New empirical correlations for the viscosity of selected organic phase change materials

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Abstract Although there are many methods and instruments for measuring viscosity, it is still difficult to determine a reliable value of the dynamic viscosity of complex chemicals such as paraffins and fatty acids. This is due to the complex and heterogeneous structure of these compounds in the case of commercial products. On the other hand, the measuring instrument should be selected very carefully, including its measuring principle and measuring range. This paper presents results of viscosity measurements of three organic PCMs (phase change materials) obtained in four different research institutions. Commercial products: paraffin, myristic acid (97%) and mixture of palmitic acid (55%) and stearic acid (45%) were selected.

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as PCMs. Four different viscometers, namely Fungilab V-Pad, Rheotest LK 2.2, Rheometer Anton Paar MCR 102, and Brookfield DV-II + Pro have been used to determine temperature dependent dynamic viscosity of the tested PCMs. Using a large database of present measurement results, correlations were developed to calculate the dynamic viscosity of fatty acids and paraffins, which predict the experimental data within a band of ±20%.

**Keywords:** PCM; Viscosity; Viscometers; Temperature; Shear rate

**Nomenclature**

- \( c \) – specific heat, J/(kgK)
- \( D \) – diameter, mm
- \( L \) – length, mm
- \( n \) – speed of rotation, 1/min
- \( r \) – heat of phase transition, J/g
- \( t \) – temperature, °C

**Greek symbols**

- \( \mu \) – dynamic viscosity, mPa·s

**Subscripts and superscripts**

- \( c \) – cooling
- \( h \) – heating
- \( l \) – liquid
- \( m \) – mean
- \( \text{max} \) – maximum
- \( \text{min} \) – minimum
- \( p \) – constant pressure
- \( s \) – solid
- \( r \) – initial
- \( n \) – final

**Acronyms**

- DSC – differential scanning calorimetry
- PCM – phase change material

## 1 Introduction

Thermal energy storage with phase change materials (PCMs) is of key importance in many areas, such as building [1], heating and air conditioning [2], cooling of portable electronic devices [3], preventing overheating of batteries [4], refrigeration [5], thermoregulated textiles [6] or improving the efficiency of cogeneration systems [7]. Such common use of PCMs requires
knowledge of their thermophysical properties, including viscosity. Although there are many methods and instruments for measuring viscosity, it is still difficult to determine a reliable dynamic viscosity of complex chemicals such as paraffins and fatty acids. This is due to the complex and heterogeneous structure of these compounds in the case of commercial products. Data regarding viscosity of organic PCMs are very sparse. Noureddini et al. [8] measured the viscosity of a few vegetable oils and fatty acids. Correlations for viscosity in the temperature scope from 24°C to 110°C have been proposed. Valeri and Meirelles [9] determined a kinematic viscosity of a number of fatty acids and triglycerides. The measurement results for pure components were generalized in the form of correlations as a function of temperature. Correlations for calculating the kinematic viscosity of mixtures of fatty acids and triglycerides have also been developed. González et al. [10] measured viscosity of several fatty acids in a wide temperature range: from melting point up to 100°C. Correlations for calculating a dynamic viscosity have been proposed. Rabelo et al. [11] determined viscosity of selected pure fatty acids and their mixtures. Measurements were realized in the temperature scope from 20°C to 90°C. A complex correlation for calculating the dynamic viscosity was developed, taking into account the atomic structure of the tested compounds. Ayranci and Akgul [12] measured viscosity of several fatty acids in 2-butanol as a function of concentration in the temperature range from 20°C to 60°C. It was established that for given temperature and concentration viscosity of all tested mixtures increased with the carbon number of the fatty acid. Ferrer and Barreneche et al. [13] determined viscosity of a number of fatty acids within the temperature range from 40°C to 100°C. Among the several types of equations tested, it turned out that polynomials give the best results in correlating the obtained experimental data. Ferrer et al. [14] and Barreneche et al. [15] measured viscosity for a few paraffins. A complex correlation has been developed to calculate the viscosity of a large group of paraffins, taking into account the melting point. Delgado et al. [16] proposed an approach for measurement viscosity of almost pure octadecane. Moreover Delgado et al. [17,18] presented results of viscosity measurements of the Parafol 18–97 and paraffin conducted by independent institutions. The measurements were realized within temperature scope 25–80°C and large shear rate range 1.65–1000 s⁻¹. The highest deviations were observed when uniform temperature throughout the sample was not preserved. Outside of design goals, reliably measured viscosity may serve as benchmark for new categories of thermal fluids, as nanocomposites [19,20], microencapsulated slurries [21,22], shear
thickening fluids [23,24], re-melted suspensions [25,26], non-Newtonian fluids [27], or nanofluids [28–30].

