The Influence of K-Value and Plasticizer Type on the Rheological Behaviour of Plastisol Used in Coated Fabrics

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ABSTRACT

Coating offers a wide variety of methods by which one can process textile and film webs for various end uses. The materials to be processed, the coating, the required properties of the finished product, and the cost-effectiveness of manufacture often dictate in choosing the best method. A best system is ultimately the one that produces the relevant product, manufactured by the most economical method. In this research work major coating techniques used in coating fabrics were briefly mentioned and their rheological requirements were outlined. Coating pastes need to have very specific rheological properties because of the methods in which they are applied. In this study, rheological measurements of paste using DOP and DOA plasticizer and PVC-E with three K-values (69, 70 and 75) were studied. The results indicated that the PVC K-value and plasticizer type could influence the rheological behaviour. Under studied condition the coating pastes were non-Newtonian pseudoplastic to Newtonian behaviour. The information presented here could help the right selection of coating and laminating method.

INTRODUCTION

Coating machinery and techniques as applied to continuous web processing can essentially be divided into three main sections:
- knife coating,
- roll coating,
- specialty coating.

Knife coating techniques and equipment cover the range from knife over roll, floating knife, knife over blanket or apron, and knife over plate. These techniques were considered to be the most straightforward type of coating. The gap between the
knife and either the roll or support surface determines the thickness of coating to be applied to a substrate.

Roll coaters are more sophisticated and are generally considered to include gravure (direct, reverse, indirect and offset), kiss, Mayer rod (wire wound bar), and ultimately reverse roll coating.

Specialty coating techniques would involve the use of hot melt coaters, slot dye coater, etc [1-10].

**Knife Coating**

Knife coating is one of the most fundamental and oldest forms of coating. It essentially applies a coating or adhesive to a web substrate by the action of the web moving beneath the knife, thereby spreading the coating. Because of the different types of webs that are coated using this method, various knife coaters are used. Generally, the acute angled knife is used for light, thin, non-penetration coatings, wide or rounded bevel knives, for thick coatings; heeled knives, for precise coatings (Figure 1) [7-10].

Some of the most important features involving knife coating include gap control, by which the coating thickness is basically determined; coating blade configuration, which controls the penetration and surface finish of a coating; the position and angle of the coating blade with respect to the substrate; and the tension in the web being coated. Of equal importance are the viscosity and physical characteristics of coating viscosities, from approximately 5000 cps to well over 100000 cps [9].

As mentioned above the knife coating can be subdivided into several methods. A brief description for these methods are presented here:

Knife over roll coating is shown in Figure 2. In this method the web is supported over driven anvil roll as it passes beneath the knife to be coated.

In floating knife coating, the web tension is the most important factor.

In knife over blanket coating, the blade configuration, and blade angle play an important role in the coating of the product.

In knife over plate coating the substrate is caught between the blade and the support plate [1-12].

**Roll Coating**

Roll coating offers a different technology one which not only allows the direct application of a coating to a substrate as seen in knife coating, but also, one which
allows a metered amount of coating to be applied in a uniform manner, even to a non-uniform substrate. In this method substrate usually passes between the nip of two rolls, or has a measured thickness of coating applied from a roll by the transfer method. Roll coating is predominately used for low to mid-range viscosity (100-2000 mPas) applications, over a wide range of coating speeds. Variations within the systems include kiss coating, gravure, offset and reverse roll coating. Each of the latter methods plays a role in the smoothness of the roll coating as well as in its thickness.

In roll coating, the important features include the type of application (gravure, direct, kiss or reverse roll); the gap between rolls used for metering such a coating, the relative speed of the coating roll to the substrate; and the viscosity as well as physical characteristics of the coating itself. As in knife coating, web tension is again an important feature [2].

Kiss coating as shown in Figure 3, applies materials to a web without the use of back-up roll for the web. Generally, kiss coaters are used as adhesive applicators and not coaters in a strict sense [3].

Gravure method, as shown in Figure 4 involves the use of various engraved applicator rolls, each of whose engraving offers a given amount of coating application based upon the properties of the coating [1-3].

In unsmooth coating, metering devices such as wire-wound (Mayer) rods are used [1-2].

Offset gravure coater, is primarily used for higher speed applications [1,2,4,5].

Direct Roll coating as shown in Figure 5; as well as reverse roll coater with additional means of controlling coating thickness are the most versatile of coating techniques [1,4].

Specialty Coating
In addition to the above coating equipment, there are a series of systems such as dip, calendaring, screen, air knife, extrusion and hot melt coating used for special applications [7,8].

Important rheological parameters for most of the above coating techniques are presented in Table 1 [13].
According to the above descriptions, each applicator produces a different shear to the coating pastes at various machines; therefore, coating pastes need to have specific rheological properties to perform well. The viscosity range involved can clearly be seen and the shear rate can be calculated using the gap and speed data presented [8,10].

