

Gel Permeation Chromatography of Vegetable-Oil-Based Printing Ink Vehicles

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SYNOPSIS

The apparent weight-average molecular weights (\overline{M}_w) of ink vehicles made from soybean, safflower, sunflower, cottonseed, and canola oils were compared by gel permeation chromatography (GPC), and the correlation between viscosity and \overline{M}_w of these vehicles was established. Apparent \overline{M}_w of vegetable oil gels that were used in vehicle preparation were also obtained by GPC. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

The petroleum oil shortage in the 1970s stimulated research to find alternatives to mineral oil and other petroleum products in ink formulations.

Inks containing vegetable oils have been formulated for various applications.¹⁻⁴ The industry, represented by the American Newspaper Publishers' Association as well as individual companies, has continued to seek non-petroleum-based printing ink vehicles that would: (a) be cost competitive with petroleum-based inks, especially black; (b) require no petroleum-derived component; (c) resist ruboff on hands and clothing; and (d) enable formulation over a wide range of viscosities required by various printing applications. We have succeeded in making vegetable-oil-based printing ink vehicles that meet and exceed these industry standards.⁵

To further characterize the gels and ink vehicles prepared from vegetable oils, the viscosities and apparent \overline{M}_w of these vehicles were determined. These vehicles were prepared from vegetable oils by two methods. In the first method, vegetable oils were heat-bodied at a constant temperature in nitrogen atmosphere to a desired viscosity. In the second

method, the heat bodying reaction was permitted to proceed to a gel point, and then the gel was mixed with vegetable oils to obtain a desired viscosity. The apparent \overline{M}_w of both the heat-bodied vehicles and the gels were determined by gel permeation chromatography (GPC).

EXPERIMENTAL

Polymer Standards

Polystyrene standards from Polymer Laboratories LTD had the following specifications [peak average molecular weight (\overline{M}_p) and molecular weight distribution (MWD)]: 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; 2880000, 1.04.

GPC Analysis

The samples were dissolved in tetrahydrofuran (THF) (0.4% w/v), filtered through 0.5- μm Teflon filters, and then injected into the HPLC (Model 8100, Spectra Physics). Chromatography operating conditions were: flow, 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 were reported.

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Vehicles

Alkali-refined soybean oil was obtained from Rice-land Foods, Stutgard, AR, and Archer Daniels Midland, Decatur, IL. Alkali-refined canola oil and cottonseed oil were purchased from Bunge Oil, Bradley, IL. Alkali-refined safflower oil was obtained from Pacific Anchor Chemical Co., Cumberland, RI. Alkali-refined sunflower oil was obtained from Archer Daniels Midland, Decatur, IL.

Alkali-refined vegetable oil (300–1600 mL) was placed in a 0.5–2 liter four-necked reaction flask equipped with a mechanical stirrer. The oils were heated with stirring at $330 \pm 3^\circ\text{C}$ under nitrogen atmosphere to obtain the desired viscosity. In selected preparations heating was continued until the oil gelled. These reactions were discontinued at the transition point when clumps of gel began to climb the shaft of the mechanical stirrer.

Viscosity Measurements

The viscosity of all samples were measured by the Gardner Bubble Viscometer by ASTM D1545-63.

The iodine values (IV) were obtained by AOCS Cd.I.25 Wijs method and peroxide values were obtained by AOCS Cd.8.53 tentative method.

