Freezing as a Storage Process for Aqueous Polymer Solutions

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Abstract:
There is often a need to perform rheological tests on dilute polymeric liquids at a time long after their initial preparation, for example if a more sensitive or novel method of measuring a material property (such as uniaxial/biaxial extensional viscosity or second normal-stress differences) becomes available. An inexpensive method of storing such fluids which prevents any form of deterioration (e.g. bacteriological) would therefore be of great value. This study explores the potential of freezing as that storage process by investigating whether the freeze-thaw process itself leads to rheological changes. The rheological properties of three polymeric liquids: 0.25% xanthan gum, 0.125% polyacrylamide and a 0.1%/0.1% carboxymethylcellulose/xanthan gum blend commonly used in non-Newtonian fluid flow studies were determined in both shear and oscillation before and after a freeze-thaw process. Within the uncertainty of the rheometer used, the rheological properties of the polymers studied were found to be unaffected by the freeze-thaw process leading to the conclusion that this storage method is indeed a practical possibility.

Zusammenfassung:
Häufig besteht Bedarf, rheologische Messungen mit verdünnten Polymerlösungen lange nach der erstmaligen Probenherstellung durchzuführen, z.B. wenn ein genaueres oder neues Messverfahren einer Materialeigenschaft zur Verfügung gestellt wird (wie uniaxiale/biaxiale Dehnviskosität oder zweite Normalspannungsdifferenz). Eine kostengünstige Methode zur Lagerung solcher Fluide, die jegliche Zerstörung (z.B. bakteriologische) verhindert, würde daher von einem sehr grossen Nutzen sein. Diese Untersuchung erörtert das Potential des Gefrierens als Lagerungsmethode durch Ermittlung, ob das Gefrieren und Tauen zu rheologischen Veränderungen führt. Die rheologischen Eigenschaften von drei polymeren Flüssigkeiten, 0,25% Xanthangummi, 0,125% Polyacrylamid und ein 0,1%/0,1% Carboxymethylzellulose/Xanthangummi-Blend, die überlicherweise in Untersuchungen über nicht-Newtonische Flüssigkeiten verwendet werden, wurden in Scherung und Oszillation vor und nach dem Gefrier- und Tauprozess bestimmt. Es wurde gefunden, dass die rheologischen Eigenschaften dieser Polymere im Rahmen der Messgenauigkeit der verwendeten Rheometer von dem Gefrier- und Tauprozess nicht beeinflusst wurden, was zur Schlussfolgerung hat, dass diese Lagermethode in der Tat eine Anwendungsmöglichkeit darstellt.

Résumé:
Il y a souvent un besoin d’effectuer des tests rhéologiques sur des liquides polymères dilués à un temps long après leur préparation initiale, par exemple lorsque une méthode plus sensible ou bien plus récente de mesurer une propriété du matériau (comme la viscosité extensionnelle uniaxiale/biaxiale ou la seconde différence de contraintes normales) devient disponible. Une méthode bon-marché pour conserver de tels fluides et qui empêche toute forme de détérioration (par exemple bactériologique) serait alors de grande valeur. Cette étude explore la congélation comme moyen de conservation en recherchant si le procédé congélation-décongélation lui-même conduit à des changements rhéologiques. Les propriétés rhéologiques de trois liquides polymères: 0,25% de gomme de xanthane, 0,125% de polyacrylamide et un mélange à 0,1% / 0,1% de carboxyméthyle cellulose/gomme de xanthane, communément utilisés dans les études d’écoulement de fluides non-Newtoniens, on été déterminées en cisaillement et en oscillation avant et après le procédé de congélation-décongélation. Dans la limite du domaine d’incertitude du rhéomètre utilisé, les propriétés rhéologiques des polymères étudiés se sont avérées être non affectées par le procédé de congélation-décongélation, ce qui conduit à la conclusion que cette méthode de conservation est de fait une possibilité pratique.

Key words: Freeze/thaw process, long-term storage for polymer solutions

1 INTRODUCTION

There is often a need to perform rheological ‘tests’ on polymeric solutions a considerable time after their initial preparation and so a method of storing these fluids is required in such a way that any form of chemical or bacteriological deterioration is avoided. We are unaware that any such method is currently available. Preparing a nominally identical fluid from powder form at a later date is unsatisfactory due to inevitable batch-to-batch variations between samples and manufacturers. Aqueous samples stored at room temperature are also unusable as they naturally deteriorate with time, primarily due to bacteriological action.

