Formulation and Characterization of Textile Inks for Ink Jet Printing

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Abstract

In this paper, novel methods for measuring ink rheological properties which appear to be an improvement on the conventional steady-state viscosity measurement are described. Ink rheological characteristics which are a result of molecular weight or conformation of polymeric constituents are described from a phenomenological viewpoint as dynamic moduli and apparent elongational viscosity. The magnitude of these variables are shown to depend on ink composition. Finally correlations between ink rheological properties and print quality are proposed and discussed.

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Introduction

The recent technological achievements in ink jet printing have not found until now widespread use in the textile industry. This is mainly due to the difficulties encountered in the formulation of water-based inks suitable for jet printing, covering the whole range of textile needs. Indeed, this implies the development of direct and reactive dyes for cellulosic fibers (cotton, viscose), dispersed dyes for synthetic fibres (polyester), acid dyes for proteinic fibres (silk, wool), and pigmented inks for all above mentioned fabrics.

Studies on jet printing of textiles date back to the l970s[1], the aim being to develop a non-impact printing system and to produce multicolour designs using digital data. The potential advantages of rapid production of colour separation patterns using computer-aided design

systems without the need to produce expensive screens, coupled with the ability to change patterns or colours almost instantaneously for short runs appeared very attractive. Other desirable features also included increased productivity and reduced stocks of printed goods so as to readily cope with rapid fashion changes. However, high capital investment, technical problems linked to ink feasibility mechanical and software capabilities have hindered the fabrication of industrial textile inkjet printers until now. To this date, inkjet is only used in the textile world for producing samples or for low resolution printing on carpet products.

Developing inks with proper rheology and fixation properties is a critical factor in the application of jet printing to textiles. Inks must have physico-chemical properties suitable for drop formation while being capable of producing sharp dense and permanent images on a variety of fabrics. In earlier works on jet printing there are very few examples where the rheological properties of inks are described[2] and the measurements are essentially limited to surface tension, density and steady-state viscosity[3] whatsoever the jet technology chosen. However influenced by developments in polymer science, improved mechanical tests of materials are gaining ever-increasing significance in the imaging industry[4-5]. As stated by Forgo et al.[5] rheological measurements with rotating or capillary viscometers provide information on merely the shear viscosity of materials which may not be the only relevant parameter. The measurement of viscoelastic properties by means of dynamic and elongational measurements provides, for instance, information on the conformational behaviour of the polymers and can, therefore contribute significantly to the understanding of complex processes, such as those that occur in jet printing.

We report in this paper the formulation and rheological characterization of pigmented ultra-violet (designated UV) curable inks for continuous inkjet printers which have been carried out within the framework of an European Brite Euram project on colour jet printing of textile materials under electron beam and UV curing systems (Project No. P-3261). UV curing is chosen preferentially to thermo-curing in order to improve printing quality and to lower energy consumption. We demonstrate in this study that we can predict and control the rheology of novel dispersions making them suitable for inkjet printing.

Experimental

Materials and Inks Formulation

The solvent serves as a vehicle to carry colourants and other ingredients. Due to the requirement that the ink be conductive while having a high surface tension, and for safety considerations, water is the ideal solvent candidate. The last point is even more important for large width printing with thousands of jets where the ink must be absolutely free of health, chemical or fire hazards.

The binders are the main constituents of pigmented inks since they impart their properties to the ink. In contrast to inks made with water-soluble dyes, binders are necessary in pigmented inks in order to provide adhesion of the pigment to the fabric. The binders we use have been especially tailored for fabric inkjet printing and are hydrosoluble pre-polymers with a low molecular weight typically 1800 daltons. They are either polyester urethane acrylate (designated PUA) or urethane acrylate (designated UA). The urethane acrylate polymer was thought to have better fixing properties in the ultra-violet curing process compared to the polyester one. There is only a limited range of usable viscosities in an ink jet printer, typically 3.10^{-3} to 15.10^{-3} Pa.s so this determines the polymer concentration.

The colourants we use are commercially available carbon black (C black) particles for the black ink and organic pigments for other colours. The pigment selection has been based on chemical compatibility, colour quality, solubility, lightfastness and waterfastness. The particle size for all our UV curable inks was found to be less than 0.6 μm using photon correlation spectroscopy (Autosizer IIC from Malvern Instruments Ltd). It is important that the particles are small enough in order to avoid sedimentation. Moreover our experience in inkjet inks is that the ratio nozzle diameter over pigment particle size should not be lower than fifty in order to avoid nozzle clogging and to obtain well formed and properly charged droplets.

