

Rheological Behaviour and Printability of Water-Based Model Inks for Screen Printing

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Short abstract

The development of environmentally-friendly inks for printed electronics motivates the design of inks with limited amounts of additives, raising the question of the specific role of each ingredient in ink formulations. This work explores the individual and combined effects of binder and conductive filler on the rheology and printability of a simplified, water-based model ink adapted for screen-printing. We formulated 2-hydroxyethyl cellulose (HEC) with graphite particles inks in various concentrations and assessed their rheological behaviour and printability. The ink rheology, featuring Carreau-like behaviour and thixotropy, was mostly driven by the vehicle with corrective effect of the particles at high concentrations, under high and low shear rates. Screen printing on plain and electronic paper substrates showed that printability depends mostly on substrate type, with higher surface coverage on the former than on the latter.

Keywords: Screen printing; Water-based inks; Rheology; Thixotropy; Printed electronics

1. Introduction and background

Printed electronics enables the fabrication of functional devices using additive deposition techniques such as screen printing, inkjet printing and gravure printing (Cui, 2016). In contrast to conventional silicon-based processes which are limited to rigid materials, printed electronics allow large-area, flexible and lightweight structures to be produced on paper and polymeric substrates. Among the available techniques, screen printing is accepted as particularly suitable for conductive patterns and thick functional layers (Kipphan, 2014).

The process employs a patterned mesh stencil through which ink is transferred onto a substrate by a squeegee and subsequently dried to form the desired pattern. The transfer is governed by ink rheology and the inks are typically highly viscous ($\approx 1\text{--}1000\text{ Pa}\cdot\text{s}$), enabling them to stay on the mesh without squeegee stroke. Mesh geometrical characteristics govern ink volume deposition and print resolution, while squeegee angle, hardness, speed, and applied pressure determine the shear and pressure experienced by the ink during transfer (Kipphan, 2014; Ney et al., 2019).

Electrical conductivity arises when conductive particles form a continuous percolated network enabling electron transport. Achieving such percolation generally requires high filler loading; however, increasing solid content also raises viscosity and may introduce yield stress due to intensified particle–particle and particle–polymer interactions (Faddoul et al., 2012). This high viscosity creates a trade-off between electrical performance and printability. Under the high shear conditions imposed by the squeegee, inks display pronounced shear-thinning behaviour to facilitate transfer through the screen openings (Kipphan, 2014). Excessive viscosity may hinder this transfer. Finally, optimum thixotropy is desired to promote levelling and reduce defects, yet insufficient structural recovery after shear may lead to spreading and loss of pattern fidelity. Ink's compatibility with screen-printing is therefore highly correlated with its rheological properties. Screen-printing inks are composed of four main ingredients: a functional material (often metallic particles in conductive inks), binders (usually polymeric thickeners), stabilizers (e.g. surfactants), and a solvent. In commercial inks, the possible cross-influence of these ingredients is often empirically corrected, magnified, or complemented with additional components, to reach the desired set of properties. As a result, inks are highly complex and mostly undisclosed

formulations, often involving health-threatening (e.g. carcinogenic) or environmentally harmful (e.g. petro-sourced) materials. The development of safer and more environmentally friendly formulations, circumventing or reducing the use of these materials raises the question of the specific role of each ingredient in ink rheology and printability. Addressing this question requires to formulate a simplified, reproducible and tuneable model system to investigate rheology and printability. In this framework, the present work investigates the rheological and printing behaviour of water-based inks formulated with controlled particle and (biomass-based) binder contents.

2. Materials and methods

Water-based model inks were formulated using an aqueous vehicle composed of 2-hydroxyethyl cellulose (HEC), adding graphite powder as conductive filler. HEC and Graphite concentrations are expressed as volume fractions ϕ_{HEC} and ϕ_{C} respectively.

2.1 Formulation

Vehicles are formulated with $\phi_{\text{HEC}} \approx 2, 4, 6, 8$ and 14%. Based on viscosity and handling properties, only the 4, 6 and 8% HEC vehicles were considered suitable for printing and used as base for inks. Conductive inks are formulated by adding graphite particles (average size: 37 μm) to the vehicles, in three concentrations ($\phi_{\text{C}} \approx 17, 24$ and 30%) leading to nine formulations. The (8% HEC; 30% graphite) composition was excluded after preliminary printing trials due to insufficient penetration through the screen mesh. Sodium dodecyl sulfate (SDS) was included in the vehicle at its critical micelle concentration for stabilisation. Formulations are thick opaque black liquids with a shine attributed to graphite.