New rheological tests could be necessary for numerous reasons: inevitably instrumentation improves with time both in terms of range and accuracy and also in ability to determine previously unmeasurable material properties. One example of a property for which until recently no commercial instrument was available is extensional viscosity (see Dontula et al 1997 for a discussion of the inadequacies of the then-current methods of measuring extensional viscosity for dilute solutions). If extensional viscosity could be measured accurately and routinely for viscoelastic polymer solutions such as polyacrylamide, it might open the way for a significant improvement in our understanding of the phenomenon of drag reduction and even correlations based upon existing data (Escudier et al 1999)). Indeed since the time of the paper by Dontula et al, there has been significant progress in this area with advances in both filament-stretching rheometers and capillary-breakup devices to the extent that a commercial device based on the later technique has been launched recently (the CaBER instrument from Thermo Haake see e.g. McKinley and Tripathi 2000 for a concise description). It is also the case that if samples could be stored without degradation, fluid samples could be saved routinely during fluid-flow investigations, their rheology then measured subsequently and shear-degradation effects monitored more closely. Freezing of samples followed by thawing at a much later date is suggested here as a suitable and economically viable long-term storage process. This paper is concerned with investigating the freeze-thaw mechanism on the rheological properties of three aqueous polymer solutions commonly used in non-Newtonian fluid-flow experiments: xanthan gum, polyacrylamide and a blend of carboxymethylcellulose with xanthan gum.

We could find no papers that investigate the rheological effects of the freeze-thaw process on purely polymeric liquids. Researchers in the food and cosmetic industries have, for obvious reasons, been long interested in the effects of the freeze-thaw process on the stability and texture (and consequently the rheology) of their products. It is well known that some foods are severely degraded by freezing such that the structure of the thawed material is significantly different from the pre-frozen article (examples include dairy cream and fruits such as strawberries and tomatoes). The dynamic viscosity of cosmetic emulsions (Hetzel et al 2000) was found to increase after the freeze-thaw process (storage at -10°C for one week) due to structural alteration of the emulsions. The effect of the freeze-thaw process on model food systems (based on starch, sucrose and water) has been studied by various authors (White et al 1989) and Ferrero and Zaritzky 2000)) and again the dynamic viscosity was found to increase after the freeze-thaw process (samples stored at both -19 and -80°C for 91 days). This increase was significantly higher for slow freezing than for quick freezing and is related to structural changes, particularly sponge formation due mainly to amylose retrogradation at slow freezing rates (Ferrero and Zaritzky). In an attempt to reduce these unwanted structural and textural changes caused by the freeze-thaw process, Ferrero and Zaritzky added a low proportion of a hydrocolloid (xanthan gum, guar gum or sodium alginate) and discovered that this addition reduced any rheological changes with quickly frozen samples “hardly differing from the unfrozen ones”. The samples containing xanthan gum and guar gum that were frozen at slow rates showed a slight reduction in dynamic viscosity and this was attributed to structural changes related to large-ice crystal formation. They did not investigate the effect of the freeze-thaw process on the xanthan gum or guar gum in a water solution alone.

Freezing is a preservation process successfully used for certain food and cosmetic products. The question we set out to answer was: would there be a detectable effect on the rheological properties of the polymers we and others use in
flow studies, of freezing in a low-cost freezer at an uncontrolled rate and to a relatively high frozen temperature of about −25°C followed by thawing? It might be anticipated, for example, that long-chain molecules would be permanently broken by freezing which would lead to molecules of effectively lower molecular weight, hence lower zero-shear-rate viscosities which would be less effective drag-reducing agents and in general, display more ‘Newtonian-like’ behaviour. In some natural gum solutions such as locust bean gums for example, it is well known that after the freeze-thaw process these type of gums do not return to their original structure (Kuntz 1995).

One issue that may limit the use of a low-cost freezer as an appropriate long-term storage medium is that of the true temperature at which all of the solution is frozen. As polymer solutions freeze, the dissolved solutes become freeze-concentrated in the unfrozen fluid spaces between ice crystals. In effect the melting point of the residual solution is reduced to below 0°C so that increasingly low temperatures are required to convert more water to ice. For long-term stability it may be that the frozen polymer solutions must be stored at a temperature lower than the so-called glass transition temperature or the solutes will remain suspended between ice crystals in an aqueous environment that can still allow chemical or bacteriological degradation. Given that polymer solutions at concentrations greater than a few hundred ppm are shear-thinning and, as a consequence, have high zero-shear viscosities at room temperature (for the concentrations used in the current study at least 1000 times that of water), the viscosity of the sample at any temperature below 0°C will be extremely high, and this in itself is likely to inhibit any such chemical or bacteriological degradation. A key aspect of the present study is to determine whether freeze-thaw mechanism leads to degradation and concomitant rheological changes. Clearly if this mechanism were to lead to rheological changes, freezing would not be a viable method for the storage of polymer solutions.

