

SHORT TIME SPREADING OF OFFSET PRINTING LIQUIDS ON MODEL CALCIUM CARBONATE COATING STRUCTURES

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Spreading of oils and water on porous model carbonate coating structures was studied with high speed video imaging. The results indicate a strong dependence between surface structural features of the pigment tablets and spreading of water at short times, while the oil spreading mainly depends on the liquid properties. With the exception of water, majority of results support spreading according to the molecular kinetic model. The evidence supports the hypothesis that at long times the oils absorb into the porous structure at a rate proportional to the ratio of surface tension and viscosity, provided there is no sorptive action with the binder. A combination of nanosized pores and high permeability is useful for providing high absorption capability for carbonate based coatings.

Introduction

Liquid–solid interactions are important for numerous natural and industrial processes in agriculture, coating, filtration, painting and printing. Understanding the effects of sequential absorption of oil components and water, in various arrangements, on porous coatings during the very short time it takes for a paper to pass through a printing machine is a prerequisite for a successful printing operation. Phenomena in the printing nip occur under far from equilibrium conditions, and therefore the interactions of liquids with the coating should also be studied in nonequilibrium conditions.

When a droplet of liquid is placed on a surface its spreading is controlled by the balance of driving and resisting forces. The driving force for initial impact spreading is kinetic energy of the droplet, whereas flow resistance is provided by viscosity and surface tension of the liquid. As the kinetic energy of the impact dissipates, the wetting forces become important. Spreading of a liquid on a specific solid surface is also influenced by chemical heterogeneity and surface topography. On porous surfaces, the spreading mechanics is further complicated by capillary absorption into the porous structure.

Numerous studies have investigated both droplet spreading on non-porous surfaces and liquid absorption into porous structures [1–8]. Simultaneous spreading and absorption has not received as much attention. Computational modeling of liquid spreading and sorption on a porous surface utilizing lubrication approximation has been done for example by Davis et al. [9] and Alleborn and Raszillier on thick [10] and layered [11] substrates. Volume-of-fluid method has been used to study the droplet impact spreading and absorption on horizontal and inclined solid surfaces [12], over saturated pores [13] and on topographically irregular surfaces [14].

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Hydrodynamic theory and the molecular kinetic model have been contrasted to explain the behavior of an advancing droplet edge after initial inertial spreading of a droplet [15–20]. The molecular kinetic model suggests that the wetting line moves as the individual liquid molecules interact with the solid at the three-phase zone. Hydrodynamic theory on the other hand proposes that the droplet spreading is controlled by an energy balance between the capillary driving force and the hydrodynamic resistance to spreading. It has also been suggested that these two theories would co-exist at different time scales [18]. The droplet kinetics can be followed by measuring the contact diameter of the droplet on the surface. A power law type of behavior is seen in log/log plots of the contact diameter as a function of time. The scaling of the contact diameter is $D \sim t^{1/2}$ for the inertial regime, for the capillary regime right after that $D \sim t^{1/10}$ according to the hydrodynamic theory, and $D \sim t^{1/7}$ according to the molecular kinetic model.

The main objective of this work is to understand the short time interactions of offset ink oils and water with calcium carbonate pigment coating structures, with a specific application to offset printing of pigment coated paper.

Materials and Methods

In offset printing, mineral oils and linseed oils are typical components of inks, and water is used in so-called fountain solution. Properties of the liquids and experimental parameters are given in table 1.

