CREEP AND STRESS-STRAIN BEHAVIOUR OF COATING COLOURS

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ABSTRACT

Paper and board are often coated with an aqueous mineral-based suspension, called the coating colour, in order to improve the optical and printing properties of the product. The rheological properties of the colour are of great importance with regard to the runnability of the coating operation. Normally these mineral suspensions exhibit a rather complicated rheological behaviour which can be attributed to the fact that they are concentrated and contain several components. At low deformation rates, they are clearly a viscoelastic material with a storage modulus that depends on the amount of water-soluble polymer in the system.

In this presentation, the creep behaviour of the coating colours, its dependence on the concentration and the amount of water-soluble polymer in the colour will be discussed. In addition to that, it will be shown that these suspensions exhibit a post-yield phenomenon in the form of a maximum in the stress-strain curve at rather large deformations. This maximum is paralleled by a corresponding maximum in the complex modulus as measured during dynamic-mechanical analysis. This has been attributed to the appearance of a deformation-induced structure in the coating colour. The significance of this post-yield phenomenon with regard to the runnability of the blade coating process will be discussed.

INTRODUCTION

Rheological studies on coating colours are required to assess rheological models. This is needed to predict the flow behaviour during the coating operation, e.g. close to the blade when blade-coating the substrate. At high shear rates, it is still debate as to whether the colours exhibit a viscoelastic character. At low shear rates, however, the colours are clearly viscoelastic and this behaviour has been suggested to influence fibre coverage during application of the coating layer[1]. Measurements at low-shear is a powerful tool to characterise aggregation, which affects the whole coating process. Although in blade-coating the deformation rates may be very high ($10^6 s^{-1}$), the residence time under the blade is extremely short (10^{-5}s). Hence, the deformation under the blade is of the order of 10 (product of deformation rate and time to pass under the blade), and coating colours are then, in a sense, best characterised by low deformation rheological tests.

In this study we have performed several creep experiments. Some of these were carried out at a certain (usually low) stress, leading to a small deformation within or slightly beyond the viscoelastic region as given by dynamic-mechanical measurements performed at 1 Hz. These creep studies were supplemented by stress-strain measurements carried out using a constant strain rate to reach rather large deformations, about 1. It has been suggested that the results from these latter experiments are related to the dewatering rate during coating. This will be discussed in the following.

EXPERIMENTAL

Materials

All pigments and chemicals used were commercial grades. An English coating clay (Speswhite from ECC international Ltd., England) was used as the pigment. Sodium polyacrylate (Dispex N 40 from Allied colloids Ltd., England) was used as the dispersant for the pigment. Carboxymethyl cellulose (CMC), with an average molecular weight of 45000 (FF5 from Metsä-Serla Oy, Finland) was used as water retention aid. A carboxylated styrene-butadiene latex (DL 935 from Dow Rheinmünster Gmbh, Germany) was used as a binder.

Methods

The clay pigment was dispersed in water for 30 min at a solids content of 67% by weight, using 0.3 parts of dispersant per 100 parts of clay (pph) and 0.15 pph NaOH. A CMC solution with a concentration of 10% was prepared by dissolving CMC powder in water. Polymer solution (0, 0.3, 0.7, 1.0 or 1.5 pph) and latex dispersion (10 pph) were added slowly to the slurry, in that order. Finally, water was added to reach the desired solids content (55%, 58%, 60% or 62%). The suspensions were left to equilibrate overnight and the final pH value was adjusted to about 8. A strain-controlled Bohlin VOR rotational viscometer (Bohlin Reologi AB, Sweden) was used for the experiments carried out at a constant rate. A stress-controlled Stresstech rheometer (Reologica Instruments AB, Sweden) was employed for the creep-recovery experiments as well as for the dynamic measurements. A constant temperature of 25°C and a bob-and-cup geometry was used at all times.

RESULTS AND DISCUSSION

Fig. 1 shows a plot of creep- and recovery compliance versus time for different applied shear stresses. The coating colours had a solids content of 58% and a CMC content of 1.5 pph

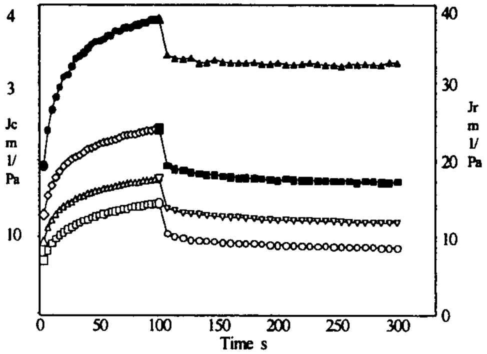

Figure 1. J(t) versus time for a coating colour. Applied stresses during the creep experiments from top to bottom: 0.5, 1.0, 2.0 and 3.0 Pa.

The compliance is defined as $J(t) = \gamma(t)/\sigma$, where $\gamma(t)$ is the strain and σ is the applied constant shear stress. Obviously, the curves do not coincide, which means that the coating colour does not behave linearly. An oscillation stress sweep measurement showed that the end of the linear viscoelastic region corresponded to a strain of about 0.025. To remain within the viscoelastic region, this value should not be exceeded during the creep experiment, i.e. $J(t) \times \sigma = \gamma(t)$ should be less than 0.025. Hence, for 100 s the applied stress (see Fig 1) should not exceed 1.0 Pa. Nevertheless, as can be seen in the figure, the discrepancies in y-position between the curves corresponding to stresses of 0.5 and 1.0 Pa, respectively, are large. Consequently, the colour does not behave linearly, although the critical stress, as measured by oscillation, was not exceeded. This could be regarded as somewhat surprising, but it certainly illustrates the complicated rheological behaviour of these suspensions. In these creep measurements, the deformations are very small. Under the blade during coating, however, the strain is of the order of 10.