Other important ingredients which enter in the formulation of our inks include the photo-initiator system which helps to start the polymerisation reaction in the presence of UV radiation. However heat generated in the printer may also initiate the reaction process leading to severe nozzle clogging. Means are provided not to exceed a temperature of 60°C. The photoinitiator system is selected such that its absorbance is not on the same wavelength as the pigments. Also, necessary especially in the the case of water-based inks, is a defoamer since foam is generated during liquid recycling which is a frequent occurrence in continuous inkjet printers. Pigmented inks are particularly prone to such foam formation because of the surface active agents they contain. Biocides are also essential in water-based inks to prevent growth of biological materials which would lead to ink spoiling. The selection of the defoamer and of the biocide is of course based on their compatibility with other materials.

Finally all the ingredients mixed together should provide a stable ink composition. After mixing, the ink is carefully filtered to eliminate all impurities and undissolved solids which would lead to nozzle clogging and reproducibility problems in droplet formation. The formulation of the binders and inks are listed in Table I**.**

Ink Rheological Characterization

Steady-state Shear Measurements. A conventional "controlled stress rheometer" (Carri-Med CSR) is used for the steady state characterization. A large cone-and-plate geometry with a radius of 30 mm, and actual cone angle of 0.0175 radians is used to perform the tests. This ensures a constant shear rate throughout the sample. A running time of 30 s is allowed prior to each measurement at various shear rates to ensure that the steady-state shear viscosities are obtained. The experiments are per-

formed in the range of stresses from 1 N/m^2 to about 15 N/m^2 and the highest shear rate attained is around 2000 s^{-1} where no obvious flow instability is observed. The test temperature (20°C) is chosen to be close to the controlled room temperature in order to minimize thermal gradients.

Table I. Main characteristics of the binders and inks

	pre-polymer (conc. g/g)	pigment (conc. g/g)	surface tens (mN/m)	conductivity (μS/cm)
binder A	PUA (11%)	none	40	
ink A	PUA (11%)	C black (10%)	36	660
binder B	PUA + UA (8% +3%)	none	40	
ink B	PUA + UA (8% +3%)	C black (10%)	36	665

High Frequency Measurements. Several different techniques for measuring theological properties of polymer solutions at high frequencies have been presented (see Harrison and Barlow[6] for a comprehensive review).

In the present investigation, we have developed and used a rheometer based on the torsional waveguide technique.[7] The quantities measured are δA and δB which are respectively the increase in attenuation in nepers per meter, and the increase in phase retardation in radians per meter. In the High Frequency Rheometer[8] (designated HFR) presented here, a pure torsional motion is generated by a Bismuth and Germanium Oxide crystal ($Bi_{12}GeO_{20}$) a more symmetric piezoelectric crystal than Quartz used in all other previous apparatuses. The electromechanical factor of the $Bi1_{2G}eO_{20}$ crystal is also higher, leading to better sensitivity. This makes the HFR particularly suitable for low viscosity fluids such as inks.

The quantities of interest in this study are *G'* the storage modulus and *G"* the loss modulus. According to McSkimin[9], one can write the following equation:

$$Z^* = \sqrt{\rho(G' + iG'')} = F(\delta A + i\delta B) \tag{1}$$

where Z* is the plane shear wave impedance, *F* a proportionality constant characteristic of the rheometer and ρ the density of the fluid under test. From equation (1), we can derive the basic equations of the torsional waveguide technique:

$$G' = \frac{F^2}{\rho}\left[(\delta A)^2 - (\delta B)^2\right] \tag{2}$$

and

$$G'' = \frac{F^2}{\rho}\left[2\delta A\,\delta B\right] \tag{3}$$

In this study, high frequency measurements have also been performed at 20°C to allow direct comparison with steady-state ones.

Elongational Measurements. The need to develop elongational rheometry has become apparent since resistance to extensional motion has been recognized as the key fluid property in certain flows of polymer solutions (see Petrie[10] for a comprehensive review).

In the present study, we follow closely Schümmer and Tebel[11] who suggested to derive the elongational properties of polymeric fluids from the capillary instability of jets, which is exactly what happens in the operation of an inkjet printer. However their simplified assumptions limit their analysis to highly elastic fluids whose jet behaviour exhibit a string of fine filaments in between spherical drop regions. This type of behaviour seldom happens with inkjet inks so we have extended their analysis to take into account situations where the filament is not homogeneous[12]. There exists a region within the jet where the flow is shear free. In this region, one can write the deformation rate $\dot{\varepsilon}$ and the axial stress σ^{ZZ} as:

$$\dot{\varepsilon} = -\frac{2}{R}\cdot\frac{dR}{dt} \tag{4}$$

$$\sigma^{zz} = \sigma^{rr} + \eta_e(\dot{\varepsilon})\cdot\dot{\varepsilon} = -p + \eta_e(\dot{\varepsilon})\cdot\dot{\varepsilon} \tag{5}$$

where R is the local radius (in the region); t, the time; σ^{rr}, the radial stress which is obtained by calculating the pressure difference (-*p*) due to the surface tension, and η_e is the apparent elongational viscosity, found by using the momentum conservation equation.

