

Influence of anisotropy on the dynamic wetting and permeation of paper coatings

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Abstract

A void network model, named Pore-Cor, has been used to study the permeation of an ink solvent into paper coating formulations coated onto a synthetic substrate. The network model generated anisotropic void networks of rectangular cross-sectional pores connected by elliptical cross-sectional throats. These structures had porosities and mercury intrusion properties which closely matched those of the experimental samples. The permeation of hexadecane, used as an analogue for the experimental test oil, was then simulated through these void structures. The simulations were compared to measurements of the permeation of mineral oil into four types of paper coating formulation. The simulations showed that the inertia of the fluid as it enters void features causes a considerable change in wetting over a few milliseconds, a timescale relevant to printing in a modern press. They also showed that in the more anisotropic samples, fast advance wetting occurred through narrow void features. It was found that the match between experimental and simulated wetting could be improved by correcting the simulation for the number of surface throats. The simulations showed a more realistic experimental trend, and much greater preferential flow, than the traditional Lucas–Washburn and effective hydraulic radius approaches.

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1. Introduction

If a porous solid is made up from a homogeneous packing of unsorted spherical particles bound together, the resulting void structure will normally be structurally isotropic—i.e., it will have approximately the same structural characteristics in any direction, and hence approximately the same permeation characteristics [1]. However, a sample made up from non-isometric particles such as clay platelets, packed in an aligned manner, would be structurally anisotropic [2]. Consequently, the rate of wetting would vary with direction. Such anisotropic permeation is relevant to the printing of paper coated with aligned anisotropic clay particles, and to other processes such as the subterranean migration of fluids in shale [3].

When designing paper coatings with optimum printing properties, manufacturers have a wide choice of mineral pigments to choose from, ranging from isotropic precipitated calcium carbonates, through ‘blocky’ clays such as Georgia kaolin, to ‘platey’ clays such as Speswhite with a high aspect factor. Each type of pigment can also be prepared with a wide range of particle sizes, and each size distribution can have a different range and skew. The problem when assessing the ink absorption properties of different pigments is that if one compares particles with different aspect factors, their size distribution changes also, and it is difficult to separate one effect from the other. So in this work a void network model has been used to highlight the effects of anisotropy and aspect factor which are otherwise hidden within experimental trends. The network model, named Pore-Cor (pore-level properties correlator), can accommodate changes in void sizes and connectivity between samples, such that additional changes caused by anisotropy can

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be revealed and studied. It has been used previously for modelling the behaviour of fluids in a wide range of materials such as porous calcium carbonate blocks [4,5] and soils [6]. A new version of the network model has been used, which generates an anisotropic three-dimensional void network of pores with a rectangular cross-section connected by throats with an elliptical cross-section. The equation for wetting was an inertially modified version of the Lucas–Washburn equation developed by Bosanquet [7].

Previous researchers have shown the dependence of wetting on the thickness of the porous layer [8] and the size of the applied droplet of fluid [9]. Others have used an effective hydraulic radius approximation [10] or the equation of state approach [11]. However, the wetting of such simple systems is totally different from that in more complex networks [12]. Nevertheless, a series of approximations had to be made to make the computation time manageable, in practice less than 30 h on a 1 GHz computer.

Wetting and consequent permeation start at the contact point or surface between the fluid reservoir or droplet and the porous solid. There is an almost instantaneous wetting jump when a wetting fluid contacts a wettable porous sample [4]. Next, the fluid has to accelerate from rest into the various void features. Many researchers have improved Bosanquet's description of initial, inertial, and continuity influences [8], and some have included a kinetic energy term [13] or used full Navier–Stokes equations [14,15]. It has been shown previously that the time-step for the wetting calculation in our network model must be no more than 1 ns [4], and consequently the calculation time would have been unmanageable if these more sophisticated effects had been included. Improvements to overcome a singularity at the tube entrance at time zero have been suggested by Szekely et al. [16], but are insignificant under the conditions of this work.

The way the fluid subsequently permeates through the structure is then controlled by a further series of factors, all of which are approximated in this work. These are the sizes and shapes of the voids [17], their connection into the network [18–20], wetting jumps [21,22], the surface energy between the fluid and the solid phase [23], and the density, viscosity and applied pressure of the fluid [24–26].

Modern printing presses feed paper through a printing nip, a few centimetres long, at speeds of up to 15 m s^{-1} . So the fluid contact time in the nip is of the order of a few milliseconds. At longer times, of the order of seconds to tens of seconds, there may be problems due to back-transfer of ink onto other rollers or ink smearing, but these effects are beyond the scope of this publication.

2. Materials and methods

2.1. Samples

In its simplest form a paper coating consists of mineral pigments, binders and air voids. The binders act as an

adhesive to bind the pigment particles together and to the substrate [27]. Typically, the weight fraction of pigment is 80–95% [28]. Assuming a pigment density of 2.6 g cm^{-3} and a binder density of 1.0 g cm^{-3} , the volume fraction of the pigment is about 70%.

Four types of commercially available pigments were studied: Speswhite and Amazon 90 SD (both Kaolin clays), and OpacarbA40 (OpA40) and Albaglos (both precipitated calcium carbonates or PCCs). Speswhite is a primary coarse-grained kaolin mineral supplied from Imerys, UK, while Amazon 90 SD is a secondary fine-grained kaolin supplied from Caulim da Amazônia S.A., Brazil. Both have a platy or foliated mineral structure. By contrast, the PCC group contains chemically synthesised calcium carbonate minerals belonging to either a calcitic or an aragonitic crystalline polymorph. OpA40 is aragonitic in structure, with an acicular (or needle-like) crystal habit. Albaglos contains a calcitic structure, with a rhombohedral crystal habit. The aragonite and Albaglos pigments were supplied by Specialty Minerals Nordic Oy, Finland.

In the coating preparation, sodium polyacrylate (Dispex N 40 from Allied Colloids Ltd., UK) was used as a dispersant for the pigments. A carboxylated styrene-butadiene latex (DPL 935 from Dow Rheinmünster GmbH, Germany), with a diameter of $0.15 \mu\text{m}$ and a glass transition temperature T_g of 8°C , was used as a binder, and carboxymethyl cellulose (CMC), with an average molecular weight of 45000 (FF5 from Noviant, Finland), was used as water retention aid. The kaolin pigments were received in a dry form and were dispersed in water under conditions suggested by the manufacturers.

The samples for the permeation experiments were coated onto an impermeable plastic backing known as Synteape (Arjo Wiggins Ltd., UK). This has a slightly rough, hooked surface on which the coating can adhere, producing the flexible but stable surface necessary for the permeation experiments.

The pigment suspensions contained 1 pph CMC and 10 pph latex. All suspensions were prepared in a conventional manner to 60% solids content by weight and a pH value of 8.5. They were drawn down onto the Synteape using a wire-wound rod in a bench coater (K-coater, RK Print-Coat Instruments Ltd., Royston, UK), to a coat weight of around 80 g m^{-2} in each case. Synteape is permeable from the side, so for porosimetry the suspensions were bench-coated onto the aluminium backing foils to a coat weight of about 18 g m^{-2} . All coating and drying was carried out at room temperature. Each coated sample strip had dimensions of $4 \times 25 \text{ cm}$.

2.2. Techniques for characterising particle and void size distributions

Particle diameters and the widths of their size distributions were measured by X-ray monitoring of sedimentation rate (Micromeritics Sedigraph 5000), and by light scattering

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