2 MEASURING PROGRAMME AND FLUID PREPARATION

The polymers used in this investigation were a 0.25% (all concentrations are by weight in water) food-grade xanthan gum (XG) solution supplied by Keltrol TF from Kelco (CAS 11138-66-2), a 0.125% polyacrylamide (PAA) solution (Separan AP 273 E supplied by Floreger) and a 0.1%/0.1% blend of XG with sodium carboxymethylcellulose (CMC, supplied by Aldrich Chemical Co Grade 9004-32-4, Catalogue No 32,306-3). The concentration levels were chosen to achieve relatively high levels of both viscosity and viscoelasticity in order to improve the accuracy of the rheological measurements. Each of these polymers has been used extensively in investigations of fluid flow in our laboratory (Escudier et al (1999), Poole and Escudier (2003)) and elsewhere (e.g. den Toonder et al (1997), Pereira and Pinho (2000), Rudman et al (2004) and Gampert et al (2004)).

All of the solutions were prepared in the same manner: the polymer was added slowly at 20°C to 1 kg of non-filtered tap water contained in a 5 litre vessel. During this process the mixture was agitated gently (to avoid air entrainment and unnecessarily high shear) by a four blade rotating impeller for one hour, by which time the solution was visibly homogenous. The mixture was then allowed to stand for 24 hours to ensure complete hydration of the polymer molecules. To retard bacterial degradation, 100 ppm of formaldehyde solution was added to each of the solutions. To further reduce bacterial degradation effects the solutions were stored in sealed containers at 20°C and exposed to the air only when a sample was required for rheological testing.

Once a batch of polymer solution had been mixed and was fully hydrated it was agitated for 30 s to re-homogenise it. This fluid batch was then split into two: one for immediate ‘fresh’ testing and one for testing following freezing and subsequent thawing. Freezing of a sample (volume ≈ 100ml) was achieved by placing it in a domestic freezer operating at −24 ± 0.5°C. Although the sample took less than three hours to freeze, solutions were kept frozen for a minimum period of 24 h and once removed from the freezer were left for 24 h at room temperature to thaw prior to testing. Both fresh and thawed solutions were agitated for 30 s prior to testing in order to achieve full homogenisation (while not degrading the sample by excessive shearing). Each sample was fully tested within three days of mixing for fresh samples and within three days of thawing for frozen samples.
3 MEASURING EQUIPMENT

All rheological measurements were carried out using a TA Instruments Rheolyst AR 1000 N controlled-stress rheometer. A 40 mm diameter parallel plate geometry was used to achieve the highest shear rates achievable with our rheometer. For a range of intermediate shear rates a 60mm diameter, 2° acrylic cone was used. The lowest shear rates were achieved using a 41.2 mm mean diameter double concentric cylinder arrangement in steady shear and in creep mode to extend the range still further. Creep data were also obtained at higher shear rates for comparison with other steady-shear data to confirm the validity of the procedure. All measurements were carried out at 20°C. Temperature control of the rheometer is achieved via a plate that utilises the Peltier effect to control the temperature of the sample within ± 0.1°C. The instrument is capable of performing measurements of the viscometric viscosity in steady shear and of the dynamic viscosity in oscillatory shear. A detailed uncertainty analysis, performed for the double concentric cylinder geometry, can be found in Escudier et al (2001). The outcome from this analysis is that for shear rates greater than 1 s⁻¹ the total uncertainty is about 2%. For the cone-and-plate and parallel-plate geometries at high shear rates, the same values of total uncertainty apply because in that range the uncertainty is dominated by the angular speed contribution which is independent of the geometry used.

4 RESULTS AND DISCUSSION

4.1 VISCOMETRIC VISCOSITY

The variation of viscometric viscosity with shear rate can be seen in Figure 1 for both fresh and thawed samples of 0.125 % PAA (Fig. 1a), 0.1 % CMC/0.1 % XG blend (Fig. 1b) and 0.25 % XG (Fig. 1c). All three flow-curves show shear-thinning behaviour to a greater (PAA and XG) or lesser (CMC/XG blend) extent with a 2.5 to 3.5 decade reduction in viscosity over a 5 - 8 decade range of shear rate.

