

# Viscoelasticity of Water/Ink Emulsions at Low and High Frequency

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**Keywords:** emulsion, viscoelasticity, droplet relaxation, ink, fountain solution

## Abstract

The deformation frequencies in a rolling Nip and during cavitation and filamentation correspond to  $10^3$ - $10^4$  Hz. The viscoelastic properties of neat inks have been relatively well characterized only in the range of low frequencies, ie less than 50 Hz. On a conventional printing press, inks are emulsified with fountain solution and the viscoelastic parameters of the ensuing emulsions also constitute a relevant information. The rheology of both neat and emulsified inks in the high frequency domain is mostly unexplored because the conventional cone/plate rheometers are not reliable above 50 Hz. An experimental rheometer able to measure viscoelastic parameters in the range 0.1- $10^4$  Hz was therefore used to characterize model ink/water emulsions. Three distinct rheological responses were obtained at 25°C as a function of the frequency range applied, viz.: (i) at low frequencies (0.1-10 Hz), increasing the volume fraction  $\phi$  of the emulsified droplets drastically enhanced the elastic modulus  $G'$  of the emulsion; (ii) in the 10-100 Hz range, a relaxation plateau, corresponding to the shape relaxation of the droplets, was observed on the  $G'$  modulus; and (iii) at the higher frequencies (100- $10^4$  Hz), both the elastic and viscous moduli decreased when  $\phi$  was increased. These trends are discussed and related to the various events related to the history of the emulsified ink on a printing press.

## Introduction

The viscoelasticity of printing inks has been a topic of great interest for years and was shown to be a dominant factor in determining print quality. Voet & al (Voet & al., 1953) showed the ink tack to be determined by the viscoelastic response of long-chain molecules responding to a rapid stress. Oitinnen (Oitinnen, 1976) performed an extensive study on the viscoelastic properties of

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lithographic inks and on how they influence ink transfer, ink coverage and printing defects such as “picking”. Zang & al (Zang & al., 1991) and Aspler & al. (Aspler & al., 1993) developed the concept of “Printing Tack” of neat inks and defined it as the maximum tensile stress (i.e. the negative pressure) the ink can withstand during film splitting at the nip exit. These authors showed that there is no universal correlation between the “printing tack” and the viscous flow properties of the ink, but that tack mainly depends on the amount of dissolved polymer in the ink. They suggested that the initiation of film splitting, i.e. the cavitation process, and the resulting tack are the viscoelastic response to the stress imposed on the ink by the receding cylinder, whereas filament elongation and break-up would be more affected by viscous flow properties (De Grace, 1992).

Hayashi (Hayashi & al., 1993) and Amari (Amari & al., 1994; 1995) characterized the effects of pigment, gelling agents and molecular weight of the polymers on the viscoelastic properties of model inks and on the internal network structure.

Unfortunately, only a few scientific studies are available on the effect of emulsified water droplets on the viscoelastic properties of inks. Hayashi (Hayashi & al., 1993) showed with model compounds that increasing the fraction of water droplets in the ink decreases the tack and the filament break-up length and increases the elasticity in the low frequency range. However, no data are to be found in the literature at short deformation times, i.e.  $10^{-3} - 10^{-4}$  s, which represent in fact the characteristic situation in a rolling Nip and during cavitation.

In a broader context, several studies, both theoretical and experimental, have been devoted to the viscoelastic behavior of water-in-oil, oil-in-water and polymer-in-polymer emulsions (Orechioni & al, 1984; Mellema & al, 1987; Graebing & al, 1993; Eshuis & al, 1984). A typical droplet shape-relaxation was predicted by theoretical models (Oldroyd, 1953; Palierne, 1990) and confirmed by experimental studies which took into account the polydispersity of the emulsion (Graebing, 1993). These authors showed that for an emulsion polydispersity with  $R_v/R_n < 2$  (where  $R_v$  and  $R_n$  are the volume-average and the number-average radii), the effect of the polydispersity on the viscoelastic behavior was negligible. The driving parameter influencing the relaxation time was the ratio  $\gamma/R$  of the emulsion,  $\gamma$  being the interfacial tension between materials and  $R$  the average radius of the droplets. In a previous study (Aurenty & al, 1995) we used this relaxation phenomenon in the low frequency range (< 250 Hz) to quantify the interfacial tension in a water-in-alkyd-resin emulsion.

The purpose of this study is to provide a better insight into the knowledge of the viscoelasticity of model water-in-ink emulsions over a range of frequencies ( $10^{-1}$

to  $10^4$  Hz) large enough to cover the whole set of deformation times imposed on the emulsion during the printing process.

## I. Experimental

### I.1 Materials

#### *The alkyd resin*

Because we wished to understand the effect of emulsification of water droplets in the ink, it was decided not to incorporate any pigment into the model ink and therefore to work first with a very simple system consisting of an alkyd resin. The alkyd LV807 supplied by Lawter International, already extensively used as model compound (Aurenty, 1996), was shown to be a mixture of low molecular weight polyesters resulting from the polycondensation of monomers like isophthalic acid, glycerol and stearic acid. This resin had a weight-average molecular weight  $M_w$  of 19000 and a polydispersity index  $I_p$  of 5.9, indicating a broad range of macromolecular sized, which is not surprising for a material resulting from a non-linear polycondensation. A Newtonian behavior was observed in shear, with a viscosity of 76 Pa.s at 25°C. Dynamic mechanical measurements at room temperature, carried out between 1 and  $10^4$  Hz showed the typical behavior of a low molar-mass polymer in his terminal zone. The alkyd surface tension was measured around 100°C and the extrapolated value at 21°C was  $31.1 \pm 0.5$  mN/m. Contact angle measurements on reference surfaces allowed the calculation of the polar part of the surface energy as  $5.7 \pm 1.4$  mN/m. Its interfacial tension with water was measured in the emulsion *in situ* (Aurenty & al, 1995) and was found to be  $8.5 \pm 0.5$  mN/m.