One of the main reasons for using a plastisol, vinyl solution is to take advantage of the ease processing, and usually low equipment costs, that are inherent fluid sys-

### Table 1. Features of coating methods.

<table>
<thead>
<tr>
<th>Coating method</th>
<th>Base materiala</th>
<th>Coating compositionb</th>
<th>Usual coating speed (m min⁻¹)</th>
<th>Viscosity range (mPas)</th>
<th>Wet-coating thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air knife</td>
<td>B, D</td>
<td>R, T, X</td>
<td>15-600</td>
<td>1-500</td>
<td>25-60</td>
</tr>
<tr>
<td>Calender</td>
<td>A, B, D, E</td>
<td>U, V, W</td>
<td>5-90</td>
<td>100-500</td>
<td>50-500</td>
</tr>
<tr>
<td>Cast-coating</td>
<td>A, B</td>
<td>Q, R, S, TV, Y</td>
<td>3-60</td>
<td>1000-5000</td>
<td>50-500</td>
</tr>
<tr>
<td>Curtain</td>
<td>A, B, C, D, E, F</td>
<td>R, S, V, X, Z</td>
<td>20-400</td>
<td>100-20000</td>
<td>25-250</td>
</tr>
<tr>
<td>Extrusion</td>
<td>A, B, D, E</td>
<td>T, U, V, W</td>
<td>20-900</td>
<td>30000-50000</td>
<td>12-50</td>
</tr>
<tr>
<td>Floating knife</td>
<td>A, B</td>
<td>R, S, T, V, X, Y, Z</td>
<td>3-30</td>
<td>500-50000</td>
<td>50-250</td>
</tr>
<tr>
<td>Kiss roll</td>
<td>A, B, C, D, E, F</td>
<td>R, S, V, X, Z</td>
<td>30-300</td>
<td>100-20000</td>
<td>25-125</td>
</tr>
<tr>
<td>Knife-over-blanket</td>
<td>A, B</td>
<td>R, S, T, V, X, Y, Z</td>
<td>3-30</td>
<td>500-50000</td>
<td>50-250</td>
</tr>
<tr>
<td>Offset gravure</td>
<td>B, D</td>
<td>R, S, T, Z</td>
<td>30-600</td>
<td>50-500</td>
<td>12-25</td>
</tr>
<tr>
<td>Reverse-smoothing roll</td>
<td>A, B</td>
<td>R, T, X</td>
<td>15-300</td>
<td>1000-5000</td>
<td>25-75</td>
</tr>
<tr>
<td>Sprays</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Airless spray</td>
<td>A, B, C,D,E,F,G</td>
<td>S, T, V, X, Y, Z</td>
<td>3-90</td>
<td>C</td>
<td>2-250</td>
</tr>
<tr>
<td>Air spray</td>
<td>A, B, C,D,E,F,G</td>
<td>S, T, V, X, Y, Z</td>
<td>3-90</td>
<td>C</td>
<td>2-250</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>A, B, C,D,E,F,G</td>
<td>S, T, V, X, Y, Z</td>
<td>3-90</td>
<td>C</td>
<td>2-250</td>
</tr>
<tr>
<td>Squeeze roll</td>
<td>A, B, C, D, E, F</td>
<td>R, S, T, U, V, X, Y</td>
<td>30-700</td>
<td>100-5000</td>
<td>25-125</td>
</tr>
<tr>
<td>In situ polymerization</td>
<td>A, B, C,D,E,F,G</td>
<td>Y, Z</td>
<td>Undetermined</td>
<td>Liquid or vapour</td>
<td>6-25</td>
</tr>
<tr>
<td>Powdered resin</td>
<td>A, B, C, E, F, G</td>
<td>Q</td>
<td>3-60</td>
<td>Liquid or vapour</td>
<td>25-250c</td>
</tr>
<tr>
<td>Electrostatic spray</td>
<td>A, B, C, E, F, G</td>
<td>Q</td>
<td></td>
<td></td>
<td>25-75c</td>
</tr>
<tr>
<td>Fluidized bed</td>
<td>E, G</td>
<td>Q</td>
<td></td>
<td></td>
<td>200-2000c</td>
</tr>
</tbody>
</table>

(a) Key: A = woven and nonwoven textiles; B = paper and paperboard; C = plywood and pressed fiberboard’s; D = plastic films and cellophane; E = metal sheet, or foil; F = irregular flat items; G = irregularly shaped.

(b) Key: Q = powdered resin composites; R = aqueous latex, emulsions, dispersions; S = organic lacquer solutions and dispersions; T = plastisol and compositions; U = natural and synthetic rubber compositions; V = hot-melt compositions; W = thermoplastic masses; X = oleoresinous compositions; Y = reacting formulations, e.g., epoxy and polyester; Z = plastic monomers.

