Iranian Polymer Journal
13 (5), 2004, 371-379

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

Ali Zadhoush, Mohammad A. Alsharif, and Pouyan Esmailzadeh Boukany

Department of Textiles Engineering, Isfahan University of Technology, Isfahan-84154, I.R. Iran

Received 12 May 2003; accepted 2 June 2004

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.

Key Words:
coating techniques;
poly (vinyl chloride);
rheological properties;
plastisol;
coated fabrics.

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

---

(∗)To whom correspondence should be addressed.
E-mail: zadhoush@cc.iut.ac.ir

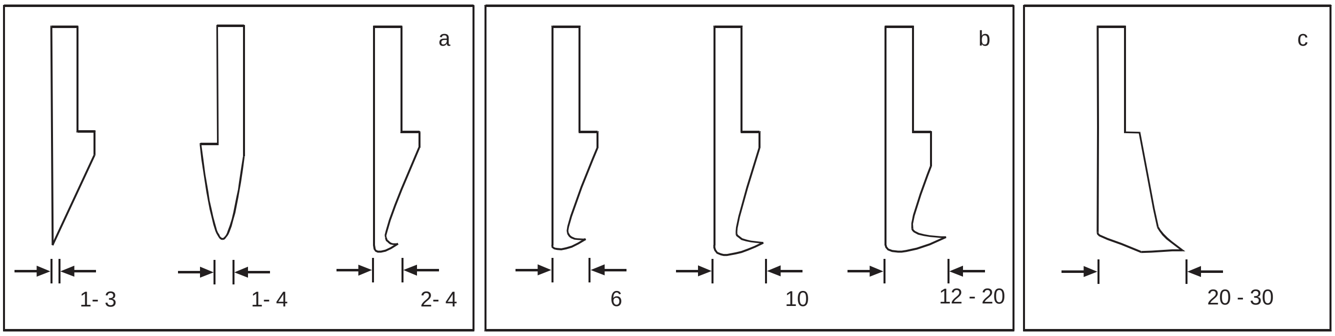


Figure 1. Shape of knifes. (a) air knife, (b) knife on rubber blanket, and (c) knife over roll.

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

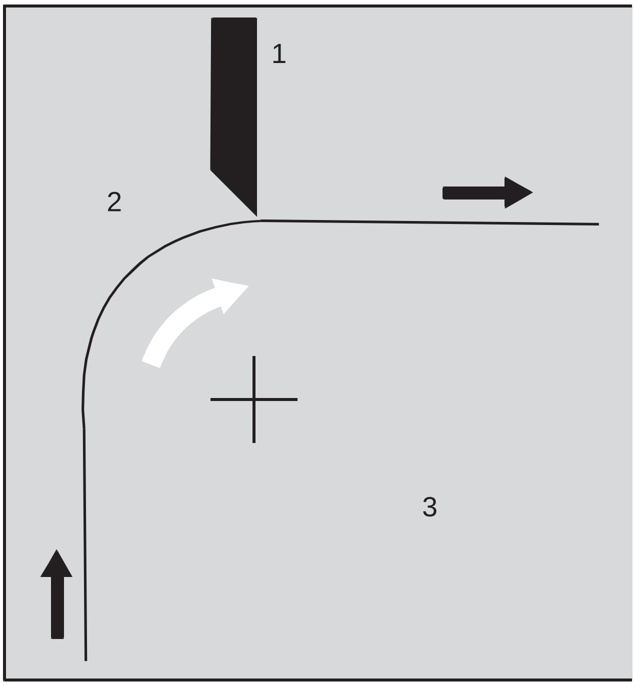


Figure 2. Schematic knife over roll coater: (1) coating knife; (2) coating liquid; and (3) backing roll.

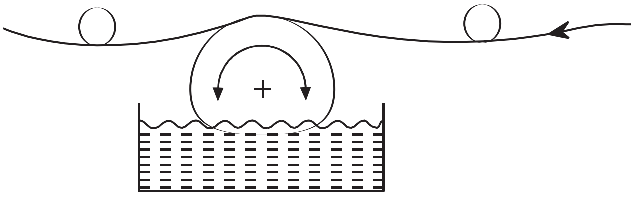


Figure 3. Schematic kiss roll coating.

