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The thermo-viscous properties of the linseed oil modified with pentaerythritol

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ABSTRACT

In this study, the thermo-viscous properties of the linseed oil modified with pentaerythritol were measured with a rheometer and modeled by several equations. Results showed that the linseed oils generally appeared as either Newtonian fluid in the non-zero shear region, or shear thinning near the zero shear. The Cross and Ellis models can fit this property, whose zero shear viscosity and infinite shear viscosity showed a positive correlation with the pentaerythritol dosage. It was believed that the shear thinning of the linseed oils was attributed to the chain entanglement. Based on the authors' formula for the temperature dependence of the viscosity, novel two-dimensional thermal-viscous models for the linseed oil were constructed as functions of temperature and shear rate/stress. These models quantitatively characterize the thermo-viscous property of the linseed oil, and form an advanced base for further rheological study and industrial application in the production and process control about the linseed oil.

1. Introduction

Linseed oil, also known as flax seed oil, is a clear to yellowish oil obtained from the dried ripe seeds of the flax plant (*Linum usitatissimum*, Linaceae). As a renewable resource from agriculture, the application knowledge of the linseed oil as industrial products has received much attention. In 1965, the triglyceride composition of linseed oil was determined by a combination of several chromatographic techniques (Vereshchagin and Novitskaya, 1965). After that, the oxidation of the linseed oil was reported by several groups (Hess and O'Hare, 1950; Nunn and Smedley-Maclean, 1938; Juita Dlugogorski et al., 2011; Güler et al., 2004). And then, the drying property was investigated with various methods and influencing factors (Tuman et al., 1996; Lazzari and Chiantore, 1999; Mallégol et al., 2000; Stenberg et al., 2005). Some more complexed systems from the linseed oil were also applied to penetration of concrete (Blankenhorn et al., 1979), and characterized with spectroscopy (Sharma et al., 2008). Recent interest of materials science, focusing on producing environmentally friendly products that substitute the oleo-chemical derived ones, points out a new route to the area of technical significance for the linseed oil. An important set of such product is the polyhydroxy alcohol fatty acid ester, obtained by modifying the linseed oil with pentaerythritol as complex ester of glycerol and pentaerythritol. This complex ester possesses many benefits in practical use, such as readily biodegradable, nonhazardous in water, good oxidation and thermal stability, low odor intensity, excellent lubricity with viscosity–temperature characteristics. They can be used as environmentally friendly water-proofing material for wood and concrete, low odor putty, sealants, wood finishes, oil cloths, rust inhibitor, plasticizer for biodegradable system, and so on. However, many important physicochemical properties about this complex ester have not been investigated up to now.

Viscosity is an essential parameter in the theoretical investigation and industrial use for liquid. The viscosity of linseed oil plays an especially important role on the stage of science and engineering of the oil. So many previous researchers have carried out studies concerning the viscosity of linseed oil, such as the rheological characterizations of some vegetable oils (Blayo et al., 2001), the empirical equations for oxypolymerization of linseed oil (Güler et al., 2004), viscoelastic properties of linseed oil-based medium chain length poly(hydroxyalkanoate) films (Ashby et al., 2000), viscosity of linseed oil as a function of mineral spirits and temperature (Gallagher et al., 1977), viscosity of linseed oil at high shearing stresses (Tollenaar and Bolthof, 1946), and so on. To the authors' knowledge, the influence of pentaerythritol on the thermo-viscous properties of linseed oil has not been investigated yet.

In this work, we studied the thermo-viscous properties of the linseed oil modified with pentaerythritol through viscosity measurement and modeling method. Quantitative formulae of the viscosity of the linseed oil as two-dimensional function of temperature and shear were constructed to form a base not only for the rheological theory about this oil, but also for its industrial application.

2. Experimental

2.1. Materials

The linseed oil used in experiment was a clear to yellowish commercial oil that had relative density (at 20 °C) 0.932 ± 0.005, melting

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Table 1
The ingredient of the linseed oil modified with pentaerythritol.

Ingredients	#1	#2	#3	#4	#5
Linseed oil (g)	50	50	50	50	50
Pentaerythritol (g)	0	2	4	6	8
Tributyl phosphate (g)	0.075	0.075	0.075	0.075	0.075

point −27 to −18 °C, boiling point 343 °C, impurity ≤0.10%, acid value ≤1.0 mg KOH/g, iodine value ≥175, and total acid ~96%. The pentaerythritol and tributyl phosphate were commercial products of chemical grade.

The modified linseed oils were made from the commercial linseed oil and pentaerythritol with tributyl phosphate as catalyst according to Table 1. The commercial linseed oil was initially heated to 150 °C. Then the pentaerythritol and tributyl phosphate were added in under stirring. After that, the temperature was gradually raised to 245 °C and kept at this temperature for 2 h. Finally, the temperature was cooled down obtaining the modified linseed oil.

The Fourier transformed infrared (FTIR) spectra of the linseed oils modified with pentaerythritol are recorded as Fig. 1 by a Nicolet AVATAR 330. The *x*-coordinate is the wave number from 4000 to 400 cm^{-1}, and the *y*-coordinate denotes the transmittance in percent. It can be seen the characteristic peaks of bending vibrations of —$(CH_2)_n$ ($n \geq 4$) at 720 cm^{-1} and —OH at 3460 cm^{-1}, stretching vibration of C═O at 1170 and 1730 cm^{-1}, deformation vibration of C—H at 1460 and 2920 cm^{-1}, respectively. The location of each peak for all the five samples was same, while the intensity changed with the dosage of pentaerythritol. For example, the characteristic peak of hydroxyl at 3460 cm^{-1} increased with increasing dose of pentaerythritol, reflecting more and more hydroxyl groups were introduced into the modified system by ester exchange reaction. The corresponding values of transmittance at 3460 cm^{-1} for sample #1–5 were 95.6, 95.5, 88.0, 81.6, 80.0%, respectively.