2.2 Rheological characterisation

To characterise the mechanical response of the formulations under shear we performed rheological measurements. We use Anton Paar MCR-302 rotational rheometer equipped with a 25 mm parallel plate geometry and a measuring gap of 1 mm. All tests are conducted at 20.0 ± 0.1 °C. Steady-shear flow curves (viscosity as a function of shear rate) are obtained by increasing steps of constant shear rates from 0.001 to 1000 s^{-1} allowing to determine the steady-state viscosity. Thixotropy, defined as time-dependent structural recovery after shear cessation, is evaluated using a Three-Interval Thixotropy Test (3ITT) (Faddoul et al., 2012). This protocol consists of a pre-shear at 1 s^{-1} for 30 s to remove mechanical history, followed by 150 s at 0.1 s^{-1} to simulate rest conditions. A high shear rate of 300 s^{-1} is applied for 15 s to simulate squeegee stroke finally followed by low shear rate of 0.1 s^{-1} for 150 s to simulate recovery stage. Viscosity recovery is then calculated by comparing the viscosity at given time to the initial low-shear viscosity.

2.3 Screen printing and post-treatment

Printing experiments were carried out using a DEK Horizon 03i screen printer equipped with a mesh of 90 threads/cm and a wire diameter of 40 μm . The off-contact distance is set to 2 mm, the squeegee pressure to 10 kg, and the squeegee speed to 190 mm s^{-1} . We compare printing on two substrates, plain paper (porous cellulose-based substrate, denoted P) and electronic paper (coated non-porous substrate, EP). After printing we sinter samples at 120 °C for 15 min.

2.4 Morphological characterisation of prints

Optical microscopy was performed at 5 $\times$ magnification to evaluate surface coverage. Image analysis provides the relative coverage as the percentage of ink-covered area after binarization. Since prints on plain paper have grey zones due to rough surface causing glare, threshold is

intensified visually until those areas are covered. Five images per case are analysed. Cross-sectional morphologies are analysed using scanning electron microscopy (SEM) at 500× magnification to assess the ink–substrate interfacial characteristics.

3. Results and discussion

3.1 Rheological characterisation

We assume the rheological behaviour of inks to be dominated by vehicle system, and graphite further influences the system due to particle interactions with the binder matrix.

3.1.1 Flow behaviour

Figure 1 presents the evolution of viscosity with shear rate for the five vehicles. All formulations feature an initial plateau, followed by shear thinning as the shear rate increases. This behaviour is fitted to a Carreau model with η_0 (Pa.s), n and λ (s) the zero-shear viscosity, flow index, and relaxation time respectively (Ouaer and Gareche, 2018).

$$\eta(\dot{\gamma}) = \eta_{\infty} + (\eta_0 - \eta_{\infty})[1 + (\lambda\dot{\gamma})^2]^{\frac{n-1}{2}} \quad [1]$$

The infinite-shear viscosity, η_{∞} , is set as the value of the solvent (1 mPa.s).

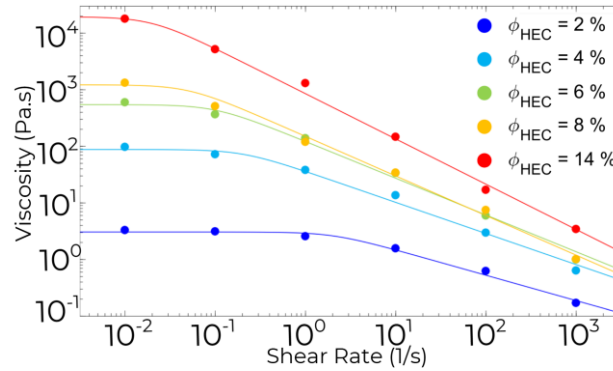


Figure 1: Flow curve of vehicle formulations

As the HEC concentration increases, the zero-shear viscosity rises from 3 to 20,000 Pa.s, and the apparent width of the plateau gradually diminishes, with relaxation time increasing from 0.5 to 50 s. Furthermore, the flow index reduces from 0.55 to 0.2 indicating an increase in shear thinning. According to Benyounes et al. (2018), increase in viscosity can be attributed to the strengthening of local structures that immobilise the fluid, preventing it from participating in the total flow. The shear thinning behaviour is interpreted as a signature of the disentanglement of the polymer coils in solution and their alignment in the direction of the flow (Clasen and Kulicke, 2001).

