Rheological Properties and Crystallization Kinetics of Biodiesel during Gelation Process

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Abstract. Variation of rheological parameters with temperature and processing time for biodiesels were studied by oscillatory rheometer. Influence of cooling rate on the gelation characteristics of biodiesel were analyzed. The gelation point lowers and the storage modulus during non-isothermal and entire isothermal processes decreases with increasing of cooling rate. Isothermal gelation kinetics of biodiesels at different conditions were estimated based on rheological measurements. It has been found the crystallization rate constants during isothermal process decreases with the increasing of temperature and decreasing of cooling rate. Activation energy of soybean oil biodiesel is greater than that of waste oil biodiesel.

Keywords: biodiesel, viscoelastic properties, cooling rate, gelation kinetics

1. Introduction

Biodiesel is mainly produced by transesterification of vegetable oils or animal fats with alcohol using alkali as a catalyst [1]. Biodiesel has several distinct advantages compared with petrodiesel: derivation from a renewable and domestic resource, biodegradability, reduction of most exhaust emissions, higher flash point and excellent lubricity [2], [3]. However, biodiesel also has some problems such as the difficulty of using at low temperatures because of the crystal crystallization [4]-[9]. Saturated fatty acid methyl esters will precipitate from biodiesel when temperature is below the cloud point, with the further decrease of temperature, the amount of precipitated crystal gradually increases and these crystals connect with each other to form a three-dimensional network full of entrapped oil [10]-[13]. The presence of crystals imparts particular rheological behavior to biodiesel such as the viscoelastic properties [14]. It is well known that the obvious aging characteristics have been observed for crude oil systems in addition to cooling gelling properties, which means the rheological parameters such as the storage modulus of crude oil gel undergo a change with time at a constant temperature [15], [16]. This phenomenon resulted in the formation of harder deposits and these aging deposits are difficult to remove by either chemical or mechanical methods [15]. For the biodiesel systems, its characteristics of cooling gelling process and the formed three dimensional network structure of precipitated crystal are almost the same to the crude oil systems, the biodiesel system also would show the aging process like waxy crude oil. So the variations of storage modulus with processing time for biodiesel systems below the gelation point were studied in this work and aging characteristics for biodiesel systems were observed.

Furthermore, the gelation kinetics analysis of biodiesel can be obtained based on the rheological measurements. A kinetics study can give a better understanding of the gelation process of biodiesel. Various experimental techniques have been used to study the gelation kinetics such as the Fourier transform infrared spectroscopy [17] and differential scanning calorimetry [18]-[20]. Rheological measurements, on the other hand, provide an alternative approach to study the kinetics of gel structure formation because of the measurement is in the linear viscoelastic regime without the network structure disruption [21]. Rheological techniques have been proved to study the gelation kinetics and used in many different systems such as
polymer gelation [22], [23], protein gelation [24], [25] or gelation kinetics of crude oil systems [26]. Using a strain within the linear viscoelastic regime, the variation of storage modulus during a process can be obtained and in many cases the kinetics of crystal structure development are evaluated by the evolution of storage modulus [25].

In the work presented here, the variation of rheological parameters such as storage modulus during aging process for waste oil and soybean oil biodiesels were studied by rheometer in the modes of small amplitude oscillatory shearing. In addition to the composition of material, the rheological properties of biodiesels are influenced by many factors such as the scan rate during cooling process, the temperatures during aging process, so the influence of temperature on aging process and effects of cooling rate on gelation characteristics of biodiesel were discussed. Based on the variation of storage modulus with time, the isothermal gelation kinetics of biodiesel was analyzed according to the Avrami model.

2. Materials and Methods

2.1. Materials

Soybean oil and waste oil biodiesels were studied in this work. Soybean oil biodiesel was prepared by traditional alkali catalyzed transesterification method and waste oil biodiesel was provided by Qingdao Furuisi biotechnology development Co Ltd. The composition of biodiesels was measured by a 6890 series gas chromatograph and listed in Table 1. It can be seen that the saturated fatty acid methyl esters concentration of waste oil biodiesel is higher than soybean oil biodiesel. The crystallization temperatures of biodiesels measured by differential scanning calorimetry method are also listed in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C16:0</th>
<th>C18:0</th>
<th>C20:0</th>
<th>C18:1</th>
<th>C22:1</th>
<th>C18:2</th>
<th>C18:3</th>
<th>Crystallization temperature/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>WME</td>
<td>17.5</td>
<td>8.7</td>
<td>1.0</td>
<td>47.8</td>
<td>1.0</td>
<td>17.4</td>
<td>6.6</td>
<td>12.2</td>
</tr>
<tr>
<td>SAME</td>
<td>10.5</td>
<td>3.6</td>
<td>0.3</td>
<td>23.4</td>
<td>0.4</td>
<td>54.7</td>
<td>7.1</td>
<td>2.2</td>
</tr>
</tbody>
</table>

