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# Precision rheological study of the effectiveness of polymer cold flow improvers for corn oil based biodiesel

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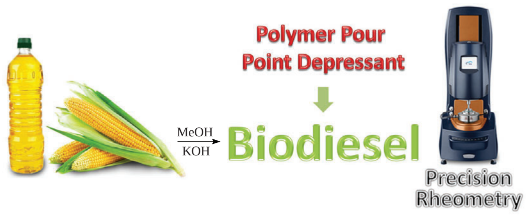
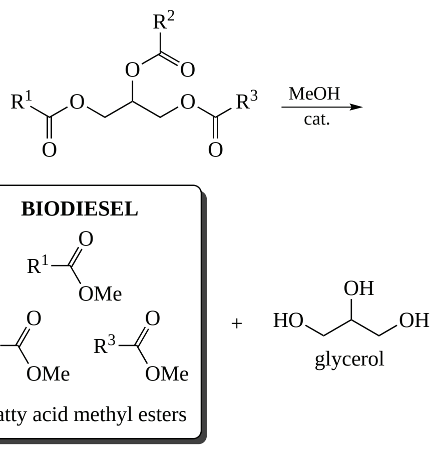
**Combination of the precision rheology and DSC helps to make an objective assessment of the effectiveness of modified copolymers of maleic anhydride with methylidenealkanes and best known commercial pour point depressants as cold flow improvers for corn oil based biodiesel.**




*Keywords*: coordination catalysis, functionalization, glycolides, lactides, organocatalysis, polyesters, ring-opening polymerization.

The search for strategies for producing fuels, lubricants and chemicals from renewable sources is one of the strategic objectives of the modern applied chemical science.[1–3] Biodiesel is an alternative diesel fuel typically obtained by methanolysis of vegetable oils, animal fats and other feedstocks with a formation of fatty acid methyl esters (Scheme 1).[1,4–8] To date, more than 95% of biodiesel is produced from edible vegetable oils, mainly rapeseed and canola oils.[9] In recent years, there is a trend of increasing the use of the corn oil as a biodiesel feedstock.[10,11] However, the use of biodiesel is affected by its poor cold flow properties (CFP) in comparison with petroleum diesel.[12] This problem is particularly relevant to the countries with cold climate. Poor CFP of biodiesel are attributable mainly to substantive content of saturated acid esters that have relatively high melting poins.[12–14]

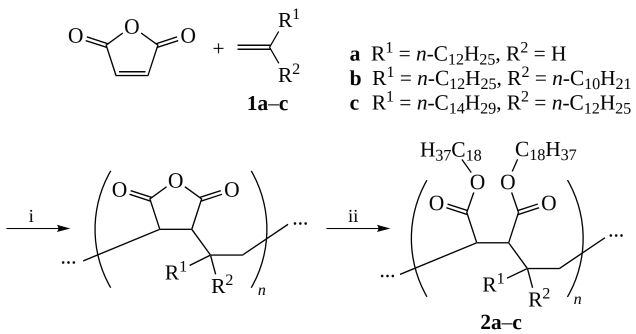



$R^1$, $R^2$, $R^3$ = alkyl, alkenyl and/or alkadienyl $C_{12}$–$C_{20}$

**Scheme 1**

Cold flow properties of petroleum diesel and other petroleum-based products might be successfully improved by the use of polymeric pour point depressants (PPDs).[15–17] The use of the polymeric PPDs to upgrade CFP of biodiesel was multiply reported[18–26] and reviewed.[27–33] However, the published data are fragmentary and often contradictory. In particular, functionalized *alt*-copolymers of maleic anhydride with α-olefins (Scheme 2), that were successfully applied for the improvement of the CFP of petroleum diesel,[35–37] have been missed with regard to biodiesel.

In the present paper, we report on the results of comparative study of the effect of conventional PPDs and functionalized *alt*-copolymers of maleic anhydride (MA) with α-olefins and α-olefin dimers on CFP of methyl esters, obtained from corn oil. The copolymers were synthesized by benzoyl peroxide induced free radical copolymerization of maleic anhydride with 1-tetradecene **1a** and with two other α-olefin dimers,[38] 11-methylidenetricosane **1b** and 13-methylideneheptacosane **1c** (see Scheme 2). The following esterification with octadecan-1-ol using modified method presented in our recent article[37] gave products **2a–c** (for details, see Online Supplementary Materials).




**Scheme 2** *Reagents and conditions*: i, $Bz_2O_2$, 105 °C, toluene, 4 h; ii, $n\text{-}C_{18}H_{37}OH$, $H_2SO_4$, toluene, reflux, 10 h.

