Fiber Thickening Phenomena in Fluid Coating with Nonlinear Rheological Solutions

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ABSTRACT

Fibers can be coated by passing them through a solution. In this paper, the thickness of the entrained film on the fiber was experimentally measured for various solutions such as water, polyacrylamide (PAA), and polyethylene glycol (PEG) aqueous solutions, and the effect of rheological properties of the solutions on the film thickness was studied. For low viscosity materials, such as water, the film thickness followed the Landau-Levich-Derjaguin (LLD) equation at low capillary number but, due to the inertial effect, it deviated away from the equation as the withdrawal velocity of fiber increased. The 3-D direct numerical simulation was performed to confirm the inertial effect on the entrained film thickness. For polymeric solution, the film-thickening rate against the capillary number was estimated by the LLD equation at low capillary number. However, the absolute value of the film thickness was far larger than that from the equation even when the withdrawal velocity was low. It could be considered the elongational deformation of polymer around fiber, which can be observed in the tubeless siphon phenomenon, affected the thickness of the polymeric film.

KEY WORDS
Fluid coating, Nonlinear rheology, Numerical simulation, Film thickening, Fiber coating

INTRODUCTION

Fluid coating is one of the key processing techniques for creating new functions in materials and adding values on the products. One of the typical fluid coating techniques is fiber coating, where a fiber is passed through a solution at a certain velocity and is coated with the entrained film. In the coating process, the thickness of the entrained film on the fiber varies according to the fiber velocity and properties of liquids as well as fiber material. Therefore, it is important to predict the thickness for realizing a stable production of fiber coating with a high quality.

There have been many researches on the prediction of the film thickness in the coating processes (Quéré, 1999), however, most of them have focused on coating with Newtonian fluids at low fiber velocity. Since in practice, fiber coating is carried out at high-speed with non-Newtonian fluids, such as
polymeric solutions (De Ryck et. al., 1998), surfactant solutions (Shen et. al., 2002) and suspensions, it is strongly desired to predict the film thickness of non-Newtonian fluid at higher fiber velocity. In this study, a fiber coating apparatus was newly developed to observe the thickness of the entrained film of several solutions. A numerical simulation was also performed by the Cubic Interpolated Propagation-Level Set (CIP-LSM) method (Y. Himeno et. al., 1999) to analyze the flow around the coated film and to understand the mechanisms of film thickening.

**EXPERIMENTS**

Fluids coating experiments were performed with water, polyacrylamide (PAA) and polyethylene glycol (PEG) aqueous solutions. The average molecular weights of PAA and PEG were 10,000 and 2,000,000, respectively. Three PAA solutions, whose concentrations were different, 0.25, 1.0, and 5.0 wt%, and two PEG solutions, whose concentration were 0.05 and 0.5 wt%, were prepared. The surface tensions were measured by the Wilhelmy method and the zero shear viscosities of solutions were measured by an Ostward viscometer and a couette rheometer (ARES, Rheometric Scientific F.E.). The resulting properties are listed in Table 1.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Concentration [wt%]</th>
<th>Surface tension [mN/m]</th>
<th>Zero shear viscosity [mPa·s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0</td>
<td>72.0</td>
<td>1.00</td>
</tr>
<tr>
<td>Polyacrylamide</td>
<td>0.25</td>
<td>63.0</td>
<td>1.005</td>
</tr>
<tr>
<td>$M_w = 10,000$ (PAA)</td>
<td>1.0</td>
<td>62.1</td>
<td>1.168</td>
</tr>
<tr>
<td>Polyethylene Glycol</td>
<td>0.05</td>
<td>63.9</td>
<td>1.767</td>
</tr>
<tr>
<td>$M_w = 2,000,000$(PEG)</td>
<td>0.5</td>
<td>63.7</td>
<td>45.00</td>
</tr>
</tbody>
</table>

Figure 1 shows a schematic diagram of the experimental setup of single fiber coating process. In the experiment, a optical glass fiber in 0.27 mm radius was used. The fiber was coated with a solution by passing it through the solution in the liquid bath, which is a cylindrical reservoir 5.0 cm in height and 2.0 cm in radius as illustrated in Fig. 1. The outer diameter of the coated fiber was measured every 1
second over 1 minute. The measuring point was located at 2 cm up from the solution surface of the liquid bath. By changing the fiber withdrawing speed from 0.2 to 1.0 m/s in each solution, the film thickness was measured.