The upturn in viscosity values for PAA (both fresh and thawed) at very high shear rates (> 10³ s⁻¹) is a consequence of secondary flows occurring in the parallel-plate geometry. Also included in Fig. 1 are curves representing the Carreau-Yasuda model fitted to the combined data sets for

Figure 1: Viscosity versus shear rate for fresh and thawed samples of (solid line represents Carreau-Yasuda model).

Figure 1a (above): 0.125 % polyacrylamide
Figure 1b (middle): 0.1 % CMC / 0.1 % XG blend
Figure 1c (below): 0.25 % xanthan gum
each fluid (not including the high-shear rate data for PAA):

$$\mu_C = \mu_0 + \frac{\mu_\infty - \mu_0}{(1 + (\lambda_C \gamma)^{\eta})^{\alpha}}$$  \hspace{1cm} (1)

$\mu_0$ being the zero-shear-rate viscosity, $\mu_\infty$ the infinite-shear-rate viscosity, $\lambda_C$ a time constant, $\eta$ a power-law index and $\alpha$ a parameter introduced by Yasuda et al (1981). In the current study we adopt the methodology advocated in the previous study of Escudier et al (2001) to determine the five model parameters. In essence this involves the minimisation of $(1-\mu_M/\mu_C)^2$ where $\mu_M$ is the measured viscosity and $\mu_C$ is the value calculated from the Carreau-Yasuda equation at the measured shear rate. It is apparent that the data of Fig. 1b could be represented by one of the simpler viscosity models, such as the Sisko model, but for the sake of consistency we have chosen to use the Carreau-Yasuda model throughout.

The aim of the present work is to identify whether measurable changes in polymer-solution rheology are caused by the freeze-thaw process. A visual inspection of the log-log plots of Figs. 1a - 1c suggests that any changes, for all three fluids, are practically insignificant. To quantify any changes we have again followed the procedure developed in Escudier et al. The Carreau-Yasuda model was fitted to the fresh and thawed data to determine the ‘inherent’ standard deviation $\sigma_I$ (i.e. the standard deviation between the model fit and an individual data set) and the Pearson correlation coefficient $R$. The inherent standard deviation $\sigma_I$ can be attributed to two sources: first measurement uncertainty, associated with the rheometer and the measurement procedure, and second the degree to which the Carreau-Yasuda model adequately characterises the viscometric viscosity of a fluid. We define the standard deviation as

$$\sigma = \sqrt{\frac{\sum_{i}(1-\mu_M/\mu_C)^2}{N}}$$  \hspace{1cm} (2)

and the Pearson correlation coefficient, as defined by Weiss and Hassett, in this case is given by

$$R = \frac{N\sum_{i}\mu_M\mu_C - \sum_{i}\mu_M \sum_{i}\mu_C}{\sqrt{\left(\sum_{i}\mu_M^2 - \left(\sum_{i}\mu_M\right)^2\right) \left(\sum_{i}\mu_C^2 - \left(\sum_{i}\mu_C\right)^2\right)}}$$  \hspace{1cm} (3)

According to Syed Mustapha et al (1999), a correlation is unacceptably poor for rheological work of the type under discussion if $R < 0.9975$. We have preferred to list $(1 - R)$ so that acceptable correlations correspond to $(1 - R) < 2 \cdot 10^{-3}$. Table 1 includes the Carreau-Yasuda model parameters for the various fits, together with the number of data points, $N$, the inherent standard deviation,