RESULTS AND DISCUSSION

For all oils studied, their viscosity (polymerization) increased with time at the heat bodying temperature of $330 \pm 3^\circ\text{C}$. The reaction time necessary to reach a desired viscosity depends on the mass and the structure of the reactants and the rate of heat transfer and agitation. As expected, oils with greater unsaturation polymerized more rapidly. Gelling times

Table I Molecular Weights of Soybean Oil Vehicles

Vehicle Viscosity	Apparent \overline{M}_w
G-H	2656
M-N	3757
T-U	4991
U-V	5133
V	6030
W	6193
W-X	7208
X-Y	8851

Table II Vehicle Molecular Weight and Viscosity

Oil Used in Vehicle	Vehicle Viscosity ^a	Apparent \overline{M}_w
Canola oil	W	5928
	W-X	6656
	X-Y	8196
Cottonseed oil	W	5364
	W-X	7046
	X-Y	7644
Safflower oil	W	7191
	W-X	7215
	X-Y	7445
Sunflower oil	W	6165
	W-X	7345
	X-Y	8827

^a Different viscosities were obtained by different heat bodying times.

for safflower (IV = 143.1), soybean (IV = 127.7), sunflower (IV = 133.4), cottonseed (IV = 112.9), and canola (IV = 110.2) oil were 110, 255, 265, 390, and 540 min, respectively. Although iodine values of cottonseed and canola oil were similar, canola oil with its greater oleic and low linoleic acid contents required a longer reaction time.

During heat bodying, conjugated dienes form by bond migration in polyunsaturated fatty acids. These can form 6-membered rings by intermolecular reaction with double bonds of other fatty acids. If these reactants come from different triglycerides, the molecular weight increases for the system. As heating continues, other conjugated groups can add to the previously formed unsaturated ring structure. Triglycerides, consisting of three polyunsaturated fatty acids at which addition may occur, introduce the possibility of forming very complex, highly branched structures and very large molecules.

The molecular weight values given in Tables I–III are shown as apparent \overline{M}_w for several reasons.

Polystyrene (PS) was used as a standard for the molecular weights without correcting for the differ-

Table III Gel Molecular Weights

Gel	Apparent \overline{M}_w
Soybean	60,423
Canola	44,924
Cottonseed	38,266
Safflower	31,772
Sunflower	15,055

ence in molecular structure between PS and the bodied oils. PS is a linear polymer, while bodied oils have varying degrees of branching. Thus, molecules of bodied oils of identical molecular weights may have different radii of gyration and therefore appear at different elution volumes on GPC. As a consequence, only apparent molecular weights are attainable. The apparent \overline{M}_w 's of relatively bulky soybean, sunflower, safflower, cottonseed, and canola oils were obtained as 1428, 1148, 1357, 1151, and 1301 respectively by this technique; however, the calculated molecular weights of these oils are ~ 880 .

Also, the GPC curves did not return to baseline at the low-molecular-weight end of the chromatograms due to minor amounts of very low molecular weight materials. These are omitted from the calculations, and therefore a degree of inaccuracy results. Weight-average values are less influenced by the area lost than number averages; therefore, apparent \overline{M}_w 's are used in tables.

Table I shows comparison values for Gardner-Holdt scale viscosities⁶ and apparent \overline{M}_w of soybean oil vehicles. Table II summarizes vehicle Gardner-Holdt scale viscosities and corresponding apparent \overline{M}_w for safflower-, sunflower-, cottonseed-, and canola-oil-based vehicles. Viscosity increases are directly proportional to increases in apparent \overline{M}_w and the degrees of polymerization. Differences of ap-