RESULTS AND DISCUSSION

1. Fiber coating with Newtonian fluid (Water)

1.1. Experimental result

Figure 2 shows that the resulting film thickness against the fiber withdrawing velocity in the case that the fiber is coated with water. In Fig. 2, the solid line represents the film thickness calculated by the classical Landau-Levich-Derjaguin (LLD) equation. The equation is given by

\[ \frac{e}{b} = 1.34Ca^\frac{2}{3} = 1.34(\eta V / \Gamma)^\frac{2}{3} \]

where \( e \) is the entrained film thickness, \( b \) is the fiber radius, \( Ca \) is the capillary number, which is defined by the ratio of the viscous to the capillary forces, \( \eta \) is the viscosity of the solution, \( V \) is the fiber withdrawing velocity and \( \Gamma \) is the surface tension of the liquid.

The LLD equation was derived from a force balance among the viscous and the capillary terms (Quéré, 1999). The equation has been used at many occasions and shows excellent predictability at low capillary number. As can be seen in Fig.2, the entrained film thickness increases as fiber velocity increases. At the low fiber velocities, the variation in the thickness was well-predicted by the LLD equation. However, at the higher velocities, the thickness became larger than that from the LLD relation. The deviation of experimentally obtained film thickness increases drastically as the velocity increases. This is due to the inertial force. To estimate the inertial effect on fiber thickness at the high velocities, the following numerical simulations were performed.

1.2. Numerical simulation of the film thickness of fiber coating with water

At low fiber velocities, the capillary force is a dominant factor of determining film thickness.
However, the inertial force becomes dominant at high-speed condition. To confirm the effects of both capillary and inertial forces on the film thickness simultaneously, a numerical simulation was performed. The simulation codes were developed by employing the Cubic Interpolated Propagation-Level set Method (CIP-LSM) (Y. Himeno et. al, 1999) so as to capture the behavior of the free surface. The governing equations of CIP-LSM are as follows: The flows in the gas and the liquid phases are expressed by the Navier-Stokes equations:

\[
\frac{\partial \rho}{\partial t} + (\mathbf{u} \cdot \nabla) \rho = -\rho \nabla \cdot \mathbf{u},
\]

\[
\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \mathbf{\Pi} + \rho \mathbf{g},
\]

\[
\rho \frac{\partial e}{\partial t} + \rho (\mathbf{u} \cdot \nabla) e = \{\mathbf{\Pi} \cdot \nabla\} \cdot \mathbf{u} - \nabla \cdot \mathbf{q},
\]

where \( \mathbf{u} \) is the velocity, and \( \rho \) is the density of fluids. \( \mathbf{g} \) is gravity acceleration. \( e \) is the energy of fluids, and \( \mathbf{q} \) is the heat flux. \( \mathbf{\Pi} \) is the stress tensor, which is given by

\[
\mathbf{\Pi} = -p \mathbf{I} + \mathbf{T}_v + \mathbf{T}_\sigma,
\]

where \( \mathbf{I} \) is the unit tensor, \( \mathbf{T}_v \) is the viscous stress tensor and \( \mathbf{T}_\sigma \) is the surface tension tensor. \( p \) is the pressure of fluids. In addition to the Navier-Stokes equation, the equation determining the interface position is required:

\[
\frac{\partial \phi}{\partial t} + \mathbf{u} \cdot \nabla \phi = 0,
\]

where \( \phi \) is a level set function, which expresses the signed distance from interface.

If the level set function \( \phi \) at a certain point inside the calculation area has a negative value, the point is in liquid phase. If \( \phi \) at the certain point is a positive value, the point is in gas phase. If \( \phi \) at the point is zero, the point is on an interface. To capture the gas-liquid interface, Eq. (6) is used. By solving these equations, both fluid and interface behavior could be obtained.