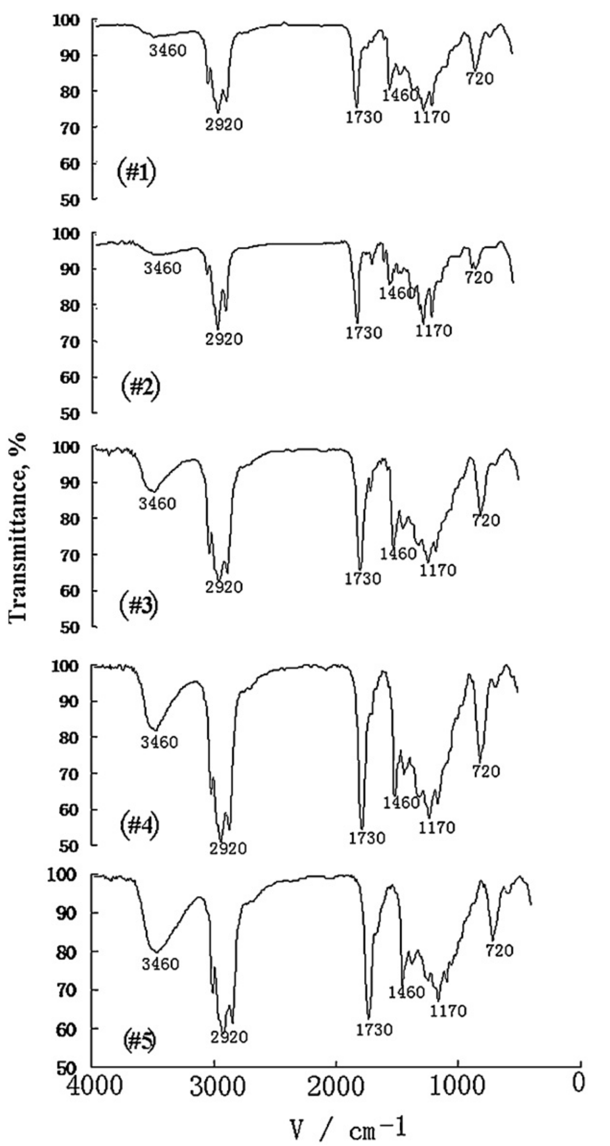

Fig. 1. The FTIR spectra of linseed oils modified at pentaerythritol additions of 0 g (#1), 2 g (#2), 4 g (#3), 6 g (#4), 8 g (#5).

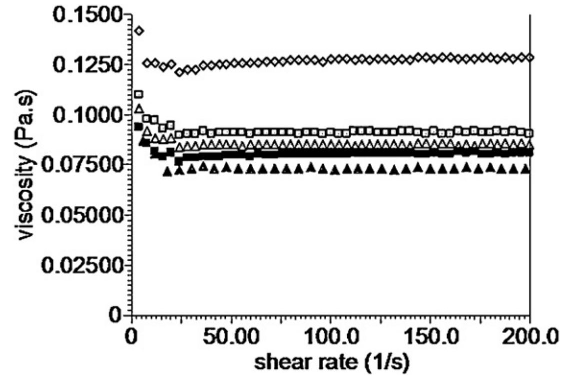

Fig. 2. The viscosity changes with shear rate from 0 to 200 s^{-1} at pentaerythritol additions of 0 g (▲), 2 g (■), 4 g (△), 6 g (□), 8 g (◊) at 25 °C.

2.2. Methods

For the above samples, steady shear measurements were carried out with a rheometer AR500 (TA instruments). A standard steel parallel plate with 1000 μm gap and 40 mm diameter was chosen. Viscosities were measured with variations of shear rate, shear stress and temperature. The recorded data was processed by the software of TA instruments, named as the Rheology Advantage Data Analysis (v3.0.24). The curve fitting method was used with various models during the data processing. The fitting results were evaluated by a standard error defined in Eq. (1).

$$\text{Error} \quad (\%) = 100 \times \frac{\sqrt{\sum (x_m - x_c)^2 / n}}{\text{range}} \tag{1}$$

where x_m is the measured value and x_c is the calculated value of x for each data point, n is the number of data points, and the range is the maximum value of x_m minus the minimum value. Generally, a reasonable fit gives a standard error ≤3%.

3. Results and discussion

3.1. Shear rate dependence

For the samples #1–5 of 0, 2, 4, 6, 8 g pentaerythritol additions, viscosities versus shear rate are measured as Fig. 2 in the shear rate region from 0 to 200 s^{-1}. For each curve, it could be divided into two parts, the main Newtonian plateau and the small shear thinning near zero shear rate. This profile means that the linseed oils modified with various pentaerythritol dosages generally appeared as Newtonian fluid in the non-near zero shear region. However, they exhibited shear thinning near the zero shear rate, where the viscosity dropped quickly with shear rate. Although zero shear viscosity was about 20% higher than the Newtonian viscosity, they existed for so short a time that a little shear pulled the viscosities down to the Newtonian value. The oil with more pentaerythritol