#### *The surfactant*

A commercial non-ionic surfactant (Surfynol 465) belonging to the 2, 4, 7, 9-tetramethyldecyne-4,7-ethoxylated diols family, was selected for this study. This surfactant is highly soluble in water because it contains 10 ethylene oxide units per molecule. It has a very high diffusion coefficient in water and an HLB value of 13. Its critical micelle concentration (CMC) is 0.7 % (wt/wt) or  $10^{-2}$  mol/l and the static and dynamic surface tension above the CMC is around 30 mN/m. Four emulsions were prepared with different surfactant concentrations referenced as WAT, CMC/3, CMC and 3 CMC corresponding to 0,  $3.3 \cdot 10^{-3}$ ,  $10^{-2}$  and  $3 \cdot 10^{-3}$  mol/l of Surfynol 465, respectively.

## I.2. Emulsion preparation

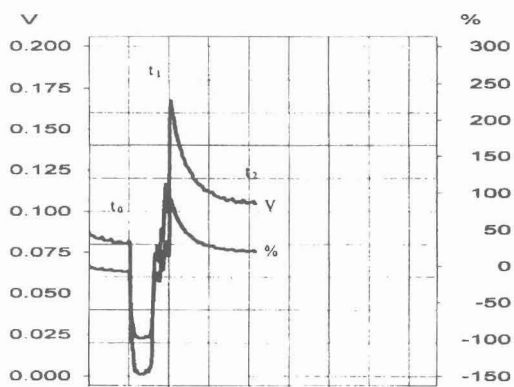
The emulsions were prepared on a Dynamic Emulsification Tester (DET) developed at Sun Chemical (Tranter, 1997). The DET consists of a mixer, equipped with a 4 cm flat propeller on which the rotation speed is imposed and the corresponding torque is measured. The device is computer controlled and a double wall connected to a water thermostat keeps the temperature constant during the emulsification procedure. Prior to emulsification, the alkyd was sheared at 1500 rpm and a stable temperature of 57°C was reached and maintained during the emulsification procedure described below:

- Weigh 20 g of neat alkyd;
- Impose speed 1500 rpm;
- Apply two minutes of pre-shear (torque equilibrium reached after 1 min.);
- At  $t_0$ , add solution drop wise for 1 min. at a flow rate of 3.5 ml/min;
- Wait until  $t_1$ , when torque reaches a maximum value;
- Continue mixing for another 2 minutes;
- Stop shearing at  $t_2$ , and collect the emulsion sample.

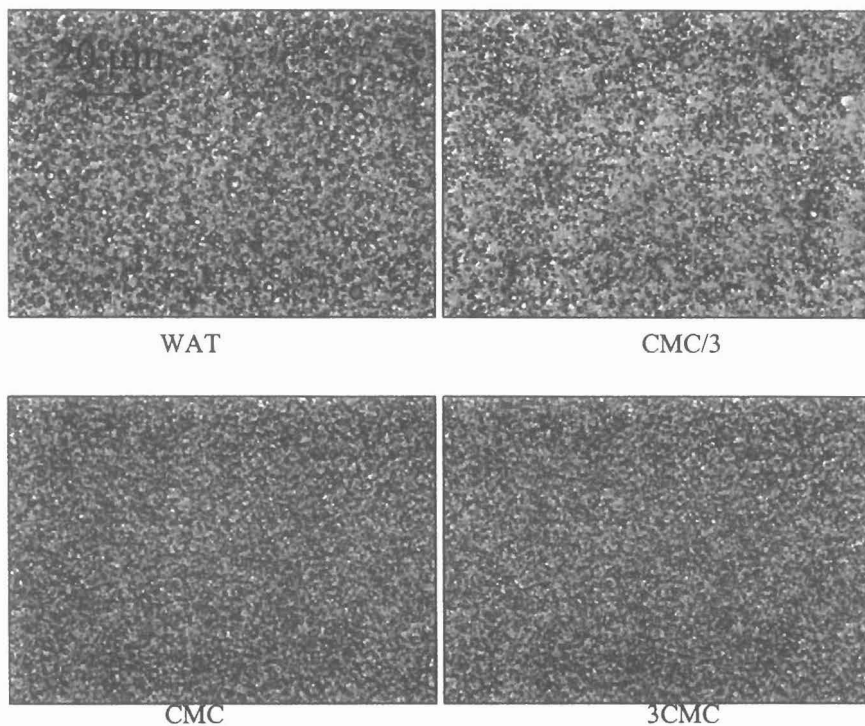
All emulsions contained 15 % of the aqueous solution in the alkyd resin. A graph of the voltage (in volt and in % change, as shown in Fig. 1), which is proportional to the torque on the mixer blade, vs. time was recorded during each complete emulsification procedure. Monitoring the voltage during emulsification was very helpful because the decrease in torque during the aqueous solution addition is related to some important slippage between the propeller and the samples at the emulsification start-up. The aqueous solution being of very low viscosity compared to the alkyd, and not being immediately emulsified, slippage certainly occurred in some "weak water layers", giving rise to very inefficient mixing. The time between  $t_0$  and  $t_1$  was therefore considered as "dead time" for the emulsification process and for that reason it was decided to start the 2-minutes mixing step after  $t_1$ , when the torque reached the maximum value. Actually, it was verified that this "dead time" varied between 1 and 2.5 minutes, depending on the surfactant type and concentration used in the aqueous solution. The addition of a non-ionic surfactant increased the "dead time".

## I.3. Optical Microscopy

An Olympus AH-D microscope with a NEOD-PLAN lens (X 50) was used for droplet size characterization (Figure 2). A rough estimate of the droplet size gives the following ranking:  $R_{WAT} > R_{CMC/3} > R_{CMC} > R_{3CMC}$  with  $R_{WAT}$  in the range of 2-3  $\mu\text{m}$  and  $R_{3CMC}$  close to 1  $\mu\text{m}$ . More precise optical microscopy evaluations were performed on similar emulsions (Aurenty, 1995) and showed a polydispersity index  $R_v/R_n < 2$  ( $R_v$  = the volume average radius and  $R_n$  = the number average radius).



