

Swelling properties of spray-dried powders made of starch and poly(vinyl alcohol)

Agneta Jansson and Lars Järnström

Department of Chemical Engineer, Karlstad University, SE-651 88, Karlstad, Sweden
Lars.Jarnstrom@kau.se, (Agneta.Jansson@kau.se)

ABSTRACT

The aim of this study was to investigate swelling properties in liquid plasticizers of two spray dried powder made of; a) starch, poly(vinyl alcohol) and glycerol and b) starch and poly(vinyl alcohol). Glycerol and poly-(ethylene glycol) were selected as liquid plasticizer for the dry powders in rheological investigations. All dispersions showed an increase in storage modulus with increasing temperature, which is the desired behaviour for plastisol pastes.

INTRODUCTION

Today, most aqueous coating techniques involve the application of a suspension at high solids content. The solids content is kept as high as possible in order to minimize drying energy. Nevertheless, the water content may be a problem due to unwanted interactions with the substrate. Therefore different types of water- and solvent-free coatings, such as plastisol coating are of interest. When making a plastisol, the powder is first gelled in the liquid plasticizer, and then heated to form a homogeneous plastic matrix film [1]. Plastisols can be used in many applications, such as textile screening and wallpaper coatings. In plastisol coating, several different unit operations can be used in the application and forming steps [2], e.g. roll application followed blade or rod metering systems, just to mention one example.

In this study, the swelling properties of spray-dried powders made of starch and poly(vinyl alcohol) (PVAL) were examined

when dispersed in glycerol and poly(ethylene glycol) (PEG). Plastisol pastes were made by mixing the dry starch/poly(vinyl alcohol)-based powder with dry poly(alkyl methacrylate) powder (PAMA) and subsequently adding a mixture of liquid plasticizers (glycerol or PEG and dipropylene glycol benzoate) to the powder mixture. The viscosity of the plastisol pastes was examined.

MATERIAL

Starch

The starch used was a hydroxypropylated and oxidized potato starch (PC-155) manufactured and supplied by Lyckeby Industrial AB, Kristianstad, Sweden. The degree of substitution with respect to the hydroxypropylation was 0.11 and the average number of carboxylic acid groups per anhydroglucose unit was 0.04, according to the supplier. The viscosity at 50°C of a 10 % (by wt.) aqueous starch solution prepared by jet cooking at 120°C was 75 mPas, as measured by a rotational viscometer (Brookfield RVT) at 100 rpm.

Poly(vinyl alcohol)

Poly(vinyl alcohol)(PVAL) (ALCOTEX 72.5) was supplied by Harlow Chemical Co. Ltd., Essex, England. The PVAL had a degree of hydrolysis of 71.5-73.5 mole %. The viscosity at 20°C of a 4 % solution was 5.6-6.6 mPas and the polymer had a molecular weight of 35,000-40,000 according to the supplier.

Other Chemicals

Poly(alkyl methacrylate) (PAMA) (Degalan M914) was a commercial polymer powder used for industrial production of plastisol-coated wall papers, delivered by Brenntag Nordic AB, Malmö, Sweden. Dipropylenglycol dibenzoate (Benzoflex 9-88), here denoted as (Dpd), which is a liquid plasticizer for PAMA, was delivered by Velsicol Chemical Ltd, England through AWL Scandinavia, Malmö, Sweden. Glycerol, puris (supplied by VWR, Stockholm, Sweden) and poly(ethylene glycol) of molecular weight of 200 (PEG 200) (supplied by UNIVAR AB, Malmö, Sweden) were used as liquid plasticizers for starch and poly(vinyl alcohol). Ethanol 99.5 %, spectroscopic grade, here denoted as EtOH, (supplied by Kemetyl AB, Haninge, Sweden) was used as co-solvent in some of the trials.

Spray dried powder

Two spray dried powders denoted as P1 and P2 were produced. The composition of P1 was 100 pph of starch, 20 pph of PVAL and 30 pph of glycerol, where pph is parts (by wt.) per hundred parts of dry starch. The composition of P2 was 100 pph of starch and 40 pph of PVAL. Some of the powders were annealed at 80°C before use.