The data needed are R and the derivative of R as a function of time. They are obtained using the laser shadowgraphy method[13]. The operating conditions of our elongational rheometer in this study are: jet velocity of 20 m/s, excitation frequency between 75 and 120 kHz, a nozzle diameter of 60 μm, and a temperature close to 23°C. Other experimental details will be reported elsewhere.

Results and Discussion

Steady-State Behaviour of Polymers and Inks

Figure 1 represents the steady-state viscosity as a function of shear rate for the four different fluids described in Table I.

The viscosities of the inks and binders are constant over a wide range of measurements demonstrating that our inks behave like Newtonian fluids. It has been suggested[2] that in this case, non-Newtonian properties will not show up under normal printing conditions in the range of several tens of kilohertz.

High Frequency Measurements of Binders and Inks

The viscoelastic data are plotted in Figure 2. The measurements were performed at 73 kHz which is the fundamental frequency of the HFR. Measurements at overtones are not reported since they are far from the operating conditions of conventional continuous inkjet printers (usually comprised between 62 kHz and 125 kHz). It can be seen from Figure 2 that the viscous moduli

G" of inks A and B are nearly identical to within 11%. In contrast their elastic moduli G' differ by an order of 3, indicating that their jet behaviour could be quite different. We also note that the addition to the binders (A and B) of pigment black (10%) tends to lower the elastic modulus and increase the viscous modulus. The reason for the decrease in G' is still unclear (polymer adsorption on the pigments, or other) and needs further investigation. Finally, the complex viscosity noted η^* equal to $\sqrt{\left(\frac{G''}{\omega}\right)^2+\left(\frac{G'}{\omega}\right)^2}$, where ω is the angular frequency is lower than the steady-state viscositiy for both inks and binders. This indicates that non-Newtonian properties (shear-thinning) may be exhibited at high frequencies.

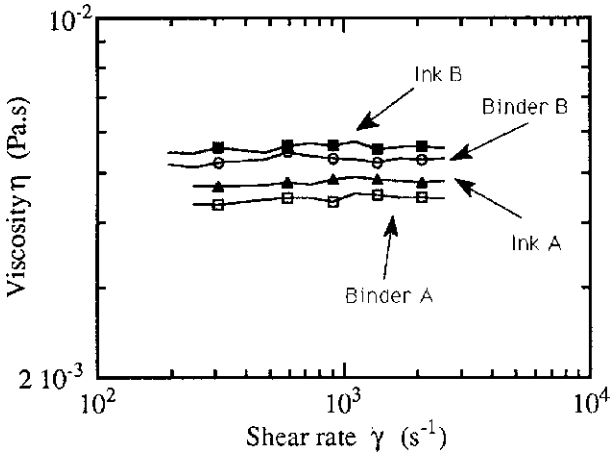

Figure 1. Shear viscosities of binders and inks

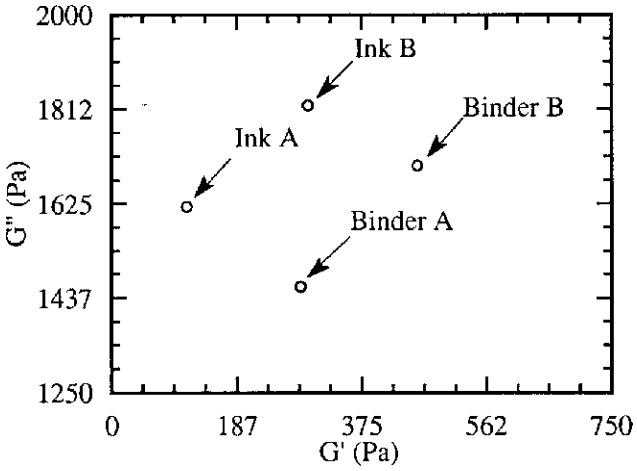

Figure 2. Cole-Cole diagram of the viscoelastic moduli of the binders and inks

Elongational Behaviour of Inks

Figure 3 gives the variation of the rate of deformation as a function of z/D for a typical experiment performed at 100 kHz where z is the considered axial location on the jet (z = 0 is nozzle exit) and D is the undeformed diameter of the jet. We can note that the strain rate never attains a steady-state before drop breakoff which for this typical experiment occurred at z/D = 145.