**Figure 1: Torque on the blade during the emulsification procedure**



**Figure 2: Optical micrographs of the four emulsions.**

#### **I.4. Rheological characterization**

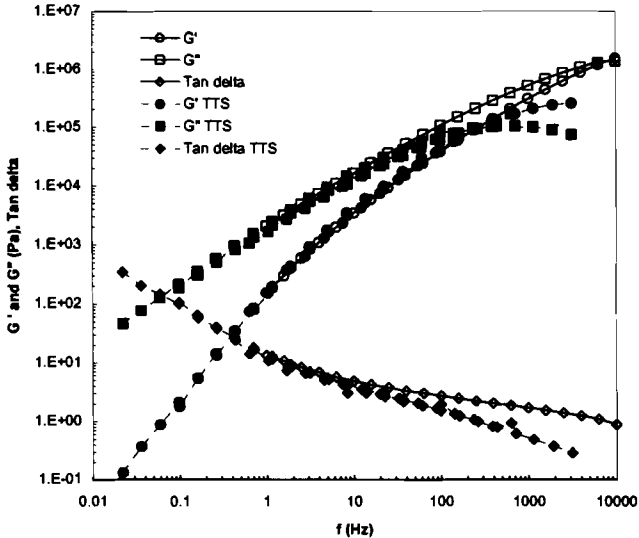
Two rheometers were used in this study, namely a controlled-stress AR-1000 from TA Instruments and an experimental PIEZO-rheometer build by Palierne. For the oscillation experiments, the AR-1000 was used with an acrylic 6-cm plate in the low frequency range, i.e. between  $10^{-1}$  and  $10^2$  Hz, whereas the PIEZO rheometer was used up to the highest frequency i.e.  $10^4$  Hz. In the PIEZO rheometer, the sample is squeezed between two piezoelectric elements, one of which is hooked to a frequency generator and can be excited between  $10^{-1}$  and  $10^4$  Hz and the other is used as a receiver by recording the transmitted oscillations. The oscillation amplitudes are so small that the measurements were always kept well within the linear range of viscoelasticity. For the data obtained on the AR-1000, it was also verified that every measurement took place within the linear viscoelastic range of the deformation. As this study mainly deals with the characterization of emulsions, two different gaps were set-up on both rheometers in order to be able to detect the occurrence of slippage artifacts during the measurements. A 20 to 30 % increase in  $G'$  was observed when doubling the gap on the AR-1000 indicating some wall slippage, whereas  $G'$  remained constant when the gap was increased from 210 to 380  $\mu\text{m}$  on the PIEZO rheometer, indicating the total absence of slippage phenomena. The creep measurements were performed on the AR-1000 with a 4 cm<sup>2</sup> degrees cone in order to impose a constant pre-shear throughout the emulsion before the measurements.

## **II. Results and discussion**

### **II.1. Time-Temperature superposition**

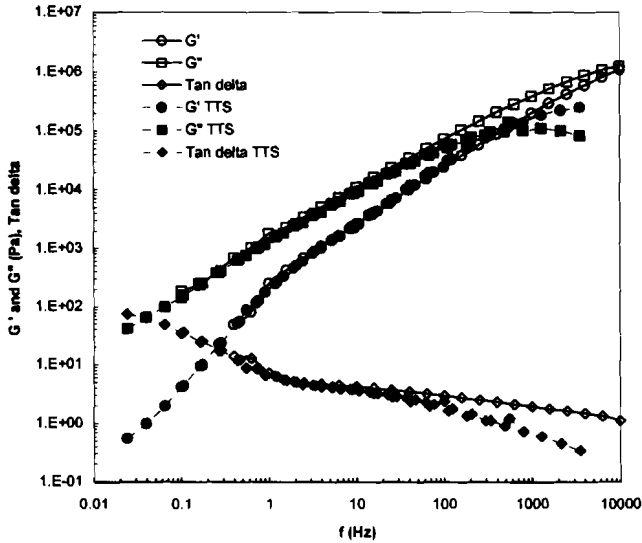
Since it was possible to conduct direct measurements at high frequencies with the PIEZO-rheometer, it was quite interesting to verify whether the time-temperature superposition (TTS) principle, extensively used in the field of polymer viscoelastic characterization, would be applicable in the high frequency range on our samples. In order to test this feature, the neat alkyd and an emulsion were characterized on the AR-1000 at 25, 15, 5 and  $-5^\circ\text{C}$ , and the data were super-imposed according to the WLF equation, taking a reference temperature of  $15^\circ\text{C}$ . Time – Temperature superposition data were plotted, along with data measured on the PIEZO-rheometer, on Figs. 3 and 4. One can easily see that whilst the TTS data matched PIEZO-rheometer data up to about  $10^2$  Hz, this was not the case at higher frequencies. In fact, in the high frequency range and for both the neat alkyd and the emulsion, the calculated TTS data lay below the measured data.  $G'$  and  $G''$  reached some sort of a plateau, suggesting some relaxation which has no physical sense for these materials and which is not observed on the real measurements. This result suggests that the WLF principle is not applicable on both the neat alkyd and the emulsion.

For the neat alkyd, the reason for such a deviation could be due to its low molecular weight, highly branched structure, and large size distribution. Indeed, according to Ferry (Ferry, 1961), the superposition principle is appropriate in the glass transition, plateau and terminal zones as long as all contributions to the measured viscoelastic properties involve the same friction coefficient  $\xi_0$ , which is the monomeric friction coefficient as defined in the Rouse theory (Rouse al., 1953). Unfortunately, at low molecular weight, the assumption of a unique friction coefficient  $\xi_0$  does not hold and  $\xi_0$  decreases with decreasing Mw because of a larger concentration of free ends (terminal groups) and its related increase of free volume (Ferry, 1961). Therefore the alkyd resin, characterized by a high concentration of end groups (low molecular weight, high extent of branching) would be characterized by a wide distribution of  $\xi_0$  which invalidates the application of the WLF principle. For low  $M_w$  polymers (typically < 30000) several anomalies like the one observed here were reported by (Fox & al., 1950) and attributed to the enhanced free volume associated with the end groups of the macromolecules. For the emulsion, the same explanation applies because the alkyd constituted 85 % of the emulsion (matrix). Moreover, in the low temperature range, i.e. just below 0°C, a phase change of the dispersed phase is expected because of the freezing of the water droplets. Such an event will definitely affect the superposition principle, which requires no structural change at all to remain valid.