METHODS

The swelling of the powders and the viscosity of the plastisol pastes were measured by a control stress rheometer (PHYSICA UDS 200, Physica Messtechnik GmbH, Stuttgart, Germany). Rheological measurements were performed with a cone (diameter 50 mm and angle 2°) and plate geometry. When measuring the swelling properties, pastes of one part of P1 or P2 were made with two parts of glycerol or PEG200. The samples were equilibrated during oscillatory strain (γ) well above the linear viscoelastic region in order to give the samples identical strain pre-histories. The equilibration took place at a constant

frequency (ω) of 1 Hz and $\gamma = 1$ during time (t) = 120 s, followed by oscillation within the linear region ($\gamma = 0.01$) during $t = 120$ s and finally a period of rest of 120 s. The measurement of the swelling behaviour were performed by small-amplitude oscillator shear at $\gamma = 0.01$ (within the linear oscillating region) and $\omega = 1$ Hz at a temperature (T) ramp from 25 to 100°C with heating rate of two degrees per minute. The storage modulus (G') is reported as mean value of two replicates.

The shear viscosity at shear rates from 0.01 s⁻¹ to 100 s⁻¹ and at $T = 23^\circ\text{C}$ were measured for compositions of plastisol pastes shown in Table 1.

Table 1. Composition of plastisol pastes expressed as % (by wt.). Gly=glycerol.

	A	B	C	D	E	F
P1	23.5	23.5				
P2			23.5	23.5	33.3	
Gly	23.5		23.5		58.3	
PEG 200		23.5		23.5		
PAMA	23.5	23.5	23.5	23.5		50.0
Dpd	23.5	23.5	23.5	23.5		50.0
EtOH	5.9	5.9	5.9	5.9	8.3	

RESULTS AND DISCUSSION

Swelling

In Fig. 1 the variation of G' with T for annealed and non-annealed samples of P1 and P2 with glycerol as liquid plasticizer are shown. The storage modulus started to increase at about 30-40°C and reach a maximum at about 45-50°C. The storage modulus decreased with further increasing temperature. This reflects that the powder had obtained its maximum degree of swelling at 45-50°C. A further increase in the temperature above 50 °C may act mainly by decreasing the relaxation time and by that lowering G' . The glass temperatures of the swelled powders are assumed to be low compared to the investigated temperatures,

which make an Arrhenius dependence quite likely [3].

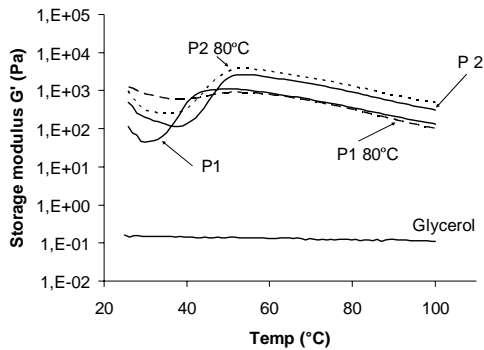


Figure 1. Storage modulus of pastes of annealed and non-annealed spray-dried powders with glycerol as plasticizer.

Fig. 2 shows the storage modulus of annealed and non-annealed P1 and P2 with PEG200 as plasticizer. The storage modulus started to increase at 70°C for P2 and at 90°C for P1. Contradictory to the behaviour in suspensions with glycerol as the continuous medium, the glycerol-free powder P2 in PEG200 swelled at lower temperatures than did the glycerol-containing powder P1 in PEG200. A maximum in storage modulus was reached at about 90°C for P2. The maximum in swelling for P1 with PEG200 was above the maximum investigated temperature.

An additional measurement was performed with P1 and PEG200 to investigate the kinetics of the swelling and if the swelling behaviour was limited by a too rapid heating rate. The sample was measured at a slower heating ramp (one degree per minute) then used in the experiment shown in Figs. 1 and 2. However, the storage modulus observed at the slower heating rate was almost the same as that shown in Fig. 2, indicating that the heating rate used in Figs. 1 and 2 was slow enough to not affect the swelling behaviour.

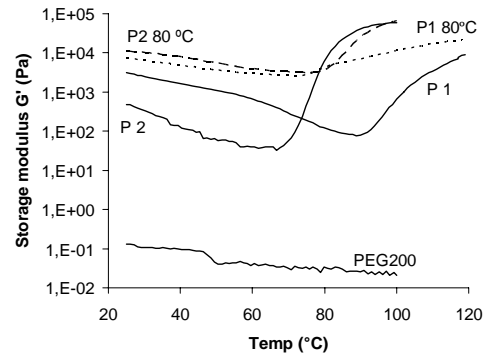


Figure 2. Storage modulus of pastes of annealed and non-annealed spray-dried powders with PEG200 as plasticizer.

The effects of annealing are included in Figs. 1 and 2. When P1 and P2 was pre-heated in an oven at 80°C, the suspensions showed higher G' at room temperature than did the corresponding suspensions based on the non-annealed powder.

