Observation and analysis of the infiltration of liquid polymers into calcium carbonate agglomerates

P. Levresse a, I. Manas-Zloczower b, D.L. Feke b, Y. Bomal c, D. Bortzmeyer c

a Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, USA
b Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH 44106, USA
c Centre de Recherches d'Auberilliers, Aubervilliers, France

Received 22 October 1998; received in revised form 26 February 1999; accepted 26 February 1999

Abstract

The dispersion of fine particle agglomerates in liquid polymer melts is influenced by the penetration of liquid into the agglomerates. It is therefore of great importance to determine the extent of polymer impregnation that can be achieved during a typical processing operation. This paper studies the infiltration of calcium carbonate agglomerates by various polymeric liquids. The kinetics of infiltration was gauged using sedimentation experiments performed in the impregnating liquids. Experimental infiltration curves proved to be well-described by a theoretical relationship based on Darcy’s law. This model was first applied assuming full saturation of the infiltrated outer layer of the agglomerate and it was considered that there was no air pressure build-up inside the dry core of the agglomerate. These assumptions had to be relaxed to account for the differences in infiltration rate observed for polymers of different chemical nature. For some of the fluids [ethylene–propylene random copolymer (EP) and styrene–butadiene random copolymer (SBR)], a partially saturated infiltrated region was envisioned. Assuming that poly(dimethylsiloxane) (PDMS) was able to fully saturate the agglomerate infiltrated layer, lower degrees of saturation (about 0.9) were found in the case of EP and SBR. These estimations were obtained considering that residual air reduced the effective permeability of the agglomerate to the polymer. A classical power law relationship was used to link this effective permeability to the degree of saturation of the infiltrated region. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Calcium carbonate; Infiltration; Molten polymers; Permeability

1. Introduction

Calcium carbonate is a widely used reinforcing filler, particularly for polyolefins. Characterized by its low cost, calcium carbonate is nonetheless able to impart strong improvement to the matrix mechanical properties, provided its dispersion in the polymer is carefully controlled. Filler content, surface treatment, and ultimate particle size have been shown to influence the mechanical behavior of calcium carbonate-filled composites [1–4]. The presence of non-dispersed or re-agglomerated clusters is detrimental to the uniformity of the product final properties [5]; therefore, understanding the mechanisms of calcium carbonate agglomerates dispersion is of high practical interest.

Since agglomerates have a permeable structure, they are subject to fluid infiltration. The infiltration of a liquid polymer into a porous agglomerate corresponds to the displacement from the agglomerate pores of a fluid (air) by a more wetting one (polymer melt). This process is driven by capillary pressure (pressure difference across the interface between the two fluids) and hydrostatic pressure but the latter can be shown to be negligible compared to the former (see Appendix A). Liquids characterized by a contact angle on calcium carbonate of less than a critical value can infiltrate calcium carbonate agglomerates, provided that the air displaced from the pores is allowed to escape. Otherwise, air pressure rises inside the agglomerate up to the point where it counterbalances the capillary pressure and consequently, infiltration stops. The critical upper limit of the contact angle for spontaneous infiltration is traditionally considered to be 90°. However, it has been observed in many systems and established theoretically in the case of orderly packed spheres or fibers that the critical wetting angle for spontaneous infiltration is less than 90°. Besides, it is sensitive to packing arrangement and infiltration direction [6].

The presence of liquid inside an agglomerate affects its cohesivity. The creation of liquid bridges leads to a sub-
stantial increase in the tensile strength of moist agglomerates [7]. Similarly, we observed in our laboratory that matrix infiltration strengthened calcium carbonate agglomerates during dispersion experiments carried out in polymer melts under simple shear flow conditions. Assessing the kinetics of matrix infiltration constitutes, therefore, a valuable tool in the analysis of the dispersion behavior of fine particle agglomerates in molten polymers.

The role of matrix infiltration in the hydrodynamic dispersion of particulate clusters was first highlighted during the study of the dispersion of carbon black agglomerates in liquid polymers. Yamada et al. [8,9] investigated the dispersion mechanisms of carbon black agglomerates in simple shear flows and found that the agglomerate erosion kinetics could be interpreted in terms of degree of matrix infiltration and agglomerate permeability. The agglomerate dispersion behavior could be successfully correlated to the ratio of the depth of the infiltrated layer to the square root of the agglomerate permeability, a characteristic length related to the thickness of the agglomerate region that can be drained by viscous flow.