**Figure 3: Viscoelastic parameters of the neat alkyd: Time –Temperature Superposition data (closed symbols) vs. measured data (open symbols).**

The present results suggest that the WLF principle cannot be applicable to ink compositions, which are a suspensions of pigments in concentrated solutions of low and high DP polymers, because such systems will always be characterized by a large distribution of  $\xi_0$  values.



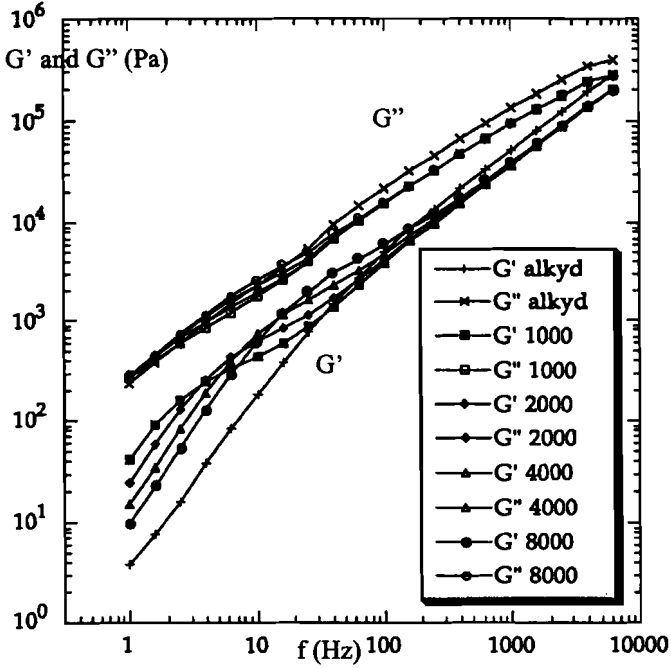
**Figure 4: Viscoelastic parameters of the emulsion CMC: TTS data (closed symbols) vs. measured data (open symbols).**

## II.2. Model calculation: effect of water emulsification on viscoelasticity

The effects on  $G'$ ,  $G''$  and  $\tan \delta$  of the emulsification of water droplets in the alkyd resin LV 807 using a theoretical model (Palieme, 1990) were already discussed in our previous papers (Aurenty & al, 1994 and 1995). In order to assess qualitatively the experimental results, the theoretical curves were plotted assuming a monodisperse emulsion and taking the complex moduli of the alkyd resin at 30°C as the moduli of the continuous phase and the viscous modulus of water for the dispersed phase. The effect on the viscoelastic parameters of the volume fraction  $\phi$ , and the ratio  $\gamma/R$  have also been discussed previously (Aurenty, 1996). As the volume fraction was kept constant in this study, only the effects of the parameter  $\gamma/R$  are shown in Figs. 5 and 6. A monodisperse droplet size  $R$  and values of  $\gamma/R$  between 1000 and 8000 Pa were chosen for the



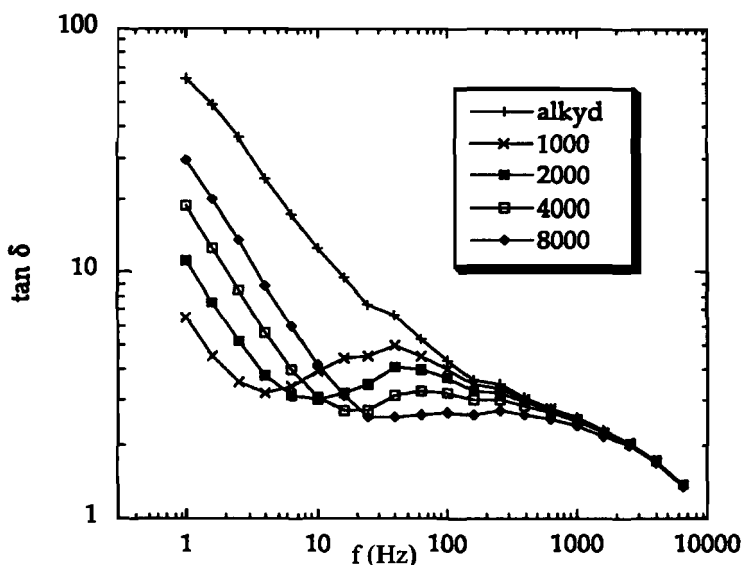
simulation, which assumed an interfacial tension between 2 and 16 mN/m for a droplet size around 2  $\mu\text{m}$ , which is a realistic value for this system.



**Figure 5: Theoretical moduli  $G'$  and  $G''$  for a monodisperse water-alkyd emulsion (20% w/w) at 30 °C.  $\gamma/R = 1000, 2000, 4000$  and  $8000$  Pa.**

### II.2.1. Low frequencies:

The well-known relaxation of the droplets shape (Graebing & al., 1993; Scholz & al., 1990; Mellema & al., 1987; Aurenty & al., 1995) is observed. The relaxation plateau on  $G'$  takes place around 10 Hz. The higher  $\gamma/R$ , the higher the relaxation frequency, indicating a faster elastic return in the case of a higher interfacial tension or a smaller droplet size.



**Figure 6: Theoretical loss tangent  $\tan\delta$  for a monodisperse water-alkyd emulsion (20% w/w) at 30 °C.  $\gamma/R = 1000, 2000, 4000$  and  $8000$  Pa.**

### II.2.2. High frequencies:

All curves merged, indicating that  $\gamma/R$  has no effect on the viscoelastic parameters of the emulsion above the relaxation frequency. The interfacial effect vanished and the only feature, as expected, was a bulk effect, viz. the presence of water droplets of negligible moduli decreased both the elastic and viscous moduli of the emulsion compared to those of the neat alkyd. The emulsification of water droplets had therefore no effect on  $\tan\delta$  at high frequency.

### II.3. Experimental results

The four emulsions and the neat alkyd resin were characterized with both rheometers at different temperatures.