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].

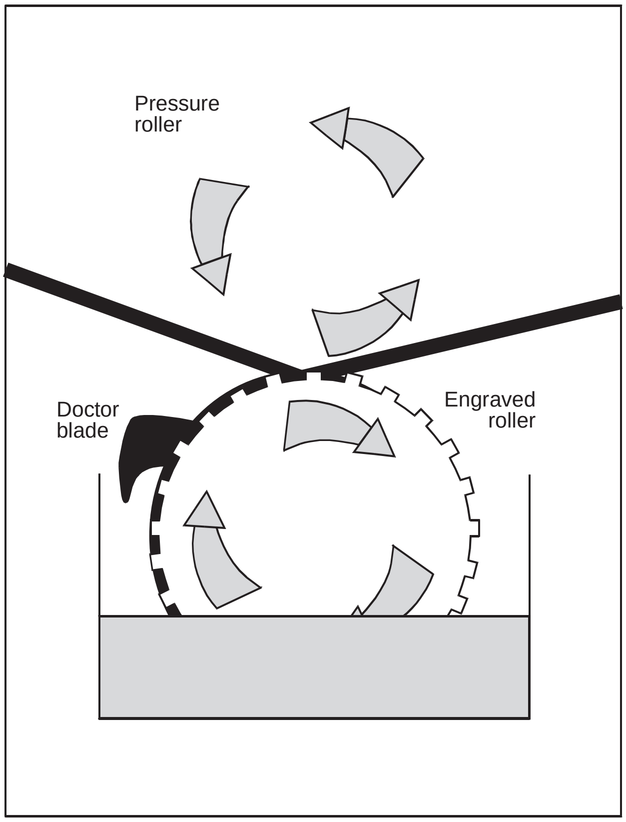


Figure 4. Gravure roll coating.

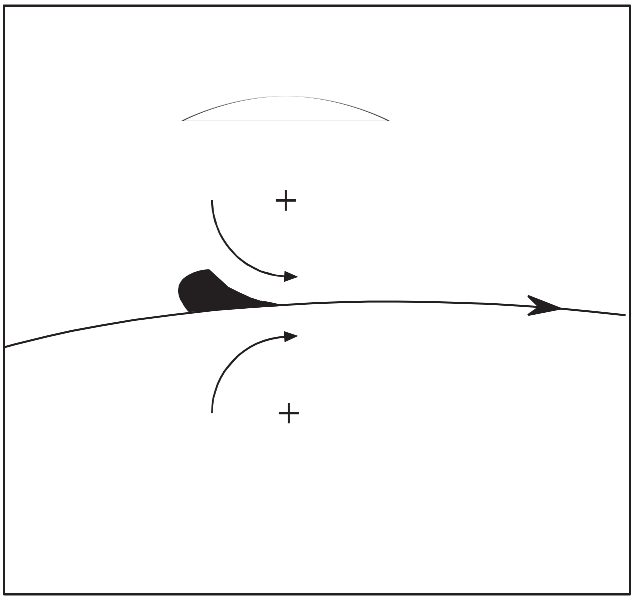


Figure 5. Direct roll coating [13].

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].

Table 1. Features of coating methods.