Adding particles does not qualitatively change this behaviour. As shown in Figure 2, all ink formulations feature a Carreau-like behaviour similar to their vehicles, almost identical at low particle concentrations (below $\sim 20\%$), with similar shear-thinning index. However, we systematically note a deviation to this behaviour at shear rates beyond $\sim 100 \text{ s}^{-1}$. Beyond the dotted lines formulations fail to adhere to Carreau model. The measured viscosity becomes significantly smaller than the one predicted by the Carreau model as if adding particles would strengthen the shear-thinning effect at high shear rate. Finally, increasing ϕ_c beyond $\sim 20\%$, the relaxation time and the zero-shear viscosity both increase.

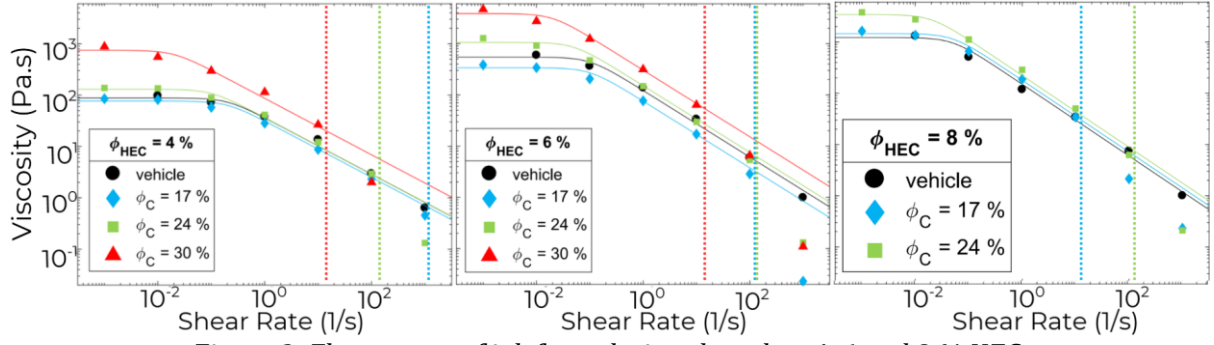


Figure 2: Flow curves of ink formulations based on 4, 6 and 8 % HEC.

Figure 3 (a) presents the evolution of the zero-shear viscosities with the particle contents for the three vehicle groups. In all cases, the viscosity remains relatively constant up to 17%, then increases by up to one order of magnitude. This trend is quantitatively similar in all vehicles as confirmed by the evolution of the viscosity normalised to the vehicle one (Figure 3 (b)). This general trend actually contrasts to particulate suspensions in Newtonian fluids, where a linear increase in viscosity at low particle loading would take place before fast divergence as the close-packing fraction approaches (Krieger–Dougherty model). Taken together, these informations suggest a structural reinforcement of the polymeric matrix by the loading particles, which is partly screened by the matrix itself at low concentrations. This interpretation is consistent with Hanif et al. (2019) who showed the thickening effect of graphite filler in HEC both due to percolation effects and particle–polymer interactions.

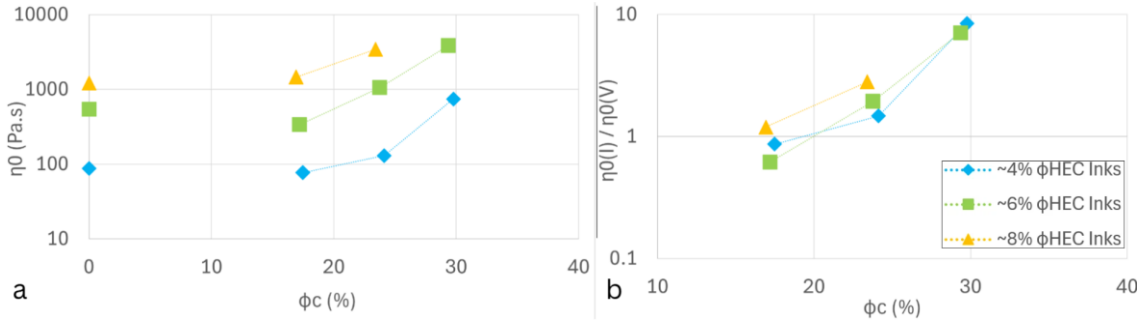


Figure 3: Evolution with ϕ_C of the (a) plain and (b) normalised zero-shear viscosity of the inks.

In summary, formulations feature a Carreau behaviour primarily driven by the binder concentration. The particulate fillers further increase the zero-shear viscosity, particularly at high concentration, and reduce the viscosity beyond 10–100 s^{-1} suggesting the emergence of a stronger shear-thinning regime.