#### II. 3.1. Below 100 Hz: droplet relaxation

First of all, a well-known drastic increase of the elasticity, attributed to the emulsified droplets, was observed at low frequency. This effect arises from an interfacial phenomenon, the droplets resisting the deformation, because of the interfacial tension.

The shape relaxation was observed between 1 and 10 Hz at 15°C and between 10 and 100 Hz at 25°C, as shown in Figs 7 and 8. The relaxation was less pronounced than on the theoretical curve. This effect is certainly due to the polydispersity of the droplet size in the real emulsions. This polydispersity leads to a distribution of relaxation times and thus flattened the global relaxation of the emulsion.

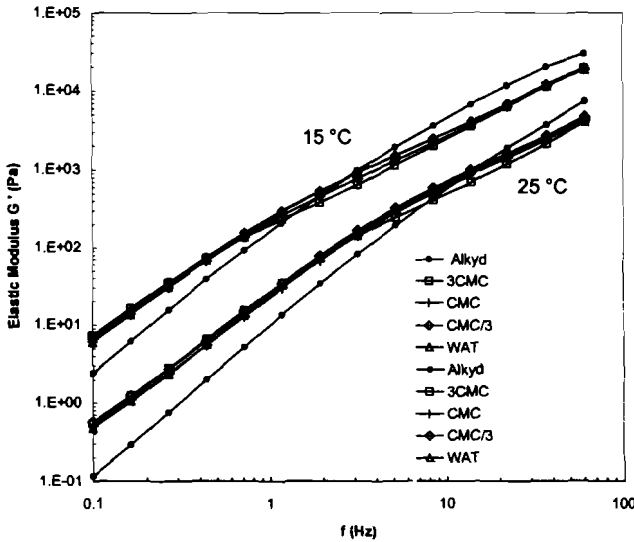
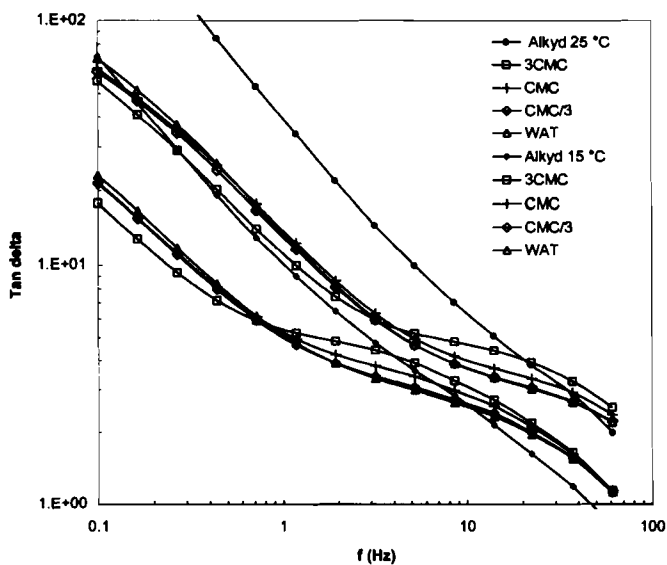


Figure 7: Elastic moduli of the emulsions WAT, CMC/3, CMC and 3CMC at 15 and 25 °C. AR-1000 data.

### II.3.1.1. Structure-properties ( $\gamma/R$ )

From the relative position of the relaxation plateau, and comparing with the theoretical curves (Fig. 5), it became possible to rank the emulsions according to their  $\gamma/R$  values. Emulsion 3CMC relaxed at lower frequency than emulsion CMC, CMC/3 and WAT. Therefore  $\gamma/R_{3CMC} < \gamma/R_{CMC} < \gamma/R_{CMC/3} \approx \gamma/R_{WAT}$ , indicating that the addition of surfactant induced a decrease in the  $\gamma/R$  ratio. As shown above, it was established by optical microscopy (Fig. 2) that the addition of surfactant tends to decrease the droplet radius  $R$  significantly. Therefore, it can be concluded that the addition of surfactant reduces the interfacial tension more significantly than it affects the radius of the droplets. Surprisingly, this trend did not stop even for surfactant concentration above the CMC, indicating that the water/alkyd interface was not yet saturated at a bulk concentration of surfactant equal to the CMC, because of the high water solubility.



**Figure 8: Loss tangent of the emulsions WAT, CMC/3, CMC and 3CMC at 15 and 25 °C. AR-1000 data.**

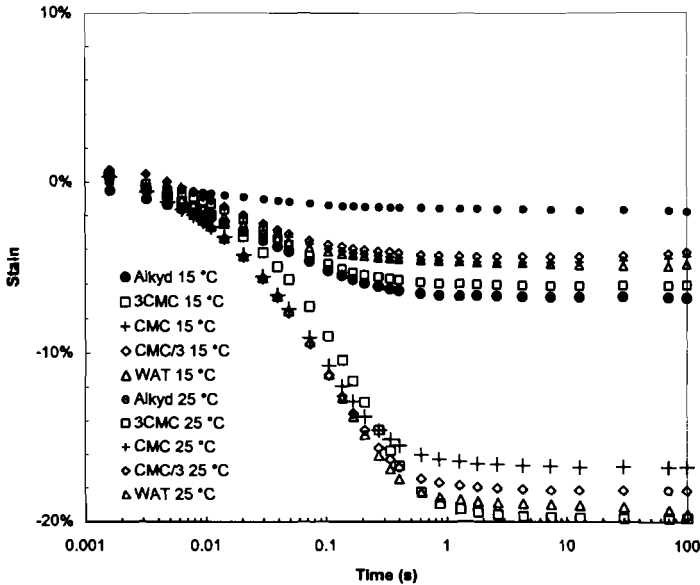
### II.3.1.2. Creep measurements

In order to confirm the droplet relaxation observed by the dynamic mechanical characterization, a creep experiment was designed on the cone and plate rheometer AR-1000, consisting of the following steps:

- Pre-shear the sample at a constant rate of  $5 \text{ s}^{-1}$  for 60 s;
- Stop stress and velocity and record % strain vs. time for 100 s.