Figure 3 shows a model of fiber coating used for numerical simulation. The region analyzed by the numerical simulation was 30 degree in the theta axis of the symmetrical cylindrical reservoir 5.0 cm in height and 2.0 cm in radius, which was the same height and radius as those of the reservoir used in experiment. A single fiber 0.5 mm in radius was located at the center of the reservoir and the size of the liquid solution phase was given as to be 2.0 cm in height and 2.0 cm in radius. As boundary conditions, non-slip condition was assumed at the solid wall of the reservoir as well as on the fiber surface, and zero-velocity gradient condition was assumed at the upper side of the analyzed region (reservoir). The initial fluid velocity was given to be zero and the contact angle of water on the fiber was assumed to be constant.

![Fig. 3 A schematic diagram of the calculation area.](image-url)
Figure 4 shows the comparison among experiments, the LLD prediction and simulation results. Figure 5 illustrates a snapshot of the velocity distribution at the water and air phases in the reservoir. The simulation results show good agreement with the experimental data over the wide range of fiber velocity. If the inertial term was excluded from the simulation equations, Eqs. (2)-(6), the simulation results by these equations far differed from experimental data. That is, the inertial force is a key factor determining the film thickness at the Newtonian fluids coating.

In addition, as the velocity increased, the unstable behavior of the film thickness became noticeable. The thickness was fluctuating owing to the inertial effect by which the water entrained on the fiber tends to slip down due to the gravity. This instability leads to a cause of the quality deterioration at practical fiber coating processes.

2. Fiber coating with Non-Newtonian fluid (PAA, PEG)

2.1 Experimental results

Figure 6 shows the experimental results of the fiber coating with PAA solutions. In the experiments, the concentration of PAA was changed from 0.25 to 5.0 wt%. Figure 7 also shows the experimental results of coating with PEG solution, which were obtained by changing the PEG concentration from 0.05 and 0.5 wt%. The film thickness obtained at the fiber coating with water is plotted for a comparison. In both figures, the solid and dotted lines respectively represent estimates of the LLD equation for the solutions of low and high concentrations. At low fiber velocity region and low concentration condition, the change in the polymer film thickness against the fiber velocity is close to...
those of the LLD equation. However, as increasing the concentration of polymer in solution, the thickness is much larger than that of the LLD even when the fiber withdrawing velocity is low. The deviation in film thickness from the LLD is more remarkable at the PEG solutions. It can be considered that a non-linear rheological character of polymeric solutions causes these film-thickening phenomena.

2.2 Rheology

To confirm the effect of the rheological properties on the film thickness, the rheological properties of the PEG solution were measured by using a couette rheometer (ARES, Rheometric Scientific F.E.). The steady shear viscosity curve of the 0.5 wt% PEG solution is illustrated in Fig. 8. The storage modulus ($G'$) and loss modulus ($G''$) of the solution are also plotted in Fig.9. The $G'$ and $G''$ of the PAA solutions could not be measured by the ARES owing to the sensitivity of the transducer.

Fig. 6 Dimensionless thickness vs. the fiber velocity for PAA solutions (●: PAA 0.25 wt%, ■: PAA 1.0 wt%, ▲: PAA 5.0 wt%, ○: water). The solid line is the LLD estimate for PAA 1.0 wt% and the dotted is for the PAA 5.0 wt%.

Fig. 7 Dimensionless thickness vs. the fiber velocity for PEG solutions (■: PEG 0.05 wt%, ▲: PEG 0.5 wt%, ○: water). The solid line is the LLD estimate for PEG 0.05 wt% and the dotted line is for PEG 0.5 wt%.

Fig. 8 Dependence of viscosity $\eta$ on shear rate at 0.5 wt% PEG solution.