Coating method	Base material[a]	Coating composition[b]	Usual coating speed (m min^{-1})	Viscosity range (mPas)	Wet-coating thickness (μm)
Air knife	B, D	R, T, X	15-600	1-500	25-60
Brush	B, C, E, F, G	R, S, X, Z	30-120	100-2000	50-200
Calender	A, B, D, E	U, V, W	5-90		100-500
Cast-coating	A, B, D	Q, R, S, TV, Y	3-60	1000-500	50-500
Curtain	A, B, C, D, E, F	R, S, V, X, Z	20-400	100-20000	25-250
Dip	A, B, D, E, F, G	R, S, V, X, Y, Z	15-200	100-1000	25-250
Extrusion	A, B, D, E	T, U, V, W	20-900	30000-50000	12-50
Blade	A, B	R, S, T, V, X, Y, Z	300-600	5000-10000	12-25
Floating knife	A, B, D	R, S, T, V, X, Y, Z	3-30	500-5000	50-250
Gravure	A, B, D, E	R, S, T, U, V, Y, Z	2-450	100-1000	12-50
Kiss roll	A, B, C, D, E, F	R, S, V, X, Z	30-300	100-2000	25-125
Knife-over-blanket	A, B, D	R, S, T, V, X, Y, Z	3-30	500-5000	50-250
Knife-over-roll	A, B, C, D, E	R, S, T, U,V,X,Y,Z	3-60	1000-10000	50-500
Offset gravure	B, D	R, S, T, Z	30-600	50-500	12-25
Reverse roll	A, B, C, D, E, F	R, S, T, U,V,X,Y,Z	30-300	50-20000	50-500
Reverse-smoothing roll	A, B	R, T, X	15-300	1000-5000	25-75
Rod	B, D	R, S, T, V, X, Y, Z	3-150	50-500	25-125
Sprays					
Airless spray	A, B, C,D,E,F,G	S, T, V, X, Y, Z	3-90	C	2-250
Air spray	A, B, C,D,E,F,G	S, T, V, X, Y, Z	3-90	C	2-250
Electrostatic	A, B, C,D,E,F,G	S, T, V, X, Y, Z	3-90	C	2-250
Squeeze roll	A, B, C, D, E, F	R, S, T, U, V, X, Y	30-700	100-5000	25-125
In situ polymerization	A, B, C,D,E,F,G	Y, Z	Undetermined	Liquid or vapour	6-25
Powdered resin	A, B, C, E, F, G	Q	3-60		25-250c
Electrostatic spray		Q			25-75c
Fluidized bed	E, G	Q			200-2000c

(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.

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 system. 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:

$$\tau = k\dot{\gamma}^{n} \qquad (1)$$

where, τ 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:

$$\log \tau = \log k + n \log \dot{\gamma} \qquad (2)$$

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, μ_a, for a power law fluid is expressed by the following formula [22,23]:

$$\mu_a = \frac{\tau}{\dot{\gamma}} \qquad (3)$$

The apparent viscosity can be written by the Ostwald-deWaele mode as follows:

$$\mu_a = k\dot{\gamma}^{n-1} \qquad (4)$$

The viscosity μ_a decreases with the increase of shear rate $\dot{\gamma}$ for $n<1$, and μ_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 89-455.68 s^{-1}. According to eqns (5-7) the shear stress (Pa), shear rate (s^{-1}) and viscosity (mPa.s) were calculated.

$$\text{Shear stress: } \tau = A.S \text{ (Pa)} \qquad (5)$$

$$\text{Shear rate: } D = M.n \text{ } (s^{-1}) \qquad (6)$$

$$\text{Viscosity } \eta = \frac{G.S}{n} \text{ (mPa.s)} \qquad (7)$$

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).

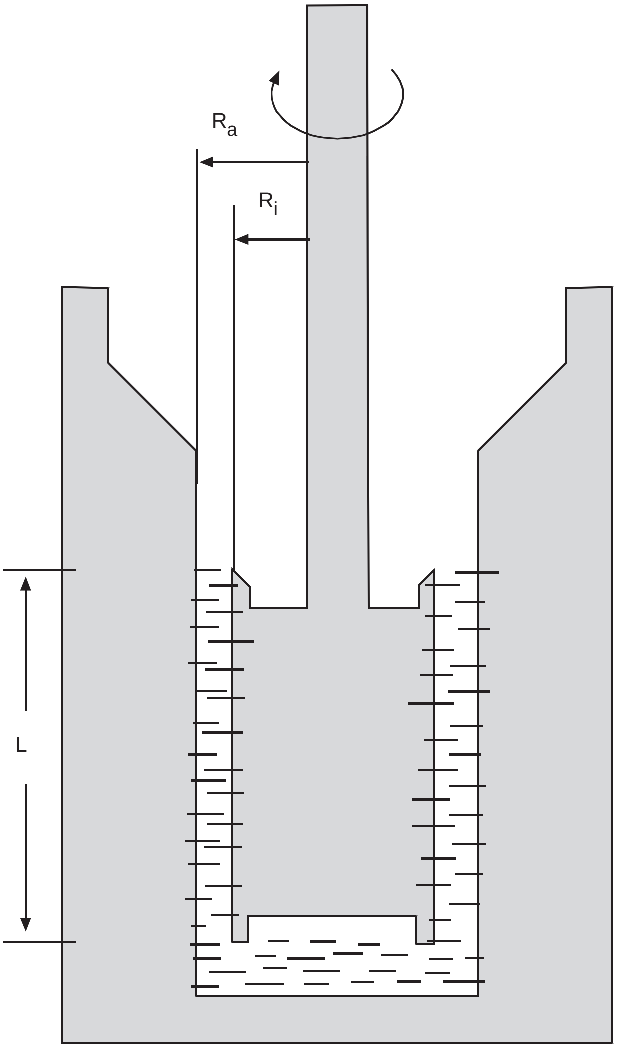
G = instrument factor, depending on the type of measuring drive unit and sensor system grad.

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

s = measuring value (scale grad.).

RESULTS AND DISCUSSION

The flow curves indicated that the pastes are character-



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

Figure 6. Hakke rotovisco RV12 coaxial viscometer.

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 τ (shear stress) versus log γ 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].

$$\log \eta_{rel} = [(\frac{75K^2 \times 10^{-6}}{1+1.5KC \times 10^{-3}}) + (K \times 10^{-3})]C \tag{8}$$

Where, η_{rel} = relative viscosity = $\frac{\text{solvent viscosity}}{\text{solution viscosity}}$,
K = K-value and C = concentration in g/100mL

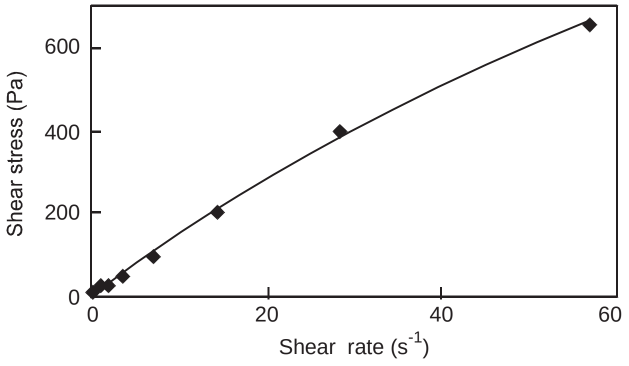


Figure 7. Plot of shear stress vs. shear rate for coating paste: PVC-E (69) and DOA plasticizer.

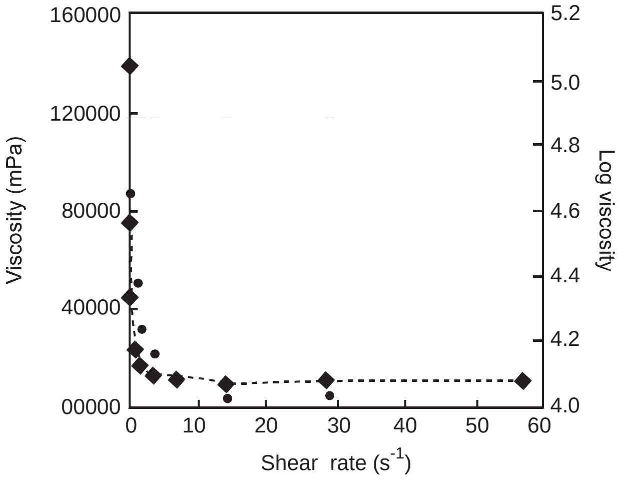


Figure 8. Plot of viscosity (mPas) vs. shear rate for coating paste: PVC-E (69) and DOA plasticizer.

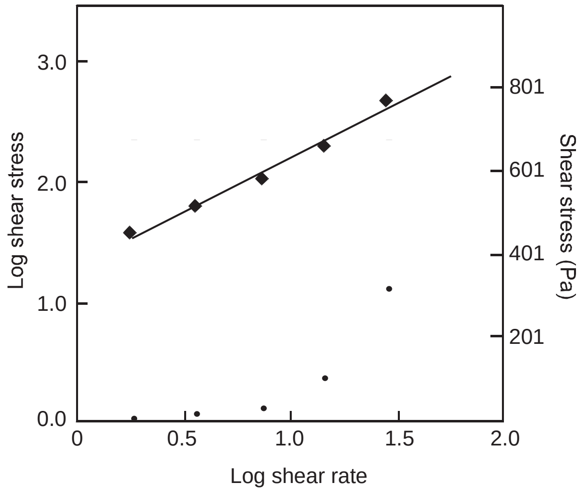


Figure 11. Plot of log shear stress vs. log shear rate for coating paste: PVC-E (70) and DOA plasticizer.

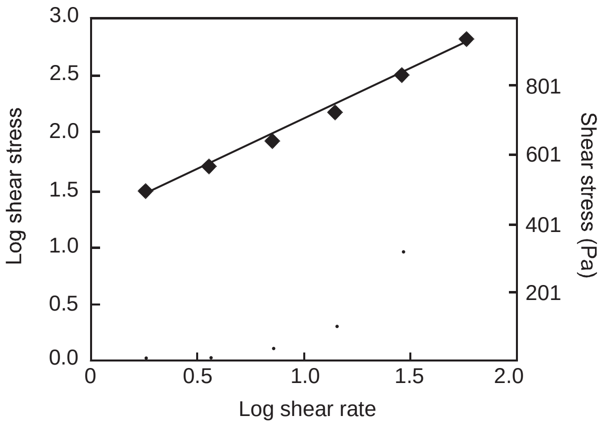


Figure 9. Plot of log shear stress vs. log shear rate for coating paste: PVC-E (69) and DOA plasticizer.

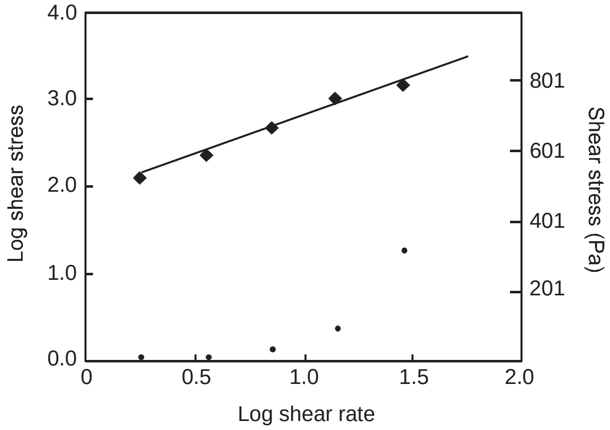


Figure 12. Plot of log shear stress vs. log shear rate for coating paste: PVC-E (70) and DOP plasticizer.

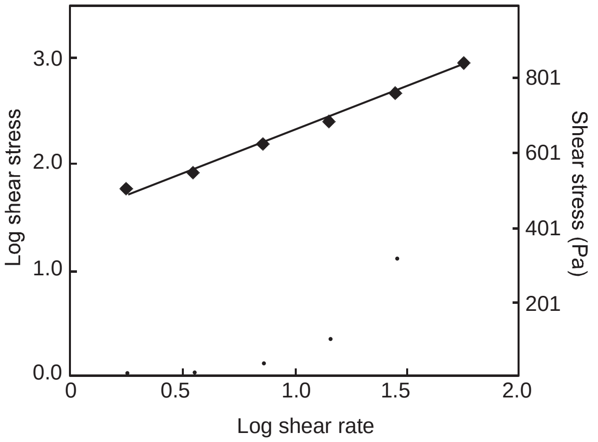


Figure 10. Plot of log shear stress vs. log shear rate for coating paste: PVC-E (69) and DOP plasticizer.

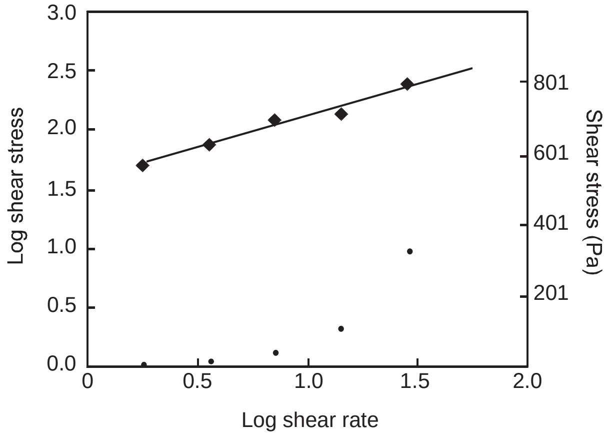


Figure 13. Plot of log shear stress vs. log shear rate for coating paste: PVC-E (75) and DOP plasticizer.

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

K-value 69				K-value 70				K-value 75	
DOA		DOP		DOA		DOP		DOP	
n	k	n	k	n	k	n	k	n	k
0.88	16.70	0.75	58.84	0.92	20.38	0.90	91.62	0.67	155.63

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.

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

1. Pasquale J.A., The many faces of coating and laminating-Is there a better way?, *J. Coat. Fab.*, **21**, 77-100 (1991).
2. Pasquale J.A., Coating machinery and techniques-A Review, *J. Coat. Fab.*, **15**, 263-274 (1986).
3. Booth G.L., Coating methods, *Mod. Plast.*, 90-99 (1952).
4. Schneider R.S., Coating of industrial fabrics, *Int. Polym. Sci. Technol.*, **21**, T/1-T/4 (1994).
5. Schneide R.S., Coating of textile fabrics, *Int. Polym. Sci. Technol.*, **21**, 616-621 (1994).
6. Satas D., Coating Technology Handbook, Marcel & Dekker, 103-111 (1991).
7. Swaraj P., Surface Coatings Science and Technology, John Wiley, New York, Chs. 7 and 8 (1986).
8. Sen K.,Coated Textiles Principles and Applications, Technomic, Pennsylvania, Ch. 3 (2001).
9. Wypych J., *Polymer Modified Textile Material*, 70-81 (1988).
10. Kerr J. and Allewelt A.L., The role of rheology in aqueous acrylate adhesive for bonding and flocking, *Text. Chem. Colour.*, **3**, 57-61 (1971).
11. Teli M.D. and Ramani V.Y., Comparative rheological study of synthetic and conventional thickeners, *Am. Dyestuff Rep.*, 26-29 (1995).
12. Zadhoush A. and Alsharif M.A., The influence of plasticizer content and type on the rheological behavior of plastisol used in coated fabrics, *J. Ind. Text.*, **30**, 1-13 (2000).
13. Rosato D.V., Plastics Processing Data Handbook, Chapman & Hall, UK, Ch. 7 (1997).
14. Den Engleson C.W., Gooijer H., Warmoerken, M.M.C.G, and Wassink J.G., Foaming of silica suspensions, *J. Coat. Fab.*, **27**, 92-104 (1997).
15. Porter N.K., Latex properties and their effect on RFL dip performance, *J. Coat. Fab.*, **25**, 268-275 (1996).
16. Zemlin J.C., Development of a 100% solids urethane fabric coating process-rheological problems, *J. Coat. Fab.*, **3**, 42-55 (1973).
17. Neag M., Wilson P., and Skerl G., Coatings characterization using multiple techniques and statistically designed experiment, *J. Coat. Tech.*, **66**, 27-36 (1994).
18. Marc V.P., *Coating*, *Industries*, Hogeschool Van Het Gemeenscgaps-ondeerwijs- CTL, Gent, Belgium, Chs. 3 and 4 (1994).

19. Boggs L.J., Law D., and Taniguchi, H., Rheological parameters of waterborne coatings, *Eur. Coat. J.*, 350-353 (1998).
20. Grolitzer M.A. and Erikson D.E., Flow modifiers: A key to developing high quality surface coatings, Australia, 20-25 (Dec. 1997).
21. Souheng W. U., Rheology of high solid coatings. I. Analysis of sagging and slumping, *J. App. Polym. Sci.*, **22**, 2769-2782 (1978).
22. Ferguson J. and Kemblomshi Z., *Applied Fluid Rheology*, Elsevire, Ch. 2 (1991).
23. Wilkinson W.L., *Non-Newtonian Fluids*, Pergamon, Ch. 1 (1960).
24. Brydson J., *Plastics Materials*, 7th Ed. Butterworth Heinemann, 320-321 (1999).
25. Edenbaum J., *Plastics Additives and Modifiers Handbook*, Van Nostrand Reinhold, Ch. 24 (1992).