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**Table 1** Composition of corn oil based biodiesel.

| Component | Mp[13]/°C | Composition (wt%) | |
|---|---|---|---|
| | | This work, GC/MS | Lit.[4] data |
| Methyl myristate | 18 | 0.1 | traces–1.7 |
| Methyl palmitate | 28–35 | 18.6 | 8–12 |
| Methyl linoleate | –35 | 34.5 | 34–62 |
| Methyl oleate | –1–2 | 38.4 | 19–49 |
| Methyl linolenate | –57 | 4.2 | traces |
| Methyl stearate | 37–41 | 4.0 | 2–5 |
| Methyl arachidate | 45–48 | 0.2 | traces |

The sample of biodiesel was synthesized by methanolysis of corn oil in the presence of KOH.† The composition and ratio of the corn oil based methyl esters were determined by comprehensive two dimensional gas chromatography/mass spectrometry-flame ionization detection (GC×GC/MS-FID, Table 1, for molecular formula, lipid codes and GC×GC/MS-FID plot see Online Supplementary Materials). As can be seen, the composition of the sample correlated with the reference data,[4] except for higher content of methyl palmitate. Thus, the sample contained more than 22 wt% of high-melting esters of saturated fatty acids.

Cold flow properties of diesel fuels are usually characterized by cloud point (CP), pour point (PP) and cold filter plugging point (CFPP),‡ determined in accordance with the internatonal ASTM standards.[12,39] However, these characteristics are no more than numerical data which do not reflect phase transitions at subzero temperatures.

Differential scanning calorimetry (DSC) is the more informative method.[40,41] Six years ago, Alike *et al*. have amply demonstrated the value of the high-precision rheometry in the study of CFP of biodiesel.[42] We proposed that both these methods can be used for comparative study of the effectiveness of different pour point depressants in the improvement of the CFP of corn biodiesel. In addition to MA-based copolymers **2a–c** which have not previously been explored as biodiesel PPDs, we have chosen ethylene/vinyl acetate (EVA) copolymer (15 wt% vinyl acetate, $M_n$ = 8.8 kDa, $Đ_M$ = 1.81) and commercial pour point depressants Keroflux 5686 (BASF) and Dodiflow 8171 (Clariant). All additives were studied in 0.1 wt% concentrations.

The results of our rheological experiments are presented in Figure 1. For pure corn biodiesel (Figure 1, line *1*) we observed rapid increase in viscosity at 8 °C. This value correlates with the first crystallization peak in DSC cooling curve (–8.61 °C, see Figure S4 in Online Supplementary Materials). The effect of **2a** additive was rather negative (Figure 1, line *2*). EVA copolymer (Figure 1, line *7*) did not alter the crystallization temperature, but reduced viscosity by an order of magnitude. All additives had no marked influence on crystallization temperature except Dodiflow 171 (Figure 1, line *6*), that lowered the crystallization temperature to –10 °C (rheometry data), DSC peak was observed at –10.83 °C (see Figure S4 in Online Supplementary Materials). On the other hand, last four additives reduced a viscosity of corn biodiesel by a factor of twenty and more. The maximum efficiency was observed for Dodiflow 8171 commercial additive and for **2c** copolymer.

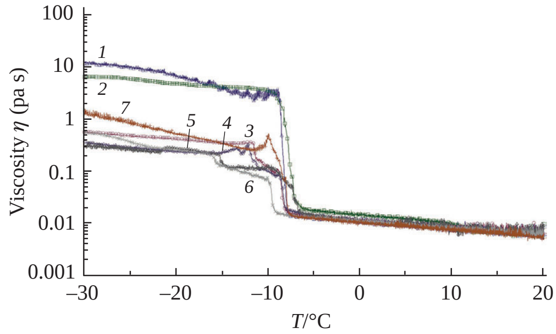


**Figure 1** Viscosity *vs*. temperature curves for corn oil methyl esters (*1*) and those containing 0.1 wt% polymer additives: with **2a** (*2*), with **2b** (*3*), with **2c** (*4*), with Keroflux 5686 (*5*), with Dodiflow 8171 (*6*) and with EVA copolymer VW353 (*7*).

In that way, one of the best commercial additive Dodiflow 8171 and copolymer **2c**, synthesized in our laboratory, demonstrated promising characteristics as a cold flow improvers for biodiesel. Note that high effectiveness was observed for maleic anhydride copolymer with long-chain branched hydrocarbon, dimer of tetradec-1-ene. Also note that the standard methods of determining CP and PP could not detect subtle differences in biodiesel rheology at subzero temperatures, a proper comparison of the effectiveness of polymer additives requires the use of more knowledge-intensive methods such as precision rheometry and DSC.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.09.039.

† Corn oil (160 g) was mixed with MeOH (108 ml, 6 equiv.) and KOH (3.2 g, 2 wt%). The mixture was heated up to 60 °C with stirring. After 4 h, the mixture was allowed to settle down overnight. The top layer was separated, washed with hot water to remove traces of glycerol, and distilled collecting a broad fraction of fatty acid methyl esters (bp 140–170 °C/0.5 Torr).

‡ CP is the temperature at which the smallest observable solid particles first occur upon cooling; PP is the temperature below which the oil loses its flow characteristics; CFPP is the temperature at which a given volume of fuel fails to pass through a standardized filtration device.

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