(c) Dry thickness.
A fluid can be anything from a substance of water-like consistency to a highly plastic like mass. There are many parameters that can influence the rheological behaviour, such as processing conditions, temperature, plastisol content, K-value, and plastisol type [11]. Paste rheology and flow behaviour are important parameters during coating applications and influence the final product’s properties. A review of literature shows the level of the importance, and many results have been published [14-21]. Importance to the process is precise control of the rheological characteristics of the coating mixture; therefore, it is necessary to have a model to represent the rheological behaviour of the mixture [21,22]. Generally speaking for Newtonian fluids, the viscosity is independent of the shear rate and can easily be calculated. For non-Newtonian fluids, however, the viscosity varies with shear rate. Thus, the viscosity must be as a function of the shear rate to represent the rheological behaviour of the coating paste. In this research work, the rheological analysis was carried out in terms of non-Newtonian power-law model (also known as the Ostwald-deWaele equation). The shear stress and shear rate relation for power-law fluids is given by:

\[ \tau = k\dot{\gamma}^n \]  

(1)

where, \( \tau \) is the shear stress, \( k \) is a constant (consistency index), \( \dot{\gamma} \) is the shear rate, and \( n \) is also a constant (named a power-law constant or power-law index). If 0<n<1, the fluid is pseudoplastic, for n=1, the fluid is Newtonian and for n>1, it is dilatant or shear thickening [11].

The degree of pseudoplasticity can be obtained by determining the shear thinning index (n) value of each paste as per the following relationship:

\[ \log \tau = \log k + n \log \dot{\gamma} \]  

(2)

Hence, by plotting \( \log \tau \) versus \( \log \dot{\gamma} \) for different pastes, the value of n for each paste is the slope of the corresponding plot. The consistency index can be determined from the intercept elevation of the corresponding curves. The apparent viscosity, \( \mu_a \), for a power law fluid is expressed by the following formula [22,23]:

\[ \mu_a = k \dot{\gamma}^{n-1} \]  

(4)

The viscosity \( \mu_a \) decreases with the increase of shear rate \( \dot{\gamma} \) for n<1, and \( \mu_a \) increases with increase of \( \dot{\gamma} \) for n>1.

EXPERIMENTAL

Materials

Polyvinyl chloride emulsion (PVC-E) with K-values of 69, 70 and 75; (VESTOLIT) stabilizer; co-stabilizer (Lankromark LZB 753, Akros Chemicals), plasticizer (dioctylphthalate (DOP) and dioctyladipate (DOA)) and calcium carbonate as filler were used for coating pastes.

Formulation

PVC-E 100 (phr), stabilizer 2 (phr), co-stabilizer 2 (phr), filler 15 (phr) and plasticizer 30 (phr).

Rheological Measurements

Rheological measurements were carried out using a Hakke Rotovisco RV12 coaxial viscometer (as shown in Figure 6). The temperature of the circulating bath was kept at 20–0.1 C. 10 Various speeds of the drive were used to produce shear rate in the range 89-455.68s\(^{-1}\). According to eqns (5-7) the shear stress (Pa), shear rate (s\(^{-1}\)) and viscosity (mPa.s) were calculated.

Shear stress: \( \tau = A.S \) (Pa)  

(5)

Shear rate: \( D = M.n \) (s\(^{-1}\))  

(6)

Viscosity \( \eta = \frac{G.S}{n} \) (mPa.s)  

(7)

where:

\( A \) = shear stress factor, depending on type of measuring drive unit and sensor system (Pa/scale grad.).

\( M \) = shear rate factor, depending on sensor system (min/s).

\( G \) = instrument factor, depending on the type of measuring drive unit and sensor system grad.

\( n \) = actual test speed (min\(^{-1}\)).

\( s \) = measuring value (scale grad.).

RESULTS AND DISCUSSION

The flow curves indicated that the pastes are character-
ized by a non-Newtonian pseudoplastic flow or Newtonian fluid under the studied condition as an example is shown in Figure 7. It can be seen, irrespective of the type of paste that the viscosity decreases on increasing the shearing rate and there is no sign of yield stress. This decrease should be attributed to better orientation of polymer particles in the direction of rotation at higher shearing rates, thereby offering less resistant to flow. In Figure 8 the changes of viscosity versus shear rate for coating paste that comprises PVC E-69 and DOA plasticizer are shown. Graphs of log \( \tau \) (shear stress) versus log \( \gamma \) for all pastes have been plotted. From the corresponding slope of the curve and intercept-elevation, values of \( n \) (power-law index) and \( k \) (consistency index) were determined (Figures 9-13).

The power-law index, \( n \), and consistency index, \( k \), of coating pastes are listed in Table 2. Consistency index is a measure of the fluid, for the higher \( k \), i.e. the more viscous fluid.