In present study, the viscosity of three organic PCMs has been measured in five different organizations. Commercial products: paraffin, myristic acid (97%) and mixture of palmitic acid (55%) and stearic acid (45%) were selected as PCMs. Four different viscometers, namely Fungilab V-Pad, Rheotest LK 2.2, Rheometer Anton Paar MCR 102, and Brookfield DV-II + Pro have been used to determine temperature dependent dynamic viscosity of the tested PCMs. The prime aim of the present study is to develop a reliable correlations for dynamic viscosity of fatty acids and paraffins.

2 Materials

Three commercial organic materials have been tested: paraffin LTP 56 supplied by Polwax S.A. Jaslo, Poland, fatty acid RT54HC supplied by Rubitherm Technologies GmbH Berlin, Germany, and fatty acid P1801 supplied by Konimpex Chemicals Konin, Poland. Table 1 shows the description of the used materials.

<table>
<thead>
<tr>
<th>Product</th>
<th>Substance</th>
<th>Formula</th>
<th>Share</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTP 56</td>
<td>Paraffin</td>
<td>$C_{19}H_{38}$–$C_{32}H_{65}$</td>
<td>100%</td>
</tr>
<tr>
<td>RT54HC</td>
<td>Fatty acid</td>
<td>$C_{14}H_{28}O_2$</td>
<td>97%</td>
</tr>
<tr>
<td>P1801</td>
<td>Fatty acid</td>
<td>$C_{16}H_{32}O_2$ Palmitic acid</td>
<td>58%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C_{17}H_{35}O_2$ Stearic acid</td>
<td>38%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>96%</td>
<td></td>
</tr>
</tbody>
</table>

The detailed chemical composition of the tested materials was determined on the basis of chromatographic tests using the GC-MS-QP2010 PLUS Shimadzu gas chromatograph (Fig. 1).

The range of phase transition temperatures, heat of phase transition, and specific heat of the tested materials were estimated by differential scanning calorimetry (DSC) method using the TA Q1000 DSC. The results of the analysis are presented in Fig. 2. As shown in Fig. 2, each tested material exhibits different ranges of the melting and solidification phase transition temperatures. During the melting cycle of LTP56 (Fig. 2a), two peaks are visible, which indicates a different chemical composition. In the case of the solidification cycle, one of the peaks was not recorded due to the limitations
of the apparatus used. RT54HC and P1801 show single peaks for both the melting and solidification cycles, which means that the individual chemical compounds of a given material have a similar phase transition temperature. The highest heat of phase transition is shown by RT54HC, which additionally has a higher heat of phase transition during the melting cycle compared to the solidification cycle.

Table 2 shows the results of the DSC measurements of the tested materials, where \( t'_h \), \( t''_h \), \( t'_c \), and \( t''_c \) represent initial and final temperature of phase transition during heating and cooling processes (Fig. 2), respectively. Specific heat at constant pressure \( (c_p) \) for solid and liquid phases and heat of phase transition for heating \( (r_h) \) and cooling \( (r_c) \) processes are presented, too.
Table 2: DSC characteristics of the tested materials.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>LTP56</th>
<th>RT54HC</th>
<th>P1801</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t'_c$</td>
<td>°C</td>
<td>51.8</td>
<td>43.6</td>
<td>52.6</td>
</tr>
<tr>
<td>$t''_c$</td>
<td>°C</td>
<td>28.1</td>
<td>51.5</td>
<td>45.5</td>
</tr>
<tr>
<td>$t'_h$</td>
<td>°C</td>
<td>31.6</td>
<td>53.1</td>
<td>53.3</td>
</tr>
<tr>
<td>$t''_h$</td>
<td>°C</td>
<td>62.4</td>
<td>63.1</td>
<td>64.9</td>
</tr>
<tr>
<td>$c_{p_{h,s}}$</td>
<td>J/(gK)</td>
<td>2.27</td>
<td>1.73</td>
<td>1.99</td>
</tr>
<tr>
<td>$c_{p_{h,s}}$</td>
<td>J/(gK)</td>
<td>2.49</td>
<td>2.09</td>
<td>2.26</td>
</tr>
<tr>
<td>$c_{p_{c,s}}$</td>
<td>J/(gK)</td>
<td>2.70</td>
<td>1.93</td>
<td>2.03</td>
</tr>
<tr>
<td>$c_{p_{c,l}}$</td>
<td>J/(gK)</td>
<td>2.20</td>
<td>2.04</td>
<td>1.97</td>
</tr>
<tr>
<td>$r_{h}$</td>
<td>J/g</td>
<td>185.9</td>
<td>195.4</td>
<td>181.9</td>
</tr>
<tr>
<td>$r_{c}$</td>
<td>J/g</td>
<td>182.2</td>
<td>200.1</td>
<td>181.4</td>
</tr>
</tbody>
</table>