2.2. Rheological Measurements

The rheological properties of biodiesel systems were measured by an Anton Par Physica MCR 302 controlled stress rheometer. Parallel aluminum plate (diameter 50 mm) was controlled by a Peltier system on the bottom plate connected with a water bath. The sample gap was set to be 1.0 mm. It must be emphasized that the applied strain is in the linear viscoelastic region so that there is no influence of oscillation shear on the gelation kinetics. A maximum target strain of 0.15% is adopted to avoid the damage of samples.

For non-isothermal gelation process, the biodiesel samples were first heated to 20°C (above the crystallization temperature of biodiesels) for 10 min and then cooled at different cooling rates (0.1, 0.5 and 1.0°C/min) with a fixed frequency of 1Hz. The storage modulus G’ and phase angle δ were measured as a function of temperature. The experimental parameters during isothermal process are the same to non-isothermal gelation, however, isothermal gelation is time scan at different temperatures below the gelation point.

3. Results and Discussion

3.1. Isothermal Gelation Process and Gelation Kinetics under Different Temperatures

The biodiesels were heated to 20°C for 10 min and cooled down to the test temperatures with a cooling rate of 0.5°C/min, then the variation of storage modulus with time for waste oil and soybean oil biodiesels at different temperatures below or near the gelation point were measured and showed in Fig.1. It can be seen that the biodiesel shows obvious aging characteristics. The aging behavior of biodiesel is possibly due to the crystals continued to grow and the crystals forming in biodiesel undergo recrystallization at quiescent conditions, which is the same to waxy crude oil, however, it is not within the scope of this article. The aging process of biodiesel at lower temperature is much faster than at higher temperature. An equilibrium storage modulus has been reached in a short time at lower temperatures. At higher temperature, the storage modulus increases sharply with time during the initial aging period. After the rapid increase period, the G’ increment slows gradually as a result of the change in the gel structure is not evident as before. However, no real
equilibrium modulus has been reached even after a long time, especially near the gelation point. The increase
amplitude of storage modulus during aging process at lower temperature is smaller than that at higher
temperature.

Fig. 1: Variation of storage modulus with time for biodiesels at different temperatures

The gelation kinetics of biodiesel during isothermal process were studied based on the rheological data
and the Avrami model as following:

\[ X(t) = 1 - \exp(-kt^n) \]  \hspace{1cm} (1)

Where \( X(t) \) is the relative crystallinity at time \( t \), \( k \) is the crystallization rate constant and \( n \) is the Avrami
exponent. The data treatment involves calculating the degree of crystallinity as a function of time using the
following equation:

\[ X(t) = \frac{G'_t - G'_0}{G'_e - G'_0} \]  \hspace{1cm} (2)

Where \( G'_t \) is the storage modulus at time \( t \), \( G'_e \) is the equilibrium storage modulus which is chosen as the
pseudo-equilibrium value in this work since it can be seen that there is almost no changes in storage modulus
at the end of experiments. Additionally, the \( G'_0 \) is chosen as the initial storage modulus. The relationship
between temperature and reaction rate constant is calculated by Arrhenius equation:

\[ k = k_0 \exp\left(-\frac{E_a}{RT}\right) \]  \hspace{1cm} (3)

Where \( k_0 \) = Arrhenius pre-exponential factor, \( E_a \) = the activation energy, \( R \) = universal gas constant.
Based on equation (1) and (3), the following equation can be obtained:

\[ \log[-\ln(1-X(t))] = n \log t + \log k \]  \hspace{1cm} (4)

Based on equation 4, a linear relationship is presented between \( \log[-\ln(1-X(t))] \) and \( \log t \) which is also
verified by Fig. 2.