3.1.2 Thixotropy

To be suitable for screen-printing process, ink must have sufficiently low viscosity at high shear rate to pass through the screen mesh and regain sufficiently high viscosity at rest to maintain the printed pattern. Structural recovery after high shear phase must balance speed and recovery: too slow recovery causes spreading or collapse, while too fast recovery causes defects (Hong et al., 2020). 3ITT is performed to emulate this process and access the recovery dynamics: the first plateau represents the rest phase prior to structural breakdown (15 s at 300 s^{-1}) corresponding to the squeegee stroke, then the viscosity gradually recovers as the structure relaxes.

Figure 4 displays the 3ITT curve for 6% HEC ink formulations. All inks feature partial recovery stabilising within ~ 30–60 s. Test is done for all formulations and the recovery efficiencies R% at 10 and 60 s after shear are summarised in Table 1.

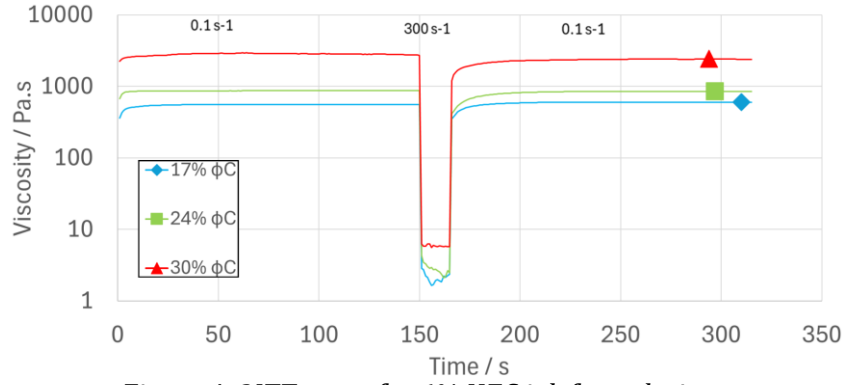


Figure 4: 3ITT curve for 6% HEC ink formulations.

In all systems, recovery generally declines with increasing graphite content, from full recovery to $\sim 80\%$ at 60 s. This decline can be interpreted as a reduction in polymer-polymer interactions due to weaker concurrent polymer-particle interactions, resulting in a weaker network that takes longer to reform within the timeframe of the test (Ouaer and Gareche, 2018). Note that one formulation (4% HEC, 24% C) featured surprisingly low recovery. Macroscopically most of the ink samples are considered printable according to thixotropic dynamics.

Table 1: Thixotropic recovery ($R\%$) of ink formulations.

ϕ_{HEC}	4%		6%		8%	
ϕ_{C}	$R\%$ at 10 s	$R\%$ at 60 s	$R\%$ at 10 s	$R\%$ at 60 s	$R\%$ at 10 s	$R\%$ at 60 s
17%	84.1	95.5	93	108.1	69.9	88.4
24%	24.4	31.8	76.9	96.8	61.3	77.7
30%	72.1	81.9	68.8	82.7		

3.2 Morphological characterisation of prints

3.2.1 Surface coverage

We first examine the printed film uniformity at sub-mm scale by optical microscopy. Figure 5 (a) and (b) show micrographs representing the deposition pattern of a (8% HEC; 17% C) ink on electronic paper (EP) and plain paper (P) respectively. Clear differences are visible between substrates. On EP, numerous whitish specks corresponding to uncoated areas show that the particle deposition is not uniform, leading to a patchy pattern with seemingly connected clusters and isolated bare spots. In several areas, a grid-like pattern is prominent, attributed to diagonal mesh geometry like the one in Figure 5 (c). In contrast, on P the deposition appears more uniform.

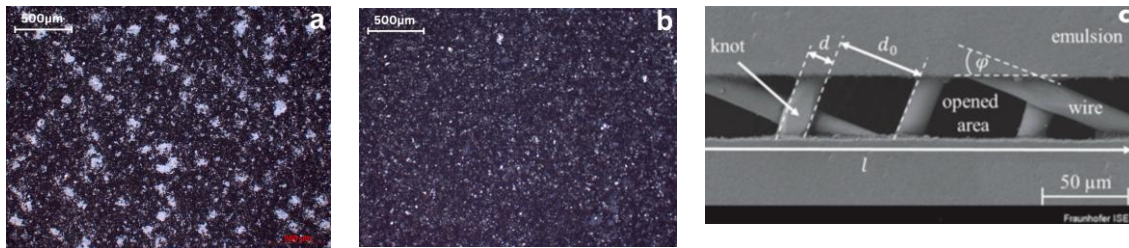


Figure 5: Optical micrographs of a print with (8% HEC, 17% C) ink on (a) EP and (b) P substrates. (c) Micrograph of mesh screen orientation (Ney et al., 2019).

