reduced from 312 min to 210 min after 2 h of metathesis. The effect of reaction time differences on drying time was best described by a parabola (Fig. 1) with a maximum of drying time at a reaction time of 5 h. The equation:

$$\text{drying time (min)} = 190.1 + 11.66 \times \text{reaction time (h)} - 1.09375 \times (\text{reaction time})^2,\ R^2 = 0.78 \qquad [2]$$

was fit to the data, and all coefficients were significantly ($P < 0.01$) different from zero.

Admixtures of soybean oil and metathesized soybean oil interacted synergistically to further shorten their drying times (min), respectively: 5%, 182 min; 10%, 186 min; 15%, 190; 20%, 190 min; 40%, 196 min; 60%, 206 min; 80%, 216 min. Drying test done by ASTM-1640 (9); 2% by weight cobalt drier was added; 2-h metathesized soybean oil was used. The addition of metathesized soybean oil to unmodified soybean oil resulted in an increase of 0.42 min in drying time for each percentage point increase of metathesized soybean oil (Fig. 2). The equation:

$$\text{drying time (min)} = 181.23 + 0.42 \times (\text{\% metathesized soybean oil});\ R^2 = 0.94 \qquad [3]$$

was fit to the data and both intercept and slope were significantly ($P < 0.01$) different from zero. Metathesized oil (5 wt%) was found to be all that was needed to decrease the drying time of soybean oil from 312 to 182 min. Additional metathesized oil did not improve drying time. This indicates that the small amount of metathesized oil acts like a coupler or bridge between the oil molecules. Increased amounts apparently result in polymerization among metathesized oils without reacting with unmodified oil.

For most ink formulations for which the drying time is critical, high-viscosity heat-polymerized oil is used (11). Improving drying properties of highly polymerized soybean oil for some applications is important. Drying times for heat-polymerized soybean oil with Gardner-Holdt viscosities of Z_1-Z_2 and Z_3-Z_4 were 71 and 75 min, respectively. The drying times (min) (drying test done by ASTM-1640 (9); 2% by weight; cobalt drier was added; 2-h metathesized soybean oil was used) for blends of metathesized soybean oil (%) and heat-polymerized soybean oil with Gardner-Holdt bubble viscosities of Z_1–Z_2 and Z_3–Z_4 were 5%, 67 min; 10%, 70 min; 15%, 77 min; 20%, 80 min; 40%, 94 min; 60%, 143 min; 80%, 146 min and 5%, 69 min; 10%, 75 min; 15%, 75 min; 20%, 76 min; 40%, 109 min; 60%, 116 min; 80%, 153 min, respectively. In both, 5% (w) metathesized soybean oil in the blend gave the best results for reducing drying time.

Addition of each percentage point of metathesized soybean oil to heat-polymerized soybean oil with Z_1-Z_2 viscosity (Fig. 3) resulted in an increase of 1.17 min in drying time. The equation:

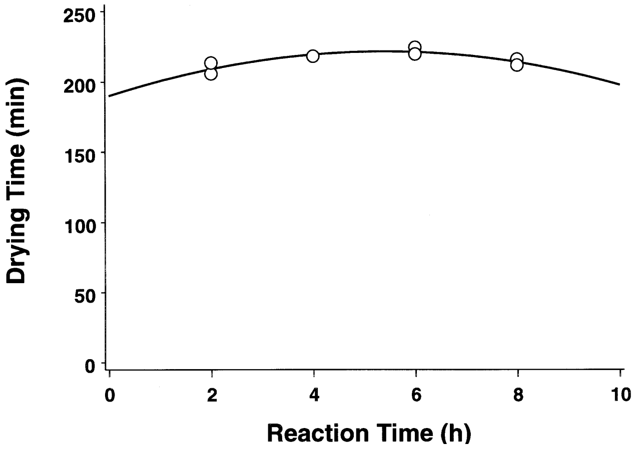

FIG. 1. The effect of metathesis reaction time on drying time of soybean oil.

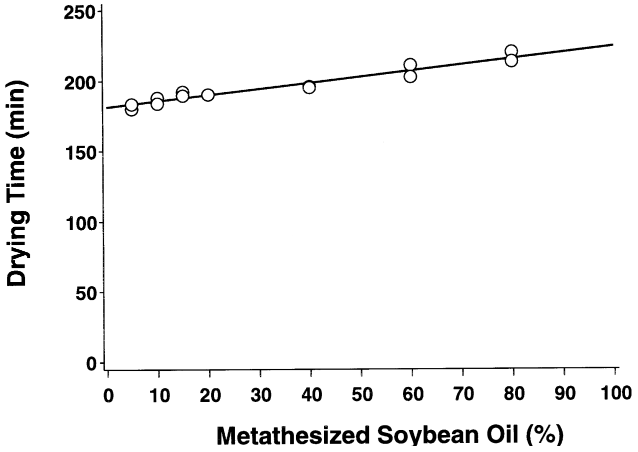

FIG. 2. The effect of percentage metathesized soybean oil on drying time.