This procedure was applied to the neat alkyd and to the emulsions CMC/3 and 3 CMC at 15 and 25°C. Right after the shear was stopped, a negative strain was observed, corresponding to an elastic return (Fig. 9). Whereas the magnitude of this return was modest with the neat alkyd, because of an essentially Newtonian behavior, the emulsions exhibited a more pronounced response. This feature constitutes a fingerprint of droplet relaxation in which the droplets are deformed and elongated under the pre-shear applied to the emulsion (Sholtz & al., 1989) and when the shear is stopped, the interfacial tension forces the droplets to recover their original spherical shape and this gives rise to a relaxation phenomenon. It was verified experimentally that the amplitude of the return depended on the amplitude of the pre-shear. Emulsion CMC/3 was submitted to two different pre-shear amplitudes of 5 and  $20 \text{ s}^{-1}$ , respectively, at 25°C. The

corresponding amplitudes of the return were 5 % at  $5 \text{ s}^{-1}$  and 17 % at  $20 \text{ s}^{-1}$  (Fig. 10), indicating a much stronger deformation and hence a much larger elastic return of the droplet when the pre-shear amplitude was increased.



**Figure 9: Elastic return after shear of the emulsions and the neat alkyd, in % vs. time and at 15 and 25 °C.**

Every creep curve in Fig. 9 has an S-shaped, with an inflexion indicating the midpoint of the relaxation phenomenon and its related abscissa value being the half-time of relaxation  $t_{r1/2}$ . The  $t_{r1/2}$  value for each emulsion was evaluated using a curve-fitting program and the results are reported in Fig. 11. According to the qualitative  $\gamma/R$  ranking obtained from the dynamic mechanical analysis (see above), and the findings summarized in Fig. 11, the higher  $\gamma/R$ , the smaller the time associated with the relaxation. This result makes a lot of sense because  $\gamma/R$  can be considered as the stress applied to the droplets by the interfacial tension. Therefore, the higher  $\gamma/R$ , the higher the stress applied to the deformed droplet and the shorter the elastic return. The time scales associated with the droplet relaxation, i.e. between 0.01 and 0.1 s at 15°C and between 0.1 and 1 s at 25°C, confirm the trends observed by the dynamic mechanical experiments.

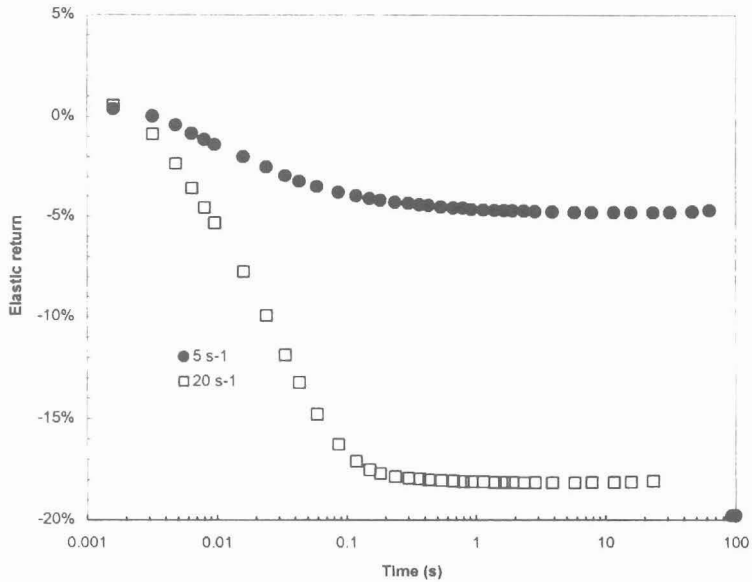


Figure 10: Effect of the pre-shear amplitude on the elastic return for Emulsion CMC/3 at 25 °C.

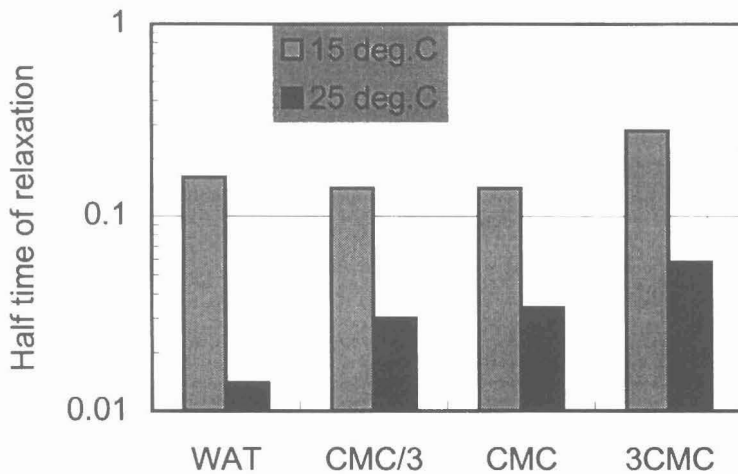


Figure 11:  $2 \times t_{r1/2}$  (time of half-relaxation) after shear vs. emulsion type.

### II.3.2. Above 100 Hz: no interfacial effect

The viscoelastic data obtained with the experimental rheometer (Figs. 12 and 13) clearly confirmed the trends obtained with the theoretical assessment of the model emulsion (Figs. 5 and 6). As long as the volume fraction of the dispersed phase was kept constant, all  $G'$ ,  $G''$  and  $\tan\delta$  curves merged, indicating that no interfacial effect took place in this frequency range, i.e. the interfacial tension  $\gamma$  and the droplet size  $R$  had no longer an effect on the viscoelastic properties of the emulsions. The only effect of the emulsified droplets was a decrease of about 30 % for both  $G'$  and  $G''$  with respect to the values related to the neat alkyd, whereas  $\tan\delta$  remained unchanged.