Fig. 9 Storage and loss modulus, $G'$ and $G''$, as functions of frequency $\omega$ at 0.5 wt% PEG solution.
The PEG solution reveals a strong shear thinning behavior. The thickness of entrained film increases as the viscosity of the solution increases. Although the viscosity of 0.5 wt% PEG solution shows a strong shear thinning behavior, the film thickness was much larger than that of the LLD estimates even at low shear rates as shown in Fig.7. The thickening phenomena observed in this fiber coating process can be explained by the elongational flow. The LLD eq. is derived under the assumption that the shear force in thin coating film balances the surface tension. The shear thinning viscosity would reduce the film thickness owing to its small shear force. On the other hand, the thickness of fiber coating film is thinning along the fiber drawing direction. As a result, the elongational deformation occurs in the direction. The elongational deformation in concentrated polymer solution makes the film drawing force larger than that in dilute polymer solution does. Consequently, surpassing the shear shining effect, the film thickness becomes thicker than the value estimated by the LLD eq. The similar situation could be observed at the tube-less siphon phenomena.

The relaxation modes of $G'$ and $G''$ shown in Fig. 9 were fitted by the linear viscoelastic model, Eq. (7). The resulting parameters values are listed in Table 2.

$$G'(\omega) = \sum_{i=1}^{N} G_i \frac{(\omega \lambda_i)^2}{1 + (\omega \lambda_i)^2}, G''(\omega) = \sum_{i=1}^{N} G_i \frac{\omega \lambda_i}{1 + (\omega \lambda_i)^2}$$  \hspace{1cm} (7)

where $\lambda_i$ is the relaxation time and $G_i$ is the relaxation modulus of $i$ mode, respectively.

<table>
<thead>
<tr>
<th>Mode $i$</th>
<th>$\lambda_i$ [s]</th>
<th>$G_i$ [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0076</td>
<td>2.9992</td>
</tr>
<tr>
<td>2</td>
<td>0.3595</td>
<td>0.0309</td>
</tr>
<tr>
<td>3</td>
<td>0.0847</td>
<td>0.1606</td>
</tr>
</tbody>
</table>

$\eta_0 = 0.0475 \text{ Pa} \cdot \text{s}$

Average $\lambda = 0.1120 \text{ s}$

Average $G = 0.4243 \text{ Pa}$

From the relaxation spectrum of the 0.5 wt% PEG solution, the average relaxation time $\lambda$ ($= \sum G_i \lambda_i^2 / \sum G_i \lambda_i$) of the solution was calculated to be 0.11s. The average elongational strain rate $\dot{\varepsilon}$ in the drawing direction is given by a decrease rate of the coating film thickness:

$$\dot{\varepsilon} = -2(V/L) \ln \left[ \varepsilon/(\text{Del}-b) \right]$$  \hspace{1cm} (8)

where, $\text{Del}$ is the initial coating film thickness at the elongational flow region. Although the $\dot{\varepsilon}$ depends on the $\text{Del}$, the order of $\dot{\varepsilon}$ is $10 \text{ s}^{-1}$ under the condition that $L = 2 \text{ cm}$, $b = 0.027 \text{ cm}$, $V=20 \text{ cm/s}$, $\varepsilon/b \sim 2$.
and $\Delta \sim 2b$ for PEG 0.5 wt %. Thus, elongational strain, $\dot{\varepsilon}_e$, became larger than one. Therefore, the PEG molecules were stretched and a strain thickening was induced by the entanglement of the molecules. Since the tensile strength of entangled polymeric liquids is larger than the normal stress induced by shear flow, the elongational flow becomes much effective on the film thickness than shear flow when low withdraw velocity for polymeric solution.

**CONCLUSIONS**

The thickness of film coating the fiber was measured by passing the fiber in several solutions, water, PAA and PEG solutions. The thickness of water coating the fiber could be predicted by the LLD equation at low capillary number. However, the inertial effect becomes effective as the withdrawal velocity increases. The 3-D direct numerical simulation confirmed the inertial effect. The numerical simulation could show the instabilities in film thickness at high-speed fiber velocity, which was also observed in our experiments. For polymer solutions, the LLD equation could not predict the film thickness even at the low velocity region. The film thickness becomes larger than that the LLD predicted. The discrepancy might be explain by the elongation deformation around fiber, however, no clear explanation was given yet. Though the current 3-D simulation performed in this study was not yet applicable to polymeric solutions due to the difficulty in dealing with viscoelastic equation for high shear rate situation, the simulation study will be a powerful tool to analyze the film thickening phenomena.

**REFERENCES**