Fig. 2 shows stress-strain curves in shear obtained at a constant rate of 0.005 s^{-1}. The shear strain is calculated as the product of rate and time. The coating colours have different solids content as shown in the graph and the CMC content is 0.7 pph. For each suspension, a maximum in the stress is observed at a strain between 0.5 and 1.0. The maximum is more pronounced at a high solids content.

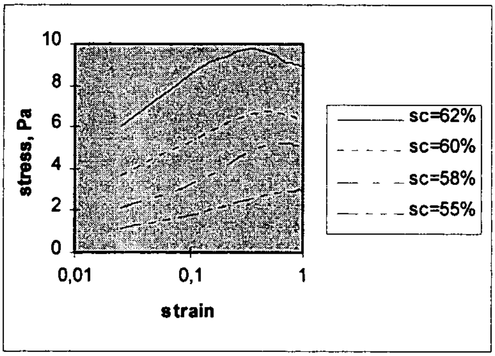

Figure2. Stress-strain curves for coating colours with 0.7 pph CMC. Measurements performed at a constant rate of 0.005 s^{-1}.

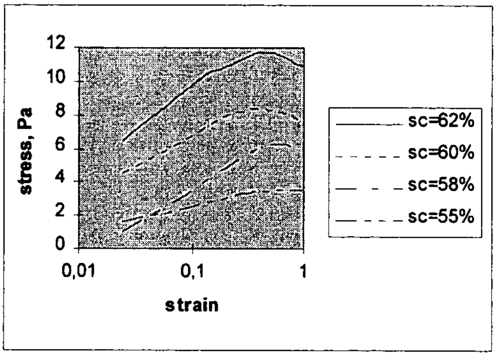

Figure 3. Stress-strain curves for coating colours with 1.0 pph CMC. Measurements performed at a constant rate of 0.005 s^{-1}.

Similarly in Fig. 3, where the addition of CMC is increased to 1.0 pph, the same trend can be observed, although the maximum appears at a higher stress for a given solids content compared to Fig. 2.

Further, the maximum seems to be shifted towards higher strains at lower solids content and lower CMC content. The stress value at the maximum (the critical stress) is clearly determined by the solids content and the CMC content. At CMC contents below 0.3 pph no maximum appeared. According to Carreau et al.[2], the maximum can be regarded as a deformation-induced energy barrier, after which the suspension starts to flow. The highest critical stress corresponds to the lowest dewatering rate under the blade. The more difficult it is for the suspension to flow, the better it retains water, trapped within the structure, and thus the coating operation can be performed at higher rates before wet streaks occur. In their experiments (Carreau et al.[2]), however, the colours are normalised by adjusting the viscosity of each colour to a certain value at a given (low) shear rate, so that a lower solids content is compensated by a higher CMC addition. A normalisation of this kind at a low shear rate is questionable, since the coating process is carried out at a high shear rate. In our own experiments, with solids content ranging from 55% to 62%, and CMC content ranging from 0 pph to 1.0 pph, the critical stress is simply a function of solids content and CMC content. In our view, more parameters and more detailed studies are needed to characterise this post-yield phenomenon and to correlate the stress maximum with dewatering and runnability data.

The dynamic-mechanical measurements, carried out at a frequency of 0.5 Hz, also show a local maximum at relatively large strains when the complex modulus is plotted against the strain, see Fig. 4. Here, the solids content is 62% and the CMC content ranges from 0 to 1.0 pph. Almost the whole effect can be attributed to changes in the loss modulus. These maxima have without doubt the same origin as the maxima in Fig. 1, although they occur at higher strains, above 1, in the dynamic-mechanical measurements. Again, the position of the maximum is shifted towards higher strains and lower complex modulus when the CMC content is lowered.

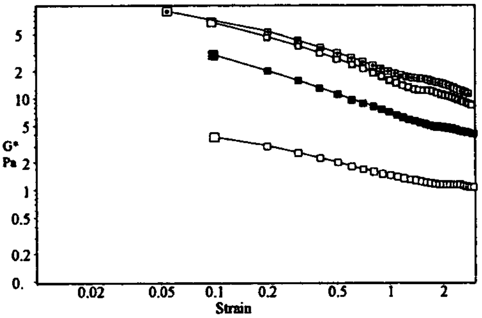

Figure 4. Complex modulus versus strain for a coating colour with 62% solids content. CMC content from top to bottom (pph): 1.0, 0.7, 0.3 and 0.

CONCLUDING REMARKS

Creep and dynamic-mechanical measurements have shown that coating colours behave non-linearly at small as well as at high deformations. Typically, a stress maximum can be observed at a strain of about 1. It has been suggested that this maximum correlates with the runnability during coating, i.e. a higher stress at the maximum corresponds to a higher degree of water retention, which makes it possible to run the coating operation at increased machine speeds. We believe that the conditions are more complicated and that more parameters are needed to correlate the maximum with the runnability.

REFERENCES

1. Fadat, G. and Rigdahl, M. (1987), "*Nordic Pulp and Paper Research Journal*", **2**, 30-38.

2. Carreau, P. J., Ghosh, T. and Lavoie, P-A. (1996), "*Tappi Coating Conference*", 303-309.