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$\mu_0$ (Pa·s)</th>
<th>$\mu_\infty$ (Pa·s)</th>
<th>$\lambda_C$ (s)</th>
<th>$\eta$</th>
<th>$\alpha$</th>
<th>$N$</th>
<th>$\sigma_I$ (%)</th>
<th>$\sigma_C$ (%)</th>
<th>$(1 - R) \cdot 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR-PAA</td>
<td>15.9</td>
<td>0.00532</td>
<td>108</td>
<td>0.706</td>
<td>1.17</td>
<td>58</td>
<td>2.97</td>
<td>3.04</td>
<td>0.33</td>
</tr>
<tr>
<td>TH-PAA</td>
<td>16.0</td>
<td>0.00602</td>
<td>96.1</td>
<td>0.721</td>
<td>1.05</td>
<td>41</td>
<td>3.05</td>
<td>3.17</td>
<td>0.22</td>
</tr>
<tr>
<td>BOTH PAA</td>
<td>16.0</td>
<td>0.00572</td>
<td>103</td>
<td>0.713</td>
<td>1.12</td>
<td>99</td>
<td>3.10</td>
<td>3.10</td>
<td>0.34</td>
</tr>
<tr>
<td>FR-CMC/XG</td>
<td>7400</td>
<td>0.00350</td>
<td>77.8</td>
<td>0.818</td>
<td>0.0704</td>
<td>47</td>
<td>2.44</td>
<td>2.47</td>
<td>0.84</td>
</tr>
<tr>
<td>TH-CMC/XG</td>
<td>18.7</td>
<td>0.00340</td>
<td>653</td>
<td>0.560</td>
<td>0.264</td>
<td>47</td>
<td>2.64</td>
<td>2.70</td>
<td>0.26</td>
</tr>
<tr>
<td>BOTH CMC/XG</td>
<td>1251</td>
<td>0.00369</td>
<td>467</td>
<td>0.739</td>
<td>0.0913</td>
<td>94</td>
<td>2.59</td>
<td>2.59</td>
<td>0.64</td>
</tr>
<tr>
<td>FR-XG</td>
<td>13.2</td>
<td>0.00199</td>
<td>60.8</td>
<td>0.693</td>
<td>0.598</td>
<td>48</td>
<td>4.19</td>
<td>4.93</td>
<td>0.63</td>
</tr>
<tr>
<td>TH-XG</td>
<td>12.0</td>
<td>0.00241</td>
<td>75.2</td>
<td>0.669</td>
<td>0.706</td>
<td>32</td>
<td>4.12</td>
<td>5.00</td>
<td>0.74</td>
</tr>
<tr>
<td>BOTH XG</td>
<td>12.5</td>
<td>0.00190</td>
<td>72.1</td>
<td>0.673</td>
<td>0.670</td>
<td>80</td>
<td>4.97</td>
<td>4.97</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Table 1: Carreau-Yasuda model parameters and correlation statistics.
As can be seen the $(1 - R)$ criterion is well satisfied in all cases, the highest value of $(1 - R)$ being $8.3 \cdot 10^{-4}$.

Also included in Table 1 are the values for the standard deviation $\sigma_C$ for both the fresh (FR) and the thawed (TH) data sets for which $\mu_C$, was calculated from the curve fit of the Carreau-Yasuda model to the combined data sets for each fluid. The curves identified as “Carreau-Yasuda model fit” in Figs. 1a - 1c were determined using parameters derived from the combined data sets. It is worth noting that the Carreau-Yasuda model parameters in Table 1 for the fresh and thawed samples of the CMC/XG blend are significantly different from each other (compare the values of $\mu_0$ for example) and yet produce virtually identical fits (in terms of $\sigma_C$) and we conclude that the fluids are indistinguishable based on the closeness of the values of $\sigma_C$ and $\sigma_I$. The seemingly anomalous behaviour of the model parameters is a consequence of the purely empirical nature of the Carreau-Yasuda model i.e. it is not derived from microstructural or other physical considerations but is simply a curve-fit to the data and therefore different combinations of the model parameters can produce essentially identical fits.

The standard deviations $\sigma_I$ and $\sigma_C$ are presented as a bar chart in Fig. 2 to illustrate that the standard deviations are practically identical for each pair of fresh and thawed samples. A systematic influence of the freeze-thaw process on the rheology of the dilute polymeric liquids chosen for this study would have to be reflected in significantly increased values of $\sigma_C$. As $\sigma_C$ is no greater than would be the case for a fit determined from the combined data from two “fresh” samples (see Escudier et al), it must be concluded that there is no systematic effect of the freeze-thaw process on the viscometric viscosity.

Fig. 2 (left): Standard deviations $\sigma_I$ (xxx) and $\sigma_C$ (xxxx) based on the Carreau-Yasuda model for the three test fluids.

Fig. 3 (above): Storage modulus $G'$ and loss modulus $G''$ for fresh and thawed samples of a) (above) 0.125 % polyacrylamide, b) (middle) 0.1 % CMC / 0.1 % XG blend, c) (below) 0.25 % xanthan gum.
4.2 OSCILLATORY TESTS

To minimise the effects of inertia, the 60 mm diameter, 2˚ acrylic cone geometry was used to provide the oscillation data. A linearity check was conducted for each fluid to determine the linear viscoelastic region prior to each frequency sweep. Frequency sweeps were performed at two different shear-stress values, both within the linear viscoelastic region, and always showed good agreement, confirming that the viscoelastic properties observed were independent of the shear-stress value.

The storage modulus, \( G' \), and loss modulus, \( G'' \), for fresh and thawed samples are shown in Fig. 3. The smooth curves in Figs. 3a - 3c represent the results of fitting a four mode Maxwell model to the \( G' \) and \( G'' \) data:

\[
G' = \sum_{i=1}^{4} \frac{\eta \lambda \omega^2}{1 + (\lambda \omega)^2}
\]

\[
G'' = \sum_{i=1}^{4} \frac{\eta \omega}{1 + (\lambda \omega)^2}
\]

In agreement with the viscometric-viscosity data (Fig. 1), the influence of the freeze-thaw process on all three samples was found to be negligible. This is illustrated by the characteristic relaxation time \( \lambda \) for each data set (shown in Table 2) estimated using the following expression:

\[
\lambda = \frac{\sum_{i=1}^{4} \lambda_i \eta_i}{\sum_{i=1}^{4} \eta_i}
\]

As can be seen in Table 2 there is no systematic influence of the freeze-thaw process on the parameter \( \lambda \). In addition, for each fluid the \( \lambda \) values determined for fresh, thawed and combined data sets agree to within better than 4%. Also included in Table 2 are the standard deviations \( \sigma_l \) and \( \sigma_C \) as well as the \((1 - R)\) values for the \( G' \) and \( G'' \) fits, these statistical measures being defined in much the same way as those for the viscosity fits. As can be seen, the standard deviations are only marginally higher than those in Table 1. With two exceptions, the \((1 - R)\) values are also higher but still well within the limits for the correlations to be regarded as good. As has been found previously, in oscillation (Walters et al (1990)) the CMC/XG blend is the least viscoelastic (\( G'' > G' \)), then 0.25% XG (at low frequencies \( G'' > G' \) and at high frequencies \( G' > G'' \) with a crossover frequency of 0.35 rads\(^{-1}\)) and that PAA is the most viscoelastic as \( G' > G'' \).

4.3 CONCLUDING REMARKS

The conclusion of this work is that for the test polymer solutions, polyacrylamide, xanthan gum and a blend of carboxymethylcellulose/xanthan gum, the freeze-thaw process has no measurable effect on either the viscometric viscosity or the storage and loss moduli. Importantly, as the freeze-process does not impart rheological changes, this allows the possibility of cheap long-term storage for polymer solutions at a temperature of about \(-25^\circ C\). We are unaware of any alternative method for long-term storage of such polymer solutions. Further investigation is required before it may be safely concluded that these polymer solutions can be stored indefinitely as frozen samples. In addition, we shall be undertaking further research into the possible effect of the freeze/thaw process on the exten-
sional viscosity and on the first-normal stress difference for polymer solutions of higher concentration than those considered here.

**NOTATION**

- \( a \) constant in Carreau-Yasuda model
- \( G' \) storage modulus (Pa)
- \( G'' \) loss modulus (Pa)
- \( n \) power-law index
- \( N \) number of data points in sample
- \( R \) Pearson correlation coefficient
- \( \dot{\gamma} \) shear rate (\( \text{s}^{-1} \))
- \( \lambda \) relaxation time (s)
- \( \lambda_i \) relaxation time in Maxwell model (s)
- \( \eta_i \) dynamic viscosity in Maxwell model (Pa\( \cdot \)s)
- \( \lambda_{CY} \) time constant in Carreau-Yasuda model (s)
- \( \mu \) shear viscosity (Pa\( \cdot \)s)
- \( \mu_{CY} \) Carreau-Yasuda viscosity (Pa\( \cdot \)s)
- \( \mu_M \) measured viscosity (Pa\( \cdot \)s)
- \( \mu_0 \) zero-shear-rate viscosity (Pa\( \cdot \)s)
- \( \mu_{\infty} \) infinite-shear-rate viscosity (Pa\( \cdot \)s)
- \( \sigma \) standard deviation
- \( \sigma_C \) standard deviation between individual measured data set and fit to combined data set (i.e. 'BOTH')
- \( \sigma_I \) inherent standard deviation between individual measured data set and fit to that data set
- \( \omega \) angular frequency (rad\( \cdot \)s\( \text{ }^{-1} \))

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