3 Methods

The devices used in each laboratory taking part in the intercomparative tests are specified in Table 3. A large dispersion of the sample volumes used in individual devices as well as the minimum ($n_{\text{min}}$) and maximum ($n_{\text{max}}$) rotation speeds of the spindle or the plate are noticeable.

Table 3: Technical specification of the used instruments.

<table>
<thead>
<tr>
<th>Organization</th>
<th>Instrument</th>
<th>Sample (ml)</th>
<th>Speed of rotation (1/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gdansk University of Technology</td>
<td>Fungilab V-Pad Spindle L1</td>
<td>600</td>
<td>0.3 250</td>
</tr>
<tr>
<td>Warsaw University of Technology</td>
<td>Brookfield DV-II + Pro Spindle SCR-21</td>
<td>7.5</td>
<td>0.1 200</td>
</tr>
<tr>
<td>Hochschule Bremen</td>
<td>Rheotest LK 2.2 Capillary 1/2: $D = 1$ mm, $L = 80$ mm</td>
<td>25</td>
<td>– –</td>
</tr>
<tr>
<td>Koszalin University of Technology</td>
<td>Brookfield DV-II + Pro Spindle SC4-18</td>
<td>6.7</td>
<td>0.1 200</td>
</tr>
<tr>
<td>Smart Fluid Inc.</td>
<td>Anton Paar MCR 102 Plate $D = 40$ mm</td>
<td>0.38</td>
<td>0.1 1000</td>
</tr>
</tbody>
</table>
Table 4 shows measurement range and measurement uncertainty according to the producers of the viscometers, where $\mu_{\text{max}}$ and $\mu_{\text{min}}^P$ represent maximum measurable viscosity and minimum measurable viscosity for given spindle (plate) and speed of rotation, respectively.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>$n$ (1/min)</th>
<th>$\mu_{\text{max}}$ (mPa·s)</th>
<th>$\mu_{\text{min}}^P$ (mPa·s)</th>
<th>Relative error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fungilab V-Pad Spindle L1</td>
<td>0.3</td>
<td>$2 \cdot 10^4$</td>
<td>3200</td>
<td>±1</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>24</td>
<td>3.84</td>
<td></td>
</tr>
<tr>
<td>Brookfield DV-II + Pro Spindle SCR-21</td>
<td>0.1</td>
<td>$1 \cdot 10^6$</td>
<td>32000</td>
<td>±1</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>50</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Rheotest LK 2.2 Capillary 1/2: $D = 1$ mm, $L = 80$ mm</td>
<td>–</td>
<td>16</td>
<td>1</td>
<td>≤ 2</td>
</tr>
<tr>
<td>Brookfield DV-II + Pro Spindle SC4-18</td>
<td>0.1</td>
<td>$32 \cdot 10^4$</td>
<td>32000</td>
<td>±1</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.6</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Anton Paar MCR 102 Plate $D = 40$ mm</td>
<td>0.1</td>
<td>$250 \cdot 10^6$</td>
<td>–</td>
<td>±3</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>$250 \cdot 10^6$</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

4 Results and discussion

In Figs. 3 to 5 dynamic viscosity against shear rate for temperature 60°C of three tested PCMs is shown. The results obtained with Fungilab V-Pad viscometer are omitted because the device is not equipped with a sample adapter, therefore it was impossible to estimate shear rate. Shear rates for capillary viscometer Rheotest LK 2.2 were not assigned, too.

