Relations of rheological measurements to sagging and sedimentation of unsaturated polyester based gelcoats

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ABSTRACT
This is a presentation of a rheological study of unsaturated polyester based gelcoats. The study concentrated on relating practical problems in use of gelcoats, such as sagging and sedimentation to the rheological data.

Correlations were found between sagging results and creep tests. The sedimentation results correlated with both the yield stress results and the stress viscometry results.

INTRODUCTION
Sagging and sedimentation of gelcoats were studied. Gelcoats are polyester based paints which are used as a surface layer of moulded parts. They are primarily used in the marine industry. Gelcoat can be applied onto the mould either by spraying or brushing.

Rheology control is essential to the successful utilization of gelcoats. Rheology has a strong influence on such problems as levelling and sagging of applied gelcoat and sedimentation of particles in gelcoat during storage.

The purpose of this work was to find correlations for sagging and sedimentation with the rheological data. Different samples were measured by Bohlin controlled stress rotational rheometer. Rheological data was compared with the results from practical reference tests for sagging and sedimentation.

THEORY
Composition of a gelcoat system
Gelcoat is a dispersion, which consists of unsaturated polyester resins, monomers, pigments, hardener and several additives.

Thixotropic properties are needed in gelcoats to prevent sagging after the coating has been applied. Thixotropy of gelcoat is created by addition of silicon dioxide. Thixotropy is formed by a network system of weak chemical bonds. The viscosity at low shear rates is formed by this colloidal structure. The structure has little strength and is easily disrupted. However, in the case of minor shear stresses, which may cause sedimentation, such structure can offer a considerable resistance to flow¹.

Sagging
Sagging is a development of uneven coating caused by gravitational forces. Shear stress for sagging can be determined by Eq. 1.

\[ \tau = \rho g x \]  

(1)

where
\( \tau \)=shear stress for sagging
\( \rho \)=specific gravity of a gelcoat sample
\( g \)=acceleration due to a gravity, 9.81 m/s²
\( x \)=coating thickness

Sagging can be simulated by performing creep tests. A shear stress, calculated from
Eq. 1 is applied on the sample. The displacement with time is recorded and can be taken as a measure of the sagging sensitivity.

**Sedimentation**

It is very important that only a limited sedimentation takes place during the storage of gelcoats.

According to the Stokes law\(^1\) the sedimentation rate for the single particle can be calculated by Eq. 2.

\[
U_s = 2.18r^2(\rho - \rho_0)/\eta
\]

where

- \(U_s\) = sedimentation velocity for single particle
- \(r\) = radius of a particle
- \(\rho\) = density of a particle
- \(\rho_0\) = density of a resin
- \(\eta\) = viscosity of a resin

In Eq. 2 the sedimentation rate can be calculated by using the value of viscosity at a very low shear rate given by the stress viscometry test.

Bergström\(^2\) studied sedimentation of flocculated alumina suspensions. Conclusion was that the higher the materials compressive yield stress, the less it sediments. Compressive yield stress is very difficult to determine. However, the assumption can be made that if the material has high yield stress when compressed, it also has high yield stress when sheared. The yield stress by shear can be determined by rotational rheometer.

The Stokes Law assumes a viscous system, which is not the case in a gelcoat system, because it has a structure. Compressive yield stress gives a better characterization of the system with a structure.

**EXPERIMENTS**

**Materials**

Gelcoat samples of different Brookfield viscosities were prepared. The viscosity was controlled by silicon dioxide content. Three different base resins were used for sample preparation. Viscosity specifications are presented in Table 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Brookfield (\text{Pa}\cdot\text{s})</th>
<th>Used SiO(_2) content / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Serie 1</td>
<td>10 000</td>
<td>1,4-1,5</td>
</tr>
<tr>
<td>Serie 2</td>
<td>7 500</td>
<td>1,1-1,3</td>
</tr>
<tr>
<td>Serie 3</td>
<td>5 000</td>
<td>1,0</td>
</tr>
<tr>
<td>Serie 4</td>
<td>2 500</td>
<td>0,6-0,7</td>
</tr>
</tbody>
</table>

**Measurement methods**

Sagging was studied by spray test and by application test with the Leneta anti-sag meter.

In a spray test gelcoat was injected on a wall by a small syringe. Sagging was evaluated in centimeters after a predetermined time.

Applicator test blade for sagging has eleven notches for different coating thicknesses between 0,36...1,52 mm. Gelcoat is mixed with a hardener and applied on a test chart. The test chart is lifted on a vertical position after application. Sagging is observed after the gelcoat has cured. The applicator and the resulting test chart are presented in Fig. 1. Sagging is evaluated by measuring the distance between stripes.

![Figure 1. Applicator blade for sagging test and the test chart.](image-url)
Sedimentation was evaluated in glass cylinders after three months time. The height of a separated clear overphase was measured.

Rheological measurements were concentrated on creep tests, yield stress tests and stress viscometry tests.

RESULTS AND DISCUSSION

Study of sagging
Constant stress tests were performed by using the actual shear stresses for sagging, calculated by Eq. 1. Rheological data was compared with the results from the sagging tests. Good correlation was found between creep compliance and spray test results. The correlation is shown in Fig. 3. Sagging results given by the application test did not correlate as well with rheological results.

![Figure 3. Correlation between creep compliance and spray test results.](image)

Study of sedimentation
Sedimentation rate was calculated by Eq. 2, based on the Stokes law. Sedimentation rate was also determined from the sedimentation test results. Correlation between theoretical and experimental sedimentation rates is presented in Fig. 4.

Sedimentation test results were also compared with the yield stress results. This correlation, which is shown in Fig. 5 is better.

This can be explained by the fact that the Stokes Law is not valid for the fluids with the structure. The good correlation between yield stress and sedimentation tells that the yield stress is related to the storage stability of gelcoats.

![Figure 4. Correlation between theoretical and experimental sedimentation rates.](image)

![Figure 5. Correlation between sedimentation results and yield stress.](image)

A defect of the found correlations is that the formulations of the gelcoat samples are quite similar as the silicon dioxide content is the only variable parameter. Different types of gelcoat formulations ought to be tested to find out if these correlations are general or not.

REFERENCES