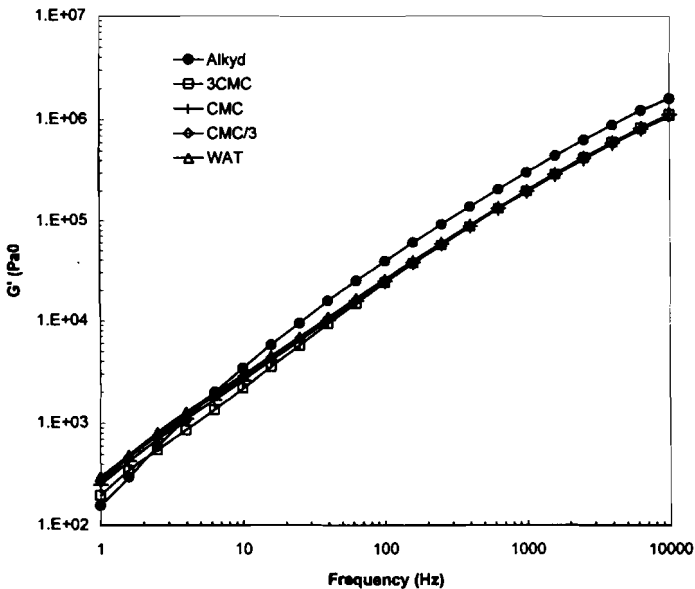
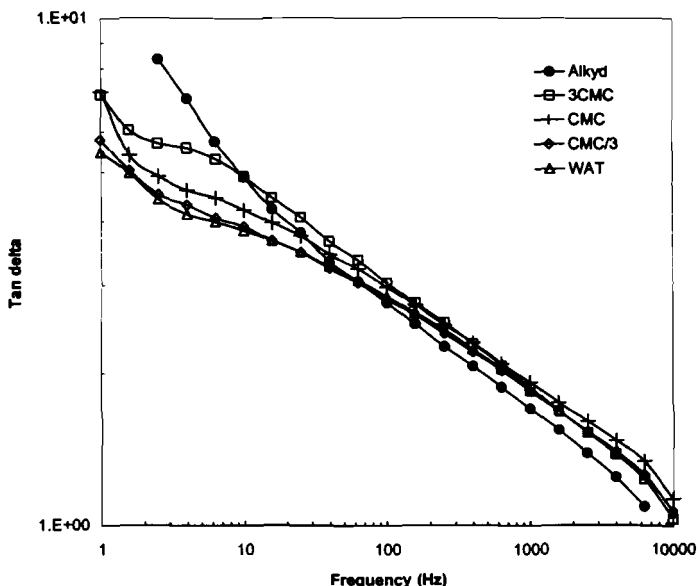


Figure 12: Elastic moduli of the emulsions WAT, CMC/3, CMC and 3CMC at 15 °C. PIEZO-Rheometer data.

#### Structure-Properties Relationship

Above 100 Hz, the emulsion is solicited on a time scale smaller than the droplet relaxation time, giving no time for the droplets to withstand the deformation. The droplets will therefore elongate in the same quantitative way as the matrix, without any shape rearrangement during the oscillation cycle. The interfacial effect seen at lower frequencies vanishes, and the only effect of the presence of emulsified droplets in the alkyd is a bulk effect, which results in a proportional

decrease of elastic and viscous moduli without affecting  $\tan \delta$ . This is attributed to the low modulus of the dispersed phase. In fact, comparing the stiffness of water with that of the neat alkyd, in this frequency range, it is obvious that the water droplets can be considered as holes in the matrix, capable of decreasing the global stiffness of the emulsion.



**Figure 13: Loss tangent of the emulsions WAT, CMC/3, CMC and 3CMC at 15 °C. PIEZO-Rheometer data.**

## II.4. Consequences for printing

### II. 4.1. Emulsified ink vs. neat ink

#### Low frequency (<100 Hz)

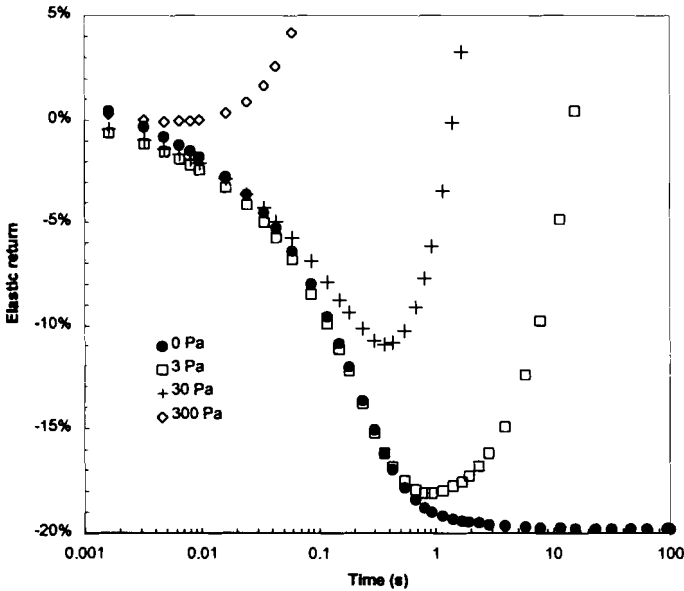
During printing, the emulsified ink undergoes various types of stresses associated with very different deformation times. Long-time deformations (low frequency region, <100 Hz) are encountered just after ink transfer to the printing substrate, e.g. during the leveling process. The surface-tension-driven film leveling is of prime importance to achieve the highest degree of print gloss (Glatter & al., 1996; Desjumeau & al., 1997). Ongoing studies (Desjumeau & al., 1998) on the effect of the rheological properties of inks on the dynamics of ink gloss suggest that the lower  $\tan \delta$  in the low frequency range, the worse is the gloss development with time. An ink with more structure in the low frequency



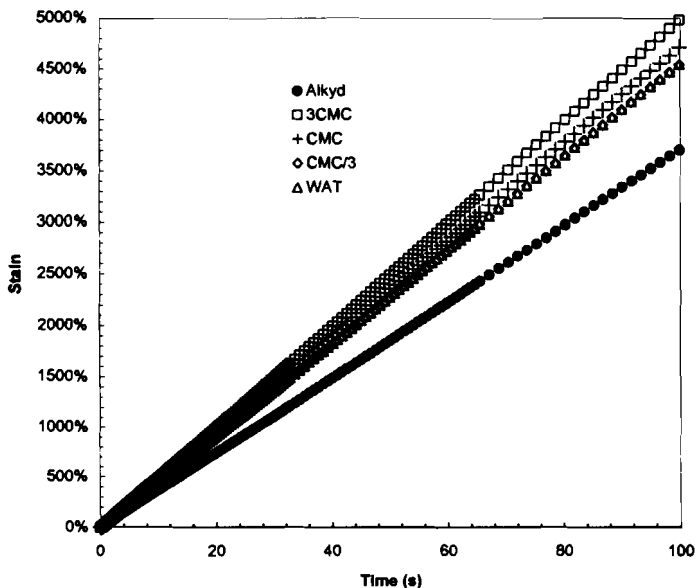
region will exhibit more resistance to the leveling stress imposed by the surface tension, and may thus retard and lower the gloss development. Since it was found in this study that the emulsification of water droplets in the ink increased drastically the elasticity in the low frequency region, some consequence is also to be expected on the printing gloss development.