Sedimentation experiments proved successful in determining the infiltration kinetics of porous agglomerates by fluids of a broad range of viscosities (from 1 to 100 Pa s) and chemical structures [10,11]. Hence, this technique appears to be the method of choice to investigate the infiltration of viscous polymers into calcium carbonate agglomerates. The purpose of this work is to measure and model the infiltration kinetics of calcium carbonate agglomerates and to study the influence of various factors affecting the rate of infiltration. The role of interfacial properties was assessed using different non-polar fluids (differing by their chemical structure and surface tension) and a stearic acid-coated powder. A first set of experiments was performed with different types of agglomerate in a given fluid. Powders of different morphologies were employed so as to generate agglomerates of equal density but different pore geometry. The influence of agglomerate packing density was examined for two of these powders. The infiltration kinetics of a powder coated with stearic acid was recorded and compared to those of the untreated powders. In a second step, a given type of agglomerate was selected and the fluid characteristics were varied in order to investigate the effects of matrix viscosity and chemistry.

2. Experimental

2.1. Materials

The powders studied here are four different commercial grades of precipitated calcium carbonate, Calofort U, Calopake F, Sturcal H and Calofort S, supplied by SMI-Lifford. The first three are untreated powders while Calofort S is a powder coated with stearic acid. This coating, applied in solution, corresponds to approximately half a monolayer surface coverage of the powder. The main characteristics of the untreated powders are summarized in Table 1. Scanning electron microscopy (SEM) observations of these powders can be found in the literature [12]. The primary particle density is 2.71 g cm$^{-3}$ for calcite (Calofort U, Calofort S and Calopake F) and 2.93 g cm$^{-3}$ for aragonite (Sturcal H).

Calcium carbonate agglomerates were prepared by compaction. The powders were used as received. Given amounts of powder were compressed unidirectionally in a cylindrical cell for 5 min and the pellets formed were carefully ejected from the cell. The pellets (0.5 cm high, 2.66 cm in diameter) were then fractured into large pieces (3 to 5 mm in size). By vibrating these pieces on sieves for up to 3 days and shaping them with a blade, nearly spherical shapes were obtained. The agglomerates selected for the infiltration experiments were characterized by diameters ranging from 2.3 to 3.6 mm. The solid volume fraction $\phi$ of the agglomerates varied from 0.26 to 0.33 (reduced density $\phi/(1 - \phi)$ of 0.36 to 0.48). All the agglomerates were dried for 24 h at 200°C (100°C for Calofort S) in a vacuum oven and stored in a desiccator prior to use.

Low-viscosity polymeric fluids, poly(dimethylsiloxane) (PDMS), ethylene–propylene random copolymer (EP) and styrene–butadiene random copolymer (SBR) were employed in this study. The main characteristics of these fluids are summarized in Table 2. Surface tensions were found in the literature [13,14]. Surface tensions of the random copolymers were estimated from the values of the homopolymers weighted by their mole fractions [15].

2.2. Procedure

Following the lead of Bohin et al. [10], the penetration of polymeric liquids into calcium carbonate agglomerates was assessed from the agglomerate sedimentation (or flotation) velocities measured in the impregnating fluid. A spherical agglomerate was placed in a glass of fluid, more than 2 cm from the glass walls and more than 3 cm from the fluid surface. The velocity of the agglomerates was measured using a charge-coupled device (CCD) video.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Crystallinity</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calofort U</td>
<td>calcite</td>
<td>spheres (around 80 nm in diameter) slightly agglomerated into micrometer scale spheres</td>
</tr>
<tr>
<td>Calopake F</td>
<td>calcite</td>
<td>micrometer scale platelets</td>
</tr>
<tr>
<td>Sturcal H</td>
<td>aragonite</td>
<td>needles agglomerated into hog-like spheres (around 10 μm in diameter)</td>
</tr>
</tbody>
</table>
camera. We adopted the convention that the velocity is positive when the agglomerate sediments. As the fluid infiltrates the porous agglomerate and increases its density, the velocity of the agglomerate increases (in algebraic value).

3. Determination of infiltration rate from sedimentation velocity

For an axi-symmetric creeping flow of an incompressible Newtonian fluid, the frictional force acting on a sphere of radius $a$ and velocity $U$ in a fluid of viscosity $\mu$ is $6\pi\mu aU$ (Stokes’s law). This expression is valid for a rigid impermeable sphere. The value of the frictional force is smaller for a permeable sphere since fluid is able to flow through it. The effect of permeability is accounted for by a factor $\Omega$, ratio of the hydrodynamic drag of a permeable sphere to that of an impermeable sphere of same size and same density. $\Omega$ is dependent on the agglomerate porosity and pore size distribution, but also on the relative amount of air and polymer inside the agglomerate because polymer flow through the agglomerate is affected by the presence of entrapped air.