Porous pigment tablets which mimic pigment coating structures were prepared by pressure filtration of pigment suspensions according to [21]. Three pigments were used, two ground calcium carbonates (Hydrocarb ME, OMYA Inc.): one with broad (BCGCC: 60 wt% < 2 μm) and one with narrow (NCGCC: 65 wt% < 1 μm) particle size distribution. The third pigment was a modified porous calcium carbonate (MCC) which creates discrete bimodal pore structures promoting rapid liquid uptake [22]. Ten parts of styrene acrylate latex (Acronal S360D, BASF) per hundred parts by weight of pigment was used as binder. Pressure-filtrated tablets were oven dried at 60 $^{\circ}\text{C}$ for 24 h after which samples were cut and polished to expose tablet centers. Optical calcite (Iceland Spar, Mexico) crystals were used as a model of solid, non-porous calcite surface. Sodium polyacrylate dispersant (Topsperse GX-N, Coatex SA, Genay, France) was adsorbed onto the calcite crystal surface as described in [23]

Pore structures of the tablets were characterized by mercury intrusion porosimetry (Pascal 140 and Pascal 440, Thermo Electron S.p.A., Milan, Italy). Figure 1 shows the pore size distributions and table 2 the pore space structural parameters. Darcy permeability was measured by pressure filtration following the method described in [24].

Droplet spreading and absorption was imaged at ambient conditions (Temperature 24 ± 2 $^{\circ}\text{C}$, RH 25-30 %) with a high speed

Table 1. The physico-chemical properties of the liquids.

	Mineral oil ^a	Linseed oil ^b	Water ^c
Abbreviation	MO	LO	H2O
η (at 100 1/s, 25 $^{\circ}\text{C}$)	4.04 (mPa s)	44.7	0.89
σ	30 (mN/m)	34	72
Drop volume	3.4 (μl)	3.4	6
Drop diameter	1.9 (mm)	1.9	2.3
Impact velocity	0.074 (m/s)	0.074	0.074
Weber number	0.27	0.27	0.17
Ohnesorge number	0.019	0.187	0.002

^a PKWF 6/9 (Haltermann Products, Germany).

^b Refined linseed oil (John L Seaton & Co Ltd., England).

^c Deionized.

Table 2. Pore space characteristics of the pigment tablets.

Pigment tablet	Accessible porosity (%)	Total pore surface area (m^2/g)	Pore diameter (μm)	k^* (m^2)
BCGCC	25.7	4.1	0.21	1.00×10^{-18}
NCGCC	27.4	6.2	0.12	5.77×10^{-18}
MCC	52.2	45.5	0.41 and 0.02	1.45×10^{-17}

* Darcy permeability constant.

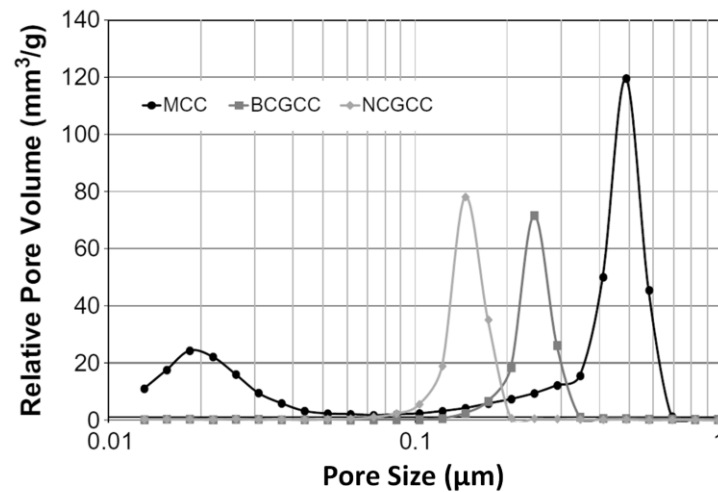


Figure 1. Poresize distributions of tablet structures.

camera (Citius C100 Centurio, Citius Imaging Ltd., Finland) positioned on the same plane as the droplet base at a grazing angle of 3°, 11 cm from the droplet center. Contact angles (left/right), volume, and contact diameter of a droplet as a function of time were extracted from the image sequences using ImageJ and a customized version of the DropSnake [25] plug-in.