To quantify this observation, we measure the relative surface coverage after binarization of the greyscale images. Figure 6 illustrates that increase in ϕ_{C} reduces the coverage, hence printability, for both substrates; this decrease enhances on EP at the highest particle concentration, reaching about 50–55%. In addition, P tends to be more printable than EP for a given formulation according

to this metrics, which suggests a more favourable deposition behaviour on hydrophilic surfaces under the present experimental conditions. However, no significant trend is identified with vehicle concentration.

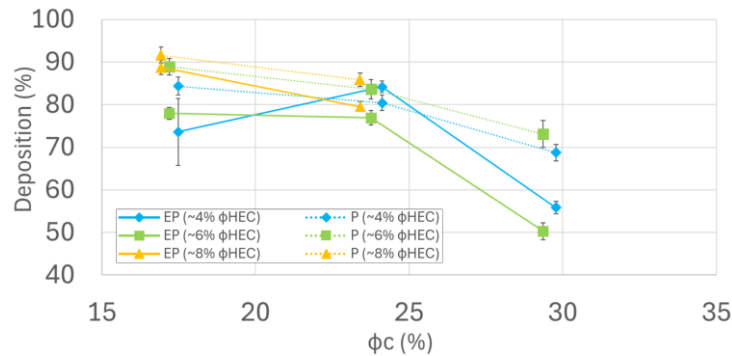


Figure 6: Evolution of the relative surface coverage with graphite and HEC content on EP and P.

3.2.2 Cross-sectional morphology

We finally evaluate cross-sectional morphology and interfacial adhesion of a film printed with (8% HEC; 24% C) ink on P and EP substrates (Figure 7). On EP, the interfacial gap between the film and the substrate indicating incompatibility and lack of adhesion is clearly visible. This substrate is indeed coated with hydrophobic layer and rejects the water in our inks. In contrast, on the porous and hydrophilic substrate P no interfacial gap is visible suggesting better adhesion. We also observe much rougher surface on P, drawing hill and valley morphology with $\sim 110 \mu\text{m}$ periodicity which corresponds to the mesh size. This pattern could be due to the partial absorption of the solvent during the recovery phase, accelerating drying and the ink structural recovery thereby reducing the levelling after transfer. SEM micrographs therefore confirm the major substrate dependence in printing.

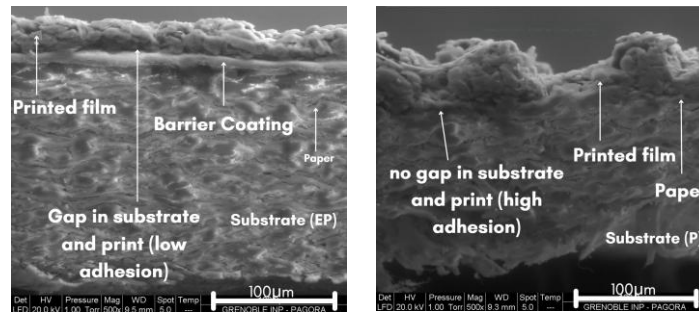


Figure 7: SEM micrographs of a print with (8% HEC; 24% C) ink on EP and P substrates.

4. Conclusions

This work aimed at establishing relationships between formulation parameters, rheological behaviour, and printability in screen printing using simplified water-based inks. Our results confirm that binder content governs the baseline rheology and structural strength of the ink, while graphite particle loading reinforces the structure in a non-linear manner, mostly above $\sim 20\%$ in volume, and decreases structural recovery after shear. The morphological analysis of printed films show that substrate properties are dominant, since porous paper (P) promotes more uniform films compared to non-porous electronic paper (EP). However, on both substrates inks with lower particle contents feature better coverage, which suggests the benefit of stronger recovery. These findings support the need for controlled formulation strategies and substrate compatibility when targeting stable deposition and functional performance with water-based conductive inks. These results show how different substrates impact the printing and direct future investigations on the independent effects of porosity, roughness, and wettability on printability.

Acknowledgements

The authors acknowledge the technical assistance provided by Mikael Party, Karine Janel and Fakhreddine Fehri. We also acknowledge the financial support of Université Grenoble Alpes and Grenoble INP-UGA.

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