From Figs. 3 to 5 it can be seen that the viscosity of LTP56 at 60°C is between 6 mPa·s and 8.5 mPa·s, while the viscosity of P1801 is between 10 mPa·s and 13 mPa·s. This means that the viscosity of P1801 is twice that of LTP56. The viscosity of RT54HC lies between LTP56 and P1801. Under the same conditions, regardless of the substance tested, the Brookfield DV-II + Pro (Spindle SCR-21) gave the lowest viscosity and the Anton Paar MCR 102 gave the highest. The measuring points for LTP56 (Fig. 3) and RT54HC (Fig. 4) at minimum shear rate obtained with Brookfield DV-II + Pro and SCR-21 spindle deviate significantly from the trend line. This may indicate that the measurements were taken performed close near to the instrument’s limit, at its lower range. It is characteristic that, regard-
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Figure 3: Dynamic viscosity of LTP56 versus shear rate.

Figure 4: Dynamic viscosity of RT54HC versus shear rate.

less of the substance tested, the viscosity measured using the Anton Paar MCR 102 and Brookfield DV-II + Pro (Spindle SC4-18) decreases slightly with increasing shear rate, whereas the results obtained using the Brookfield DV-II + Pro (Spindle SCR-21) show the opposite tendency. Changes in the
dynamic viscosity of the three PCMs tested are within the measurement error limits, so the viscosity can be considered as constant regardless of the measuring devices used. It was, therefore, assumed that LTP56, P1801 and RT54HC at a temperature of 60°C have the rheological properties of Newtonian fluids where viscosity is independent on the shear rate. Consequently, Brookfield DV-II + Pro (Spindle SCR-21) showed an average viscosity of 6.71 mPa·s (LTP56), 5.24 mPa·s (RT54HC), and 10.41 mPa·s (P1801). The average viscosity determined by using the Brookfield DV-II + Pro (Spindle SC4-18) compared to the results obtained using the Brookfield DV-II + Pro (Spindle SCR-21) was approximately 7% (LTP56), 40% (RT54HC), and 11% (P1801) higher and in comparison to the data obtained using the Anton Paar MCR 102, the average viscosity was approximately 28%, 75%, and 23% higher for LTP56, RT54HC, and P1808, respectively. It is worth emphasizing that the measurement results presented in Figs. 3 to 5 were obtained at a temperature of 60°C, i.e. a temperature close to the melting point of the tested PCMs. Thereforer, the temperature inside the tested samples could not be uniform, which in turn could affect the measurement results obtained.

In Figs. 6 to 8 dynamic viscosity against temperature of three tested PCMs is shown. First of all, there is a large variation in the results obtained with Fungilab V-Pad depending on the spindle speed. The device used was
not equipped with a commercially available sample adapter. Following the manufacturer’s recommendations the measurements were performed with sample volume 600 ml, that is very large in comparison with other devices (Table 3).

Figure 6: Dynamic viscosity of LTP56 versus temperature.

Figure 7: Dynamic viscosity of RT54HC versus temperature.
As can be seen in Figs. 6 to 8 for Fungilab V-Pad measurements dynamic viscosity increases with speed of spindle rotation. Irrespective of the PCMs tested the highest dynamic viscosity was observed for the highest speed of spindle rotation used (200 rpm). According to the manufacturer the measurement uncertainty is ±1% of the full scale range and depends on the spindle type and speed of rotation (Table 4). The Brookfield DV-II + Pro equipped with the SCR-21 spindle allowed the measurement of dynamic viscosity only for \( t = 60^\circ C \). At higher temperature the viscosity of the PCMs examined was too low. In order to check the behavior of liquid PCMs under the influence of increasing shear stress the tests were carried out for the spindle rotational speeds in the range of 40–200 rpm. As can be seen in Figs. 6 and 7 the dynamic viscosity increases slightly with spindle rotational speed for LTP 56 and P1801, respectively. For RT54HC (Fig. 8) no effect of spindle rotational speed on dynamic viscosity was observed. The use of the Brookfield DV-II + Pro equipped with the SC4-18 spindle allowed the measurement of dynamic viscosity within the temperature range 60–80°C and for spindle rotational speeds between 50 and 200 rpm. However, the measurements were made close to the minimum torque, i.e. 10%. This means that the results may be biased by a large error. This fact probably explains the contradictory influence of spindle rotational viscosity measured using the Fungilab V-Pad and Brookfield DV-II + Pro equipped with the
SC4-18 spindle. As can be seen in Fig. 6 the dynamic viscosity of P1801 measured using the Anton Paar MCR 102 is independent of rotational speed. Rheotest LK 2.2 capillary viscometer – gave the lowest dynamic viscosity values regardless of PCM type and temperature.

Using data obtained with 4 instruments, i.e. Brookfield DV-II + Pro O with spindle SCR-21, Brookfield DV-II + Pro with spindle SC4-18, Anton Paar MCR 102 and Rheotest LK 2.2, least squares regression analysis was used to establish correlation equations for predicting the dynamic viscosity of the tested PCMs at different temperatures. These correlations for LTP 56, RT54HC, and P1801 respectively have the form:

\[
\mu = 24.3e^{-2.05 \cdot 10^{-2} t}, \quad (1)
\]

\[
\mu = 21.1e^{-1.77 \cdot 10^{-2} t}, \quad (2)
\]

\[
\mu = 47.8e^{-2.39 \cdot 10^{-2} t}, \quad (3)
\]

where \( \mu \) is the dynamic viscosity in mPa⋅s and \( t \) is the temperature in °C.

In Fig. 9 a comparison of predicted data against the experimentally obtained is displayed for LTP56. For 66% of the experimental points the discrepancy between the experimental data and the values calculated from the proposed correlation is less than ±20%. In addition, Fig. 9 shows the correlation developed by Ferrer et al. [17] for paraffin RT55, for which the melting temperature is close to LTP56:

\[
\mu = \left( 0.02584 - 0.0007849t + 9.801 \cdot 10^{-6} t^2 - 4.388 \cdot 10^{-8} t^3 \right). \quad (4)
\]

As can be seen in Fig. 9, the correlation of Ferrer et al. [17] underestimates the dynamic viscosity of LTP56 by about 49% compared to the present correlation.

In Fig. 10 a comparison of the predicted data with the experimentally obtained is displayed for RT54HC. For 81% of the experimental points the discrepancy between the experimental data and the values calculated from the proposed correlation is less than ±5%. In addition, Fig. 10 shows the correlation developed by Ferrer et al. [16] for fatty acids:

\[
\mu = \left( 2.95 \cdot 10^{-2} - 7.80 \cdot 10^{-4} t + 8.37 \cdot 10^{-6} t^2 - 3.42 \cdot 10^{-8} t^3 \right) c, \quad (5)
\]

where \( c \) is a correction factor on PCM melting temperature

\[
c = 15.38 - 0.3t_m + 1.1 \cdot 10^{-3} t_m^2. \quad (6)
\]
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Here the temperature $t_m$ was assumed as the arithmetic mean of the initial melting point ($t'_{c,m}$) during the cooling process, and the final melting point ($t''_{h,m}$) during the melting process:

$$t_m = \frac{t'_{c,m} + t''_{h,m}}{2}. \quad (7)$$
Using the results of the DSC tests (Fig. 2b), \( t_m = 58.9^\circ \text{C} \) was assumed for the calculations.

As can be seen in Fig. 10, the correlation of Ferrer et al., Eq. (5), overestimates the dynamic viscosity of RT54C by about 11\% at lower temperatures and underestimates it by about 4\% at higher temperature, compared to the present correlation.

In Fig. 11 a comparison of the predicted data with the experimentally obtained is displayed for P1801. For 100\% of the experimental points the discrepancy between the experimental data and the values calculated from the proposed correlation is less than \( \pm 15\% \). In addition, Fig. 11 shows the correlation developed by Ferrer et al., Eq. (5), for fatty acids, A correction factor, Eq. (6), was calculated for \( t_m = 59.7^\circ \text{C} \) using the results of the DSC tests (Fig. 2c). As can be seen, the correlation of Ferrer et al. [16], underestimates the dynamic viscosity of P1801 by approximately 54\% compared to the present correlation.

![Figure 11: Comparison of measured and calculated dynamic viscosity of P1801.](image)

5 Conclusions

The dynamic viscosity-temperature relationships of three phase change materials (PCMs) have been determined using of three spindle rotational viscometers, one plate rotational viscometer, and one capillary viscometer.
A large scatter of results was observed, even when the same type of viscometer (Brookfield DV-II + Pro) was using, which indicates the need for very careful selection of the sample adapter. The results also indicate the need to respect the limitations imposed by the torque limit. The results obtained using the Fungilab V-Pad viscometer are characterised by the greatest uncertainty, due to the lack of precise determination of the geometry of the spindle-sample chamber system. Regardless of the type of PCM, the lowest values of dynamic viscosity were obtained with the capillary viscometer. The discrepancy between the experimental data and the values of dynamic viscosity calculated from the proposed correlation equations does not exceed ±20% for most measurement points. Taking into account the difference in chemical composition, developed correlations reproduce the present results with reasonable agreement.

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References


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