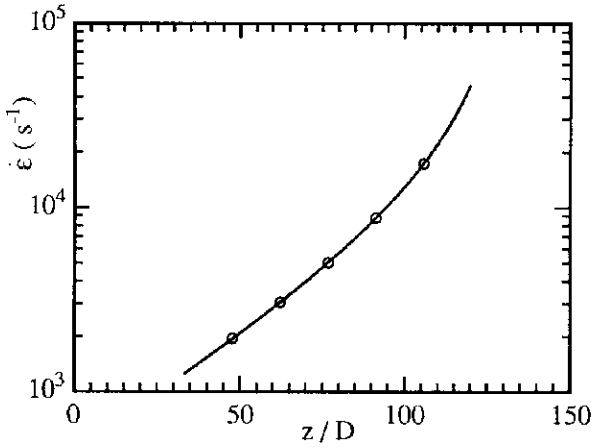

Figure 3. Variation of the strain rate as a function of distance

Figure 4 depicts the elongational behaviour of the two inks as a function of strain rate. Note that the curve for ink A is the result of two experiments performed at 75 kHz and at 103 kHz which allow to cover two orders of magnitude in strain rate. At low deformation rates, the fluid exhibits Newtonian behaviour and we recover the Trouton ratio with η_e equal to three times the shear viscosity at low shear rate. The curves for ink B also result from a set of two experiments. Their superposition denotes that there is no degradation in fluid properties. The non-linear departure happens sooner for ink B and its apparent elongational viscosity at breakoff is higher.

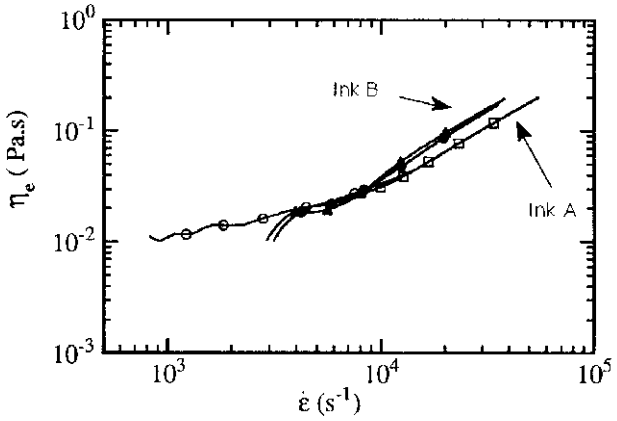

Figure 4. Variation of apparent elongational viscosity as a function of strain rate

Correlation Between Rheological Measurements and Printing Behaviour

Figure 5 shows samples printed with both inks A and B. The distance between the printhead and the substrate has been significantly increased (by an order of 5

compared to usual printing distances) to amplify drop positioning defects. Note that in the line pattern generated with ink B, some dots do not appear, others are out of line and others are merged on the substrate, whilst the printing quality in overall is good for ink A.We find that ink B, which presents a higher elastic modulus in shear and shows more pronounced non-Newtonian properties under elongation, is correlated with poor print quality. It thus appears that a qualitative prediction of printing behaviour is possible based on rheological variables such as G' and η_e measured at frequencies and deformation rates comparable to the operating conditions of the printer.

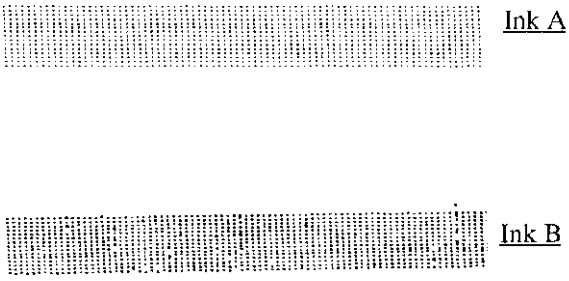

Figure 5. Line patterns printed with inks A and B

Conclusions

In this paper, we have described the formulation and preparation of pigmented inks for inkjet textile printers and disclosed means to characterize and to tailor them. The measurements with the High Frequency Rheometer and the Elongational Rheometer are easy to perform and shown to present quite high sensitivity. Using these techniques, we have demonstrated that the mixing of two binders very similar in nature and molecular weight can lead to increased elastic modulus and apparent elongational viscosity. These rheological characteristics in turn are connected to the printing behaviour. Finally, although the present work has been confined to ultraviolet curable pigmented inks for textile, the principles developed have found applications in the choice of thickeners for the formulation of disperse and reactive dyes to cite a few.

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