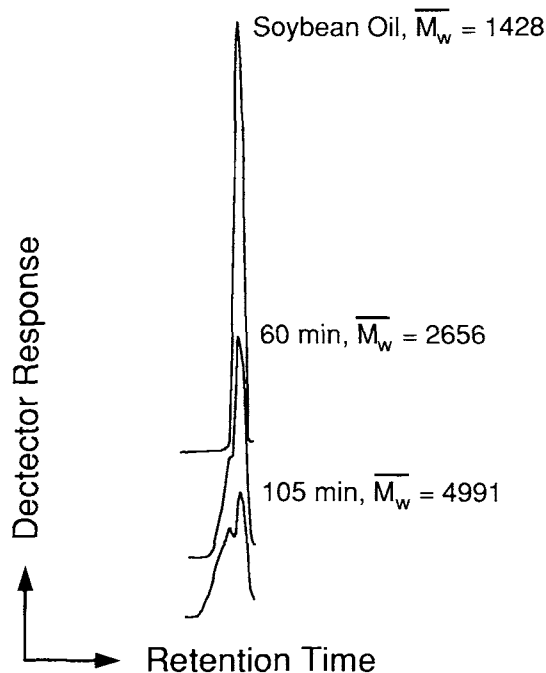


Figure 1 Gel permeation chromatograms of alkali-refined, 60 min, and 105-min heat-bodied soybean oil.

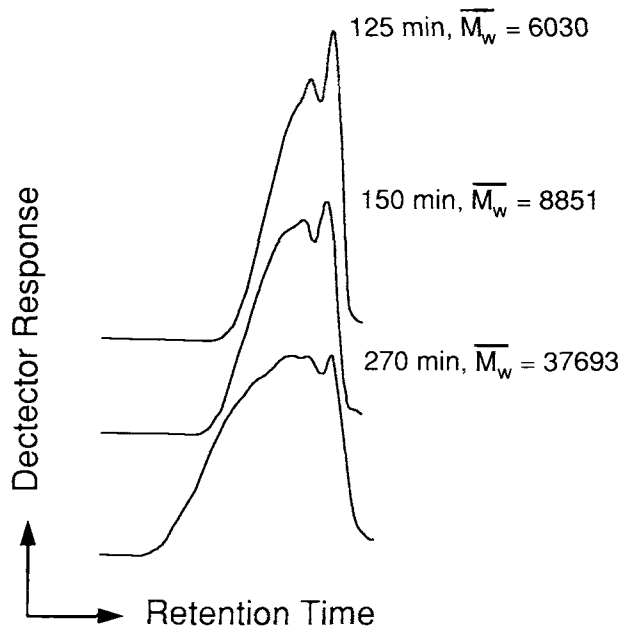


Figure 2 Gel permeation chromatograms of 125 min-, 150 min-, and 270-min heat-bodied soybean oil.

parent \overline{M}_w at the same viscosity of different oils may be due to differences in linearity of the bodied oils. As heat bodying time was increased, the ratio of polymerized oil to unpolymerized oil increased. These observations are readily shown by the plots in Figures 1-3. Apparent \overline{M}_w values of the vegetable-oil-derived gels are given in Table III. The differences among oils in apparent \overline{M}_w at the gel point suggest a decrease in the size of the gel particles as one goes from soybean oil to sunflower oil. Perhaps the gelled sunflower oil is a more linear polymer than

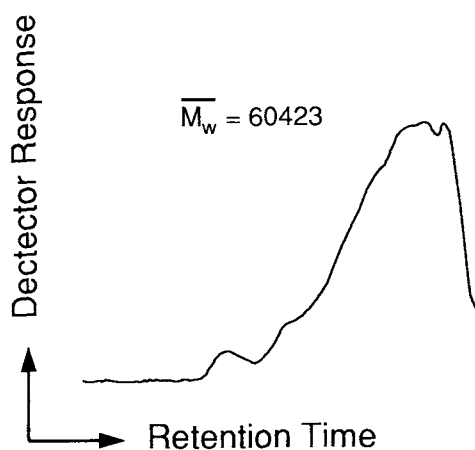


Figure 3 Gel permeation chromatograms of soybean oil gel.

other gels. Further work is required to gain insight into these observed differences.

CONCLUSIONS

There is a positive relationship between the apparent \overline{M}_w and the viscosities of heat-bodied oils, and a correlation between the shapes of the GPC peaks and the apparent \overline{M}_w of heat-bodied oils. These correlations will provide useful tools to monitor the scaleup of the process to prepare printing ink vehicles from different vegetable oils. If the vehicles are going to be prepared from the gel obtained by heat processing, then the gel point can be determined by the above methods.

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