In practice it has been common to characterize the molecular weight of a PVC polymer by its Fikentscher K-value rather than to quote an actual figure for molecular weight. This is not the same \( k \) as given in the power-law equation. The K-value is obtained from the following relationship and it is a measure of the molecular weight, for the lower the K-value the lower the molecular weight would be obtained [24].

\[
\log \eta_{rel} = \left( \frac{75K^2}{1 + 1.5KC \times 10^{-3}} \right) + \left( K \times 10^{-3} \right) C \quad (8)
\]

Where, \( \eta_{rel} \) = relative viscosity = \( \frac{\text{solvent viscosity}}{\text{solution viscosity}} \),

\[ K = \text{K-value and } C = \text{concentration in g/100mL} \]

---

**Table 2**

<table>
<thead>
<tr>
<th>Sensor system</th>
<th>SV I</th>
<th>SV II</th>
<th>SV IIIFL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner cylinder (rotor)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>radius, ( R_i ) (mm)</td>
<td>10.1</td>
<td>10.1</td>
<td>10.1</td>
</tr>
<tr>
<td>height, ( L ) (mm)</td>
<td>61.4</td>
<td>19.6</td>
<td>19.6</td>
</tr>
<tr>
<td>Outer cylinder (cup)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>radius, ( R_o ) (mm)</td>
<td>11.55</td>
<td>11.55</td>
<td>11.55</td>
</tr>
<tr>
<td>Radii ratio, ( R_o/R_i )</td>
<td>1.14</td>
<td>1.14</td>
<td>-</td>
</tr>
<tr>
<td>Sample volume, ( V ) (mL)</td>
<td>12</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>Temperature: max (°C)</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>min (°C)</td>
<td>-30</td>
<td>-30</td>
<td>-30</td>
</tr>
<tr>
<td>Calculation factors</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A ) (Pa/scale grad.)</td>
<td>12.4</td>
<td>37.6</td>
<td>28.0</td>
</tr>
<tr>
<td>( M ) (min/s)</td>
<td>0.89</td>
<td>0.89</td>
<td>-</td>
</tr>
<tr>
<td>( G ) (mPa.s/scale grad. min)</td>
<td>13920</td>
<td>42260</td>
<td>79500</td>
</tr>
</tbody>
</table>

**Figure 6.** Hakke rotovisco RV12 coaxial viscometer.
Figure 8. Plot of viscosity (mPas) vs. shear rate for coating paste: PVC-E (69) and DOA plasticizer.

Figure 9. Plot of log shear stress vs. log shear rate for coating paste: PVC-E (69) and DOA plasticizer.

Figure 10. Plot of log shear stress vs. log shear rate for coating paste: PVC-E (70) and DOA plasticizer.

Figure 11. Plot of log shear stress vs. log shear rate for coating paste: PVC-E (70) and DOP plasticizer.

Figure 12. Plot of log shear stress vs. log shear rate for coating paste: PVC-E (70) and DOP plasticizer.

Figure 13. Plot of log shear stress vs. log shear rate for coating paste: PVC-E (75) and DOP plasticizer.
The results obtained show clearly higher $k$ (consistency index) are obtained for higher K-value and deviation from non-Newtonian behaviour is reflected in the figures obtained for $n$ (power-law index).

Dioctylphthalate (DOP) has higher, molecular weight, specific gravity and viscosity than the dioctyladipate (DOA) [25]. Rheological results obtained have been influenced by these differences as reflected in the $k$ and $n$ values shown in Table 2.

Power-law index, also called shear thinning index, is a measure of the degree of non-Newtonian behaviour, and greater the departure from unity the more pronounced are the non-Newtonian properties of paste. When $n$ is close to one, the viscosity is independent of the shear rate.

<table>
<thead>
<tr>
<th>K-value 69</th>
<th>K-value 70</th>
<th>K-value 75</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DOA</td>
<td>DOP</td>
</tr>
<tr>
<td>$n$</td>
<td>$k$</td>
<td>$n$</td>
</tr>
<tr>
<td>0.88</td>
<td>16.70</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td>91.62</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table 2. Consistency ($k$) and power law index ($n$) values for different K-values and plasticizer type ($p=$ content of plasticizer (phr)).

CONCLUSION

One of the main causes for rheological behaviour of a paste is the dispersion caused by the plasticizer in diffusing into the PVC core placing itself between the PVC polymer or between the closely spaced microcrystalline areas. In this research work it has been shown that the nature of plasticizer (DOP, DOA) and polymer (K-value) can have great influence on the rheological behaviour that plays an important role in coating processes. In many instances it is necessary to increase or decrease the viscosity of the coating pastes, and this can be done by the right choice of plasticizer or PVC K-value.

REFERENCES