Results

Mineral oil, linseed oil and water droplets were placed on the three porous pigment tablets, and the absorption and spreading of the droplets was imaged in time. The times for complete absorption are given in table 3. The absorption is fastest into the MCC structure and slowest into BCGCC. The fast absorption into the MCC is due to the discrete bimodal pore size distribution which combines high capillary forces with high permeability. Absorption into BCGCC structure is slightly slower than that into the NCGCC, apparently because of the lower permeability of the former. When comparing the different liquids, the absorption speed into the porous structures is fastest for the mineral oil and slowest for water, with the exception of the BCGCC structure, into which linseed oil absorbed slowest.

On a porous surface, spreading and absorption of the droplet occur simultaneously. Figure 2a shows representative image sequences for water droplet behavior on the three porous structures. One main observation is that at short times, the surface spreading dominates over the absorption as the droplet volume losses into the tablet structures were always less than 5 % at time $t = 2$ s. Complete absorption occurs at much longer times (table 3).

Figures 2b-d represent the spreading behavior by plotting the droplet contact diameter in time. It appears that there is only a minor influence of the porous structure on the spreading behavior of the mineral oil and linseed oil. Spreading is faster for mineral oil as expected from its lower viscosity. The change of slope in the figure 2b at $t \sim 0.01$ s indicates a transition from inertial spreading to spreading driven by capillarity. The transition cannot be

Table 3. Liquid absorption times into porous tablets.

Liquid	Complete absorption					
	MCC		NCGCC		BCGCC	
	Time (s)	Normalized to MCC	Time (s)	Normalized to MCC	Time (s)	Normalized to MCC
H ₂ O	242	1.0	567	2.3	579	2.4
MO	11	1.0	40	3.6	43	3.8
LO	129	1.0	434	3.4	839	6.5