Viscosity

Fig. 3 shows flow curves for Formulations A-D.

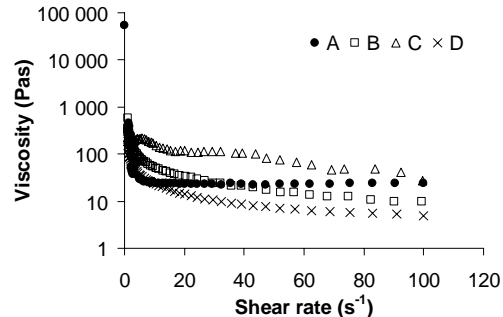


Figure 3. Viscosity vs. shear rate for starch/PVAL/PAMA- containing plastisol pastes at 23°C. Formulations A-D are defined in Table 1.

The two plastisols that contained PEG200 were smoothly shear-thinning, a feature that promotes coating at high shear rates. The flow curves of the corresponding plastisols with glycerol as liquid plasticizer were rather unstable, exhibiting regions with shear-thinning followed by constant viscosity or shear-thickening. The flow

curves of the glycerol-borne dispersions probably reflected the swelling behaviour of the powders in glycerol during shear. However, the degree of shear thinning in the two plastisol pastes containing PEG200 was probably not sufficient to eliminate all runnability problems at high shear rates. Thus plastisol coatings are likely to be most attractive for thick coating layers and low machine speeds.

The viscosity values for Formulation A-F were in general much higher than the viscosities of traditional paper coating colours (Fig 4).

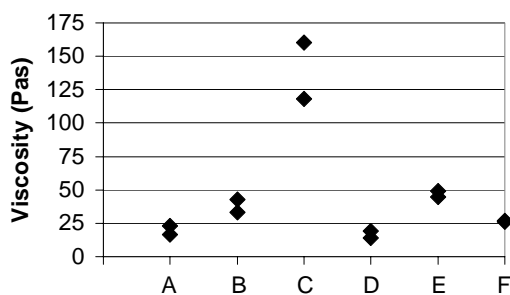


Figure 4. Viscosity of plastisol pastes at 23°C and shear rate of 20 s⁻¹. Two replicates are shown of each formulation. Formulation A-F are defined in Table 1

Formulation F is a simplified variant of a typical industrial formulation based on PAMA, although not used in the industrial coating of graphic papers. The viscosity of Formulation F (27 Pas) could be regarded as a base-line, since plastisols based on PAMA represents the state-of-the-art technology. The pure starch/PVAL paste that contained a co-solvent and relative high amounts of plasticizer (Formulation E) had only slightly higher viscosity (47 Pas) than Formulation F, indicating the positive effect of the co-solvent. The highest viscosity values of those shown in Fig. 4 were obtained for Formulation C (137 Pas), i.e. one the two plastisol pastes that combined starch/PVAL-containing powder with glycerol as liquid plasticizer. Formulation D had a viscosity of 17 Pas. Since Formulation D was the

PEG 200 counterpart to Formulation C, this indicated the positive effect of replacing glycerol by PEG 200. Replacement of glycerol by PEG 200 seemed to result in a reduction of the viscosity.

CONCLUSIONS

Rheology was found to be a useful laboratory-scaled method to predict swelling behaviour of plastisol compounds. The swelling ability of the spray-dried powder in liquid plasticizers indicated that the starch/PVAL powders may be incorporated in plastisol formulations. When glycerol was used as plasticizer, a maximum in storage modulus was reached at about 50 °C, and when PEG200 was used, the storage modulus started to increase at about 70 °C. This shows that the powder swells in these two plasticizers.

Plastisol pastes have quite high viscosity. This was also the case with the pastes investigated in the present study. Thus, plastisol coatings on paper are so far most applicable when thick coatings are desired and for coating operations performed on coaters running at low machine speeds.

ACKNOWLEDGEMENT

Financial support from the Swedish Pulp and Paper Research Foundation, the Knowledge Foundation and the Swedish Governmental Agency for Innovation Systems is gratefully acknowledged.

REFERENCES

1. Rebrovic, J.A. (2000), Plastisols as a surface coating, *Metal Finishing*, **98(6)**, 124-127.
2. Nakajima N. and Harrell E.R. (2001), Rheology of PVC Plastisols: Particle Size Distribution and Viscoelastic Properties, *J. Colloid Interface Sci.*, **238**, 105-115.
3. Morrison, F.A. (2001), *Understanding Rheology*, Oxford University Press, New York, pp. 197-206.