Deviations from linearity can be observed at the latter part of curves in Fig. 2. This phenomenon has
been observed for several crystallization systems and usually is caused by the secondary crystallization [26]-
[28] So only the initial linear part was used to study the isothermal gelation kinetics and the reaction rate
constant can be obtained from the slope after a linear regression. The relations of reaction rate constants with
temperatures for biodiesels were described by the Arrhenius relationship as shown in Fig. 3. The activation
energy of biodiesels during aging process can be obtained and the values are 239.8 kJ/mol and 285.7 kJ/mol
for waste oil and soybean oil biodiesel, respectively. The activation energy of soybean oil biodiesel is greater
than the value of waste oil biodiesel, which means the waste oil is more favorable for gelation. This is due to
the concentration of saturated fatty acid methyl esters in waste oil biodiesel is higher than soybean oil
biodiesel.
The data in Fig. 3 suggested that the reaction rate constant increases with decreasing temperature. The lower the temperature, the higher degree of supercooling and the greater driving force for crystallization, so smaller and more numerous precipitated crystal prefer to form and these crystals are more easily interconnected to form a three dimensional network structure.

### 3.2. Effect of Cooling Rate on Gelation Process

The viscoelastic parameters versus temperature for waste oil and soybean oil biodiesels with different cooling rate are plotted in Fig. 4.

For waste oil biodiesel with the cooling rate of 1 °C/min, it can be seen that the phase angle is almost a constant with a value of 90° and the value of storage modulus is lower than $10^{-2}$ when temperature is higher.
than 8.5 °C, which is suggested that the predominant liquid-like behavior is shown by waste oil biodiesel. The storage modulus starts to increase and phase angle begins to decrease when the temperature is lower than 8.5 °C and the phase angle is almost equal to 45° when the temperature decreased to 6 °C. Based on the gelation point definition [29], the gelation point of waste oil biodiesel with a cooling rate of 1.0 °C/min is 6 °C. At this temperature a gel network structure has been built up. With the further decrease in temperature, the moduli increase continuously which is attributed to the three-dimensional network structure is further strengthened. The variations of rheological parameters with temperature for soybean oil biodiesel are similar to those for waste oil biodiesel. When the cooling rate is 1.0 °C/min, the gelation point of soybean oil biodiesel is -2 °C which is lower than waste oil biodiesel. This is due to the higher concentrations of saturated fatty acid methyl esters in waste oil biodiesel. It can also be found that when the cooling rate is 0.1 and 0.5 °C/min, the gelation point of waste oil biodiesel is 8.4 °C, 7.5 °C and soybean oil biodiesel is 0.3 °C, -1 °C, respectively. The gel point temperature decreases with the increase of cooling rate.

From Fig. 4 it can also be seen that the structure development of biodiesel gel during cooling process is significantly related to the processed cooling rate. The storage modulus is higher with a slower cooling rate, which means a stronger network structure has been developed at a slower cooling rate. This phenomenon can be explained by the time needed for the growth of crystal network. Larger crystal has been formed with lower cooling rate because of there is more time for crystal growth, however, smaller crystal has been formed with higher cooling rate because of there is not sufficient time for crystal growth. Meanwhile, a stronger gel structure has been observed for network which is formed of longer crystals [30]. Thus, the gel structure becomes stronger with the decrease of cooling rate.

The effects of cooling rate on the aging process of waste oil biodiesel at 4 °C were studied as shown in Fig. 5. It is suggested that the storage modulus during aging process also decreases with the increasing of cooling rate, which is consistent with the cooling gelation process.

![Fig. 5: Effect of cooling rate on aging process of waste oil biodiesel](image)

Based on equation 4 and the isothermal gelling process of waste oil at 4°C with different cooling rates, the value of reaction rate constant for waste oil biodiesel is 0.000505, 0.000691 and 0.000835 when the cooling rate is 0.1, 0.5 and 1.0 °C/min, respectively. This means that the reaction rate constant during aging process increases with the increasing of cooling rate. This can be explained by the formation of smaller crystal during cooling process when the cooling rate is higher.

4. Conclusions

The rheological parameters such as storage modulus of waste oil and soybean oil biodiesels during cooling process and aging process at different temperatures were studied by means of oscillatory shear rheometer. The effect of cooling rate on the cooling and aging processes of biodiesels was also investigated. With the increase of cooling rate, the gel points of biodiesel decrease and the storage modulus during cooling and entire aging process also decreases.
Based on the variation of storage modulus with aging time, the gelation kinetics of biodiesel can be determined by Avrami model. The kinetic analysis of aging process for biodiesels display the reaction rate constant are dependent on the test temperature and cooling rate. The rate constants decrease with increasing temperature or decreasing cooling rate. Regardless of cooling gelling or aging process, the activation energy of waste oil biodiesel is lower than soybean oil biodiesel because of the concentration of saturated FAME of waste oil biodiesel is higher.

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6. References