In order to predict the effect of emulsified droplets on film leveling and gloss development, further creep measurements were applied to the emulsions, in order to attempt a simulation of the action of the surface tension on the rough film, right after shear and filamentation in the nip:

- Pre-shear the sample at a constant rate of  $5 \text{ s}^{-1}$  for 60 s;
- Stop stress and velocity, apply a constant stress and record % strain versus time for 100 s.



**Figure 14: Creep experiment: deformation vs. time under constant stress after pre-shear; short time after pre-shear**



**Figure 15: Creep experiment: deformation vs. time under constant stress after pre-shear; long time after pre-shear.**

In a real experiment, the stress imposed by the surface tension would decrease with the radius of curvature and therefore with time. Three values of imposed stress after the pre-shear phase were applied to the sample, namely 3, 30 and 300 Pa, the middle value being a realistic initial stress right after filamentation (Desjumeau & al., 1998). Shortly after stopping the pre-shear, the elastic return was counterbalanced by the imposed stress (Fig. 14) and the deformation became positive again after a short time. For both inks, an imposed stress of about 300 Pa actually inhibits any elastic return. For the longtime deformation (Fig. 15), the samples reached an extent of deformation which correlated very satisfactorily with the qualitative ranking of  $\gamma/R$  established above, viz. the lower  $\gamma/R$ , the higher the deformation reached at a given time. This trend confirmed the interfacial phenomena due to the droplet relaxation,  $\gamma/R$  acting like a counter-stress which resists deformation. These experiments suggest that the lower  $\gamma/R$ , the better should be the leveling and the gloss development.

Comparing the % strain reached at 100 s by the neat alkyd with that related to the emulsion, an unexpected feature emerges. In fact, although emulsions were

more elastic in the low frequency range, because of the interfacial effect, and although  $\gamma/R$  acted as a counter-stress opposing the deformation, the emulsions were displayed a higher deformation than the neat alkyd, at a given stress. This suggests that the bulk effect (decrease in viscosity due to the presence of droplets of very low viscosity in the matrix) was more important than the interfacial effect described above, with regard to leveling.

### **High frequency (>100 Hz)**

The high frequency region is more related to the type of deformation suffered by the emulsified ink in the nip and during cavitation. The finding that emulsified droplets did not affect the viscoelastic character of the material at high frequency (same loss tangent for emulsified and neat ink), suggests that the initiation of film splitting is not perturbed by the presence of water droplets in the ink.

However, the typical relaxation times of the water droplets observed in this study (10 to 100 ms at 25°C) are well above the deformation times in the nip, which indicates that during film splitting the droplets will follow the deformation of the ink matrix without any time for shape-rearrangement. A large droplet deformation could therefore be expected, which might result in some emulsion break-up during elongation. Hayashi (Hayashi & al., 1993) showed that the break-up length at nip exit decreased with increasing the water content in the ink.

The dynamic mechanical measurements were conducted assuming a linear viscoelastic response and therefore did not take into account any change in the morphology of the emulsion such as this very probable emulsion break-up under high elongation rate. In fact, the water droplets, because of their very small cohesion compared to that of the alkyd matrix, could certainly act as “weak point” in the filament and therefore initiate the rupture. Some elongational characterizations are needed in order to gain a better understanding of the behavior of the emulsion in these specific conditions.

### **II.4.2. Effect of the presence of surfactants**

This study underlined the effect of the ratio  $\gamma/R$  on the rheological properties of water-in-ink emulsions. The only variable explored was the concentration of the surfactant in the aqueous phase and the results suggested that Surfynol 465, added at the realistic concentration of  $CMC/3$ , did not induce any change in the value of  $\gamma/R$  (compared with that obtained using pure water) and therefore would not affect the rheological properties of the emulsion. Now, at higher surfactant concentrations,  $\gamma/R$  decreased, indicating that surfactant addition has a larger effect on the interfacial tension  $\gamma$  than on the radius of the droplets  $R$ . Because this  $\gamma/R$  decrease provoked a longer droplet relaxation and less resistance to flow under an imposed stress, it should promote a better leveling

behavior. Of course, this trend also depends on the specific surfactant structure and on the way the surfactant acts on the ratio  $\gamma/R$  and more work is therefore needed to unravel these questions.

### **Conclusion**

The use of a piezo-rheometer able to measure dynamic moduli in the range  $1-10^4$  Hz clearly showed that the time-temperature superposition principle according to WLF theory is not valid for system like printing inks because of a spread in the values of monomeric friction coefficient  $\xi_0$  related to the corresponding polymer.

The emulsification of water droplets affected the viscoelastic properties of the alkyd resin principally in the low frequency range ( $<100$  Hz at room temperature). The ratio  $\gamma/R$  was proven to be the parameter controlling the rheology in this low-end region. Decreasing  $\gamma/R$  by adding more surfactant in the aqueous phase increased the droplet relaxation time and the emulsion ability to be deformed under a given stress. This trend could have some beneficial effect on the film leveling process.

At higher frequencies, i.e. above the droplet relaxation frequency, the emulsification of water droplets did not change the elastic/viscous ratio of the alkyd resin, suggesting a rather small effect of the presence of emulsified droplets during the short-time deformation suffered by the emulsion in a rolling nip. No emulsion morphology or structural change, such as an emulsion break-up, was taken into account in our measurements and thus the present conclusion must be validated by a further investigation based on elongational studies.

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