At a time $t$ after its immersion in the fluid, the agglomerate steady-state velocity $U(t)$ obeys the following force balance equation:

$$
\frac{4}{3}\pi a^3 g \left[ \rho_b s(t) (1 - \phi) + s(t) (1 - \phi) \rho - \rho \right] = 6\pi \mu a U(t) \Omega(s),
$$

where $\rho_b$ is the primary particle density of the powder, $\rho$ is the fluid density and the filling factor $s(t)$ is the fraction of the overall agglomerate void volume which is filled with polymer at time $t$:

$$
s(t) = \frac{V_t}{\frac{4}{3} \pi a^3 (1 - \phi)},
$$

in which $V_t$ is the total volume of polymer incorporated within the agglomerate.

4. Determination of $\Omega$ values for completely filled agglomerates

In the case of an impermeable sphere such as a glass ball of radius $a_b$ and density $\rho_b$, Eq. (1) becomes:

$$
\frac{4}{3}\pi a_b^3 g (\rho_b - \rho) = 6\pi \mu a_b U_b.
$$

(3)

The value of $\Omega$ for a completely filled agglomerate ($s = 1$) can be readily derived from Eqs. (1) and (3):

$$
\Omega = \phi \left( \frac{\rho_b - \rho}{\rho_b - \rho} \right) \left( \frac{a}{a_b} \right)^2 \frac{U_b}{U_{s=1}}.
$$

(4)

In this equation, $U_{s=1}$ stands for the velocity of the completely filled agglomerate. The value that is accessible through experiments is the maximum sedimentation velocity $U_{max}$: after long infiltration times (several days in some instances), the sedimentation velocity of the agglomerate stabilizes at $U_{max}$, indicating that $s$ has reached its maximum. Provided that the maximum of $s$ is equal to 1, $U_{max}$ can be identified with $U_{s=1}$. In this paper, it is assumed that complete filling can indeed be attained after prolonged soaking and $\Omega$ values are derived from the equilibrium sedimentation velocity $U_{max}$. It is essential that $U_{max}$ (agglomerate velocity) and $U_b$ (glass ball velocity) be measured at the same temperature, such that the viscosity of the fluid is the same for both measurements. This condition is especially important for liquid polymers such as EP and SBR characterized by a viscosity that is strongly temperature-dependent.

Table 3 shows the values of $\Omega$ determined experimentally from $U_{max}$ for (presumably) completely filled Calopake F agglomerates in various liquid polymers. The reduced density $\phi/(1 - \phi)$ of the agglomerates was 0.43. All the agglomerates were approximately spherical: the ratio of the largest diameter to the smallest (aspect ratio) was less than 1.1. Correction factors for the drag coefficient of regular spheroids (oblate or prolate) whose main axis is parallel or perpendicular to the vertical direction are available in the literature [16]. In this study the correction factors were not employed. Instead a mean radius was calculated for each agglomerate and the values of $U_{max}$ used in the calculation of $\Omega$ were averaged over multiple

<table>
<thead>
<tr>
<th>Fluids</th>
<th>Brands</th>
<th>Viscosity (Pa s)</th>
<th>Density (g cm$^{-3}$)</th>
<th>Surface tension (mJ m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>Dow Corning 200®</td>
<td>10</td>
<td>60</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>10000 cSt 60000 cSt Blend</td>
<td>15</td>
<td>97</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Dow Corning 200®</td>
<td>150</td>
<td>97</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Rhône-Poulenc 47 V</td>
<td>150</td>
<td>97</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>150000®</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EP</td>
<td>Uniroyal Trilene CP 30®</td>
<td>200 (21°C), 145 (25°C)</td>
<td>0.83</td>
<td>31</td>
</tr>
<tr>
<td>SBR</td>
<td>Ricon Resins Ricon 181®</td>
<td>15</td>
<td>0.89</td>
<td>34</td>
</tr>
</tbody>
</table>