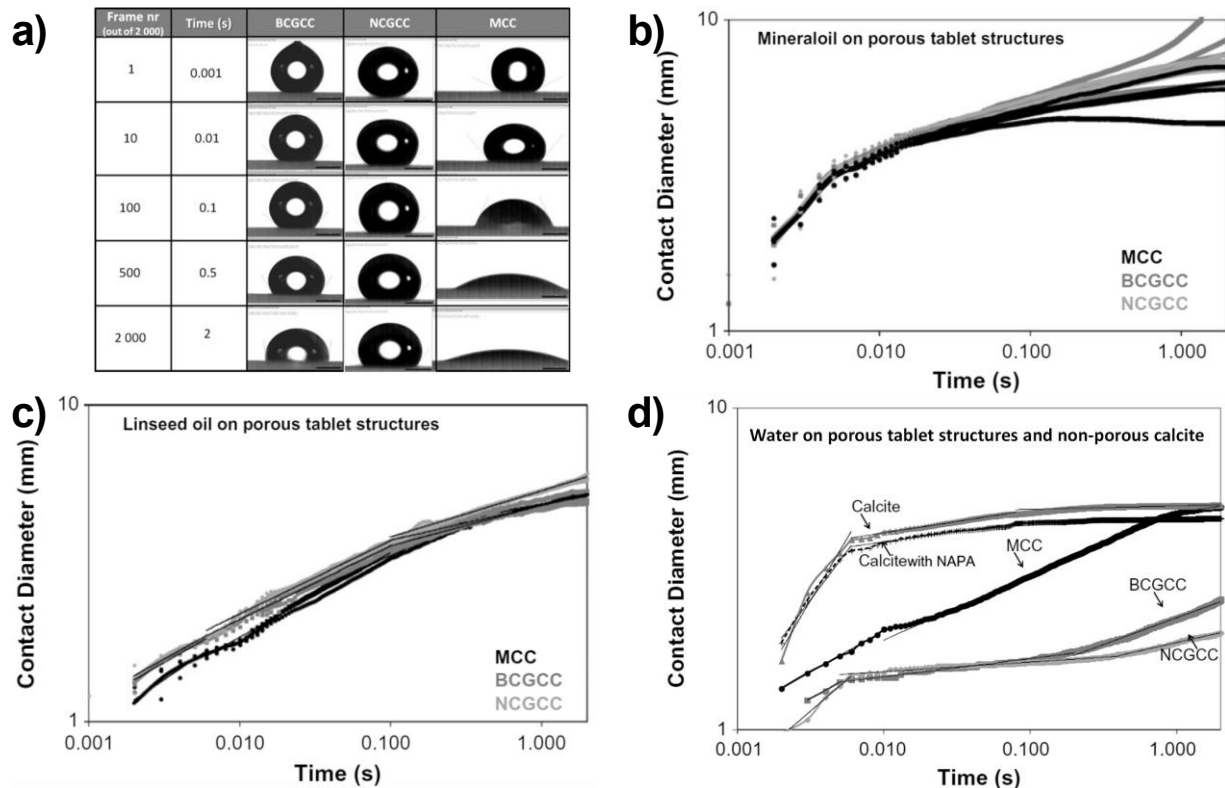


Figure 2: (a) Water droplet spreading and absorption on porous pigment tablets, contact diameters of (b) mineral oil, (c) linseed oil and (d) water on porous pigment tablets and (d) untreated and polyacrylate treated calcite surface.

observed for linseed oil (figure 2c) due to its high viscosity, which dampens the inertial effect of the falling droplet.

The spreading behavior of water differs from that of the used oils. Figure 2d plots the contact diameter of water droplets on the three porous structures together with data for droplets on non-porous smooth calcite surface. The droplet spreading on non-porous surface is clearly faster than that on the porous surfaces, where the advancing liquid front is frequently pinned by the surface roughness. The Na-polyacrylate dispersant slows down the droplet spreading slightly. The change from inertial spreading to capillary regime can easily be seen in the curves. The slope of the capillary phase spreading curve depends on the pigment used. Tablets BCGCC and NCGCC behave initially very similarly but start deviating from one another at around $t = 200$ ms, and the MCC curve is steeper throughout. The surface features of BCGCC and NCGCC are larger compared to MCC, and thus the motion of water is slower on these pigments as the water front needs to overcome larger surface features and fill up larger surface pores in order to move forward.

The results can be related to the hydrodynamic and the molecular kinetic theories, when plotting the contact diameter and the time in a log/log-graph and studying the respective slopes. The curves in figures 2b-d can be divided into two distinct regions, the first one being the inertial regime. On these porous surfaces using the three liquids: mineral oil, linseed oil and water, the slope in the inertial region was $n = 0.34 \pm 0.04$. The results agree with the work of Bliznyuk *et al.* [18] in that the duration of the inertial regime was of the order of a few milliseconds and that for more viscous linseed oil the inertial regime was even shorter. The surface porosity certainly affects the results as well, and it is suggested to be the cause of the slightly smaller value than that originally proposed by Bianco *et al.* [4]. For the solid calcite surface included in figure 2d, the slope is $n = 0.71$. The addition of sodium polyacrylate on the surface reduces the slope to $n = 0.61$. The strong interaction of water with both the calcite and sodium polyacrylate might provide a partial explanation for larger than 0.5 slope which is expected for purely inertial spreading. A supporting conclusion of higher slope being due to increased interactivity of water contacting a hydrophilic surface is found in the work of Drelich and Chibowska [19] and Wang *et al.* [5]. Sodium polyacrylate is known to give an additional hygroscopic character to a surface. The later capillary stage of the curve shows that the water droplet does not spread as far on the sodium polyacrylate covered calcite indicating support to the retarding effect of the dispersant. Analyzing the capillary regime, starting from approximately 6 ms to the final 2 000 ms, for the oils, the slopes are of the same magnitude as predicted by the molecular kinetic model, $1/7$ or 0.14. For the water droplet, the structure of the surface with a range of topographies, roughness and porosities is dominant after the inertial regime, and the molecular kinetic theory does not seem to apply.

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