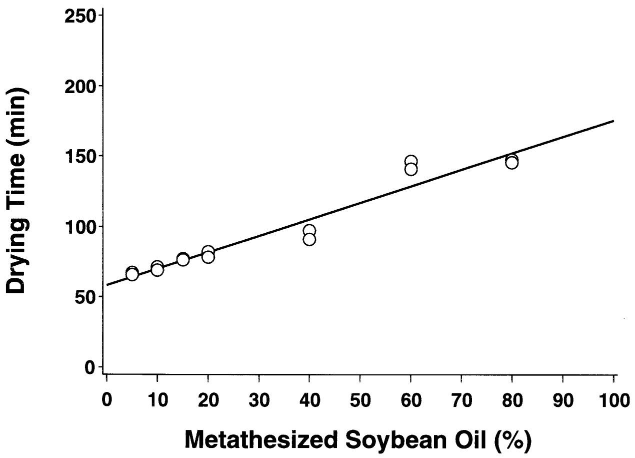

FIG. 3. The effect of metathesized soybean oil percentage on drying time of heat-polymerized soybean oil with Z_1–Z_2 viscosity.

$$\text{drying time (min)} = 58.26 + 1.17 \times (\text{\% metathesized soybean oil}); R^2 = 0.94 \quad [4]$$

was fit to the data, and both intercept and slope were significantly ($P < 0.01$) different from zero. When the metathesized soybean oil was blended with heat-polymerized soybean oil with Z_2-Z_3 viscosity (Fig. 4), the increase in drying time was 1.08 min for each percentage point increase of metathesized soybean oil. The equation:

$$\text{drying time (min)} = 60.39 + 1.08 \times (\text{metathesized soybean oil}); R^2 = 0.96 \quad [5]$$

was fitted to the data, and both intercept and slope were significantly ($P < 0.01$) different from zero. The intercept and slope of the equation for the Z_1-Z_2 viscosity oil were compared by *t*-tests (12) to the intercept and slope of the equation for the Z_2-Z_3 viscosity oil, and no ($P > 0.10$) differences were found.

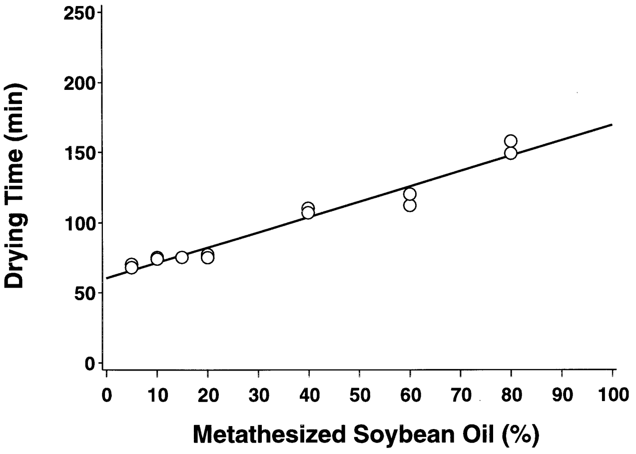

FIG. 4. The effect of metathesized soybean oil percentage on drying time of heat-polymerized soybean oil with Z_2–Z_3 viscosity.

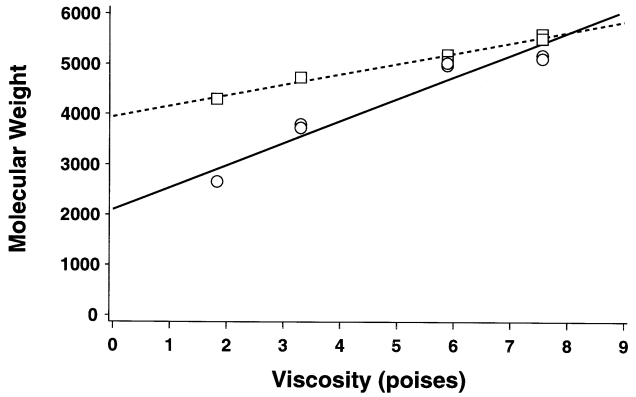

FIG. 5. Molecular weight vs. corresponding viscosities: —— heat-polymerized soybean oil; ---- metathesized soybean oil.

Initially, the molecular weight (MW) of metathesized soybean oil was higher than for heat-polymerized soybean oil (Fig. 5, intercepts were significantly different, $P < 0.01$) and increased at a lower rate with increased viscosity (slopes were significantly different, $P < 0.01$). The equations for the lines on Figure 5 are metathesized soybean oil:

$$\text{MW} = 3944 + 209 \times \text{viscosity}, R^2 = 0.98 \quad [6]$$

and heat polymerized soybean oil,

$$\text{MW} = 2104 + 437 \times \text{viscosity}, R^2 = 0.93 \quad [7]$$

Viscosity increase in metathesized soybean oil was slow. Comparison of weight-average molecular weights of heat-polymerized soybean oil and metathesized soybean oil at the same viscosity showed that the latter has higher apparent molecular weight than the former at all viscosities tested (Table 1). The metathesis reaction could occur between fatty acid groups of the same molecule (intramolecular reaction), which does not result in a larger molecule (3). However, with the intermolecular reaction, molecule enlargement does take place, and stereochemical considerations indicate that the intermolecular reaction dominates over the intramolecular.

In thermal polymerization, the MW and viscosity increases are due to the triglycerides undergoing Diels-Alder or other crosslinking reactions (13). At the temperature of heat-body-

TABLE 1
Comparison of Molecular Weights (MW) at Corresponding Viscosities

	Apparent weight-average MW[a]	
Viscosity[b]	Metathesized soybean oil[c]	Heat polymerized soybean oil[d]
G–H	4287	2656
M–N	4713	3757
T–U	5107	4991
U–V	5552	5133

[a] Obtained by gel-permeation chromatography (Ref. 3).
[b] Gardner-Holdt Bubble viscosity, ASTM D-1545-63 (Ref. 9).
[c] Two-hour metathesized soybean oil was used.
[d] Reference 4.

ing, double bonds migrate and conjugate (14). The conjugated dienes then can form 6-membered rings by reaction with the double bonds of other fatty acids. If these fatty acids come from different triglycerides, viscosity and MW increase. An essential difference between heat-polymerization and molecular enlargement by metathesis is the preservation of double bonds. While thermal polymerization considerably lowers the iodine value, unsaturation is not lost during metathesis.

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