Table 3

Experimental values of $\Omega$ for completely filled Calopake F agglomerates measured from $U_{max}$ in various fluids ($\phi/(1 - \phi) = 0.43$)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\mu_{(25°C)}$ (Pa s)</th>
<th>$\Omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>10</td>
<td>0.99</td>
</tr>
<tr>
<td>PDMS</td>
<td>15</td>
<td>0.97</td>
</tr>
<tr>
<td>PDMS</td>
<td>60</td>
<td>0.99</td>
</tr>
<tr>
<td>PDMS</td>
<td>150</td>
<td>0.96</td>
</tr>
<tr>
<td>EP</td>
<td>200</td>
<td>0.99</td>
</tr>
<tr>
<td>SBR</td>
<td>15</td>
<td>0.97</td>
</tr>
</tbody>
</table>
irrespective of the fluid, which confirms that \( V \) represents only a small fraction \( 1\pm2\% \) of the agglomerate ability spheres with varying permeability \( 18\pm20 \). However, the drag force experienced by the sphere can be analytically calculated from the velocity across the agglomerate surface and uniform velocity field. For an agglomerate of radius \( R \) the flow within the infiltrated sphere is well-described by Brinkman’s extension of Darcy’s law. The boundary conditions adapted to the geometry of the problem are continuity of velocity vectors and tangential and normal stresses across the agglomerate surface and uniform velocity field far from the sphere. The drag force experienced by the sphere can be analytically calculated from the velocity field. For an agglomerate of radius \( a \) and constant permeability \( k \), \( \Omega \) is expressed by the following formula:

\[
\Omega = \frac{2 \beta^2 \left[ 1 - (\tanh \beta / \beta) \right]}{2 \beta^2 + 3 \left[ 1 - (\tanh \beta / \beta) \right]},
\]

where \( \beta = a / \sqrt{k} \).

Other authors have conducted similar studies for permeable spheres with varying permeability \( 18\pm20 \). However, Eq. (5) will be preferred here, since it is assumed a priori that the agglomerates prepared by compaction have a homogeneous structure.

The extent to which the outside viscous flow is effective beneath the agglomerate surface is of the order of \( \sqrt{k} \) [21,22]. A simplified schematic of this boundary layer is shown in Fig. 1. For Calopake F agglomerates of reduced density 0.43, \( \Omega \) was found to be between 0.96 and 0.99. Using Eq. (5), \( \Omega = 0.96 \) leads to \( \beta \approx 25 \), \( \Omega = 0.98 \) leads to \( \beta \approx 50 \) and \( \Omega = 0.99 \) leads to \( \beta \approx 100 \). Thus, \( \sqrt{k} \) represents only a small fraction \( 1\pm2\% \) of the agglomerate.

The extent to which the outside viscous flow is effective beneath the agglomerate surface is of the order of \( \sqrt{k} \) [21,22]. A simplified schematic of this boundary layer is shown in Fig. 1. For Calopake F agglomerates of reduced density 0.43, \( \Omega \) was found to be between 0.96 and 0.99. Using Eq. (5), \( \Omega = 0.96 \) leads to \( \beta \approx 25 \), \( \Omega = 0.98 \) leads to \( \beta \approx 50 \) and \( \Omega = 0.99 \) leads to \( \beta \approx 100 \). Thus, \( \sqrt{k} \) represents only a small fraction \( 1\pm2\% \) of the agglomerate.

The intrinsic permeability \( k \) of a porous material can be calculated from the value of \( \Omega \) measured from the sedimentation velocity of a completely filled spherical agglomerate. The case of an isolated permeable sphere in uniform flow was discussed in detail by Neale et al. [17]: the Navier–Stokes equations apply outside the sphere while the flow through the partially filled agglomerate is similar to the flow through a completely filled agglomerate. This situation can be achieved when all the pores located close to the agglomerate surface are filled, provided the depth of this fully saturated outer part exceeds \( \sqrt{k} \). This is all the more likely as \( \sqrt{k} \) is small, which is the case of the agglomerates studied here. Although this will not hold true shortly after immersion of the agglomerate in the fluid, it is reasonable to assume that this condition can be satisfied for intermediate and long immersion times. For the sake of simplicity, the values of \( \Omega \) corresponding to completely filled agglomerates are used in Eq. (1) for all times. With this assumption, the filling factor \( s(t) \) of an agglomerate can be derived from its sedimentation velocity:

\[
s(t) = 1 + \frac{\phi}{1 - \phi} \left( 1 - \frac{\rho_a}{\rho} \right) \left[ 1 - \frac{U(t)}{U_{\max}} \right].
\]

The following part of this paper is dedicated to the presentation of a theoretical relationship between \( s \) and \( t \). Experimental results will be compared to this model.

### 5. Model for the kinetics of agglomerate infiltration

A mathematical model based on Blake–Koseny equation was developed by Bohin et al. [23] to describe the kinetics of agglomerate impregnation by viscous liquids. A more general version based on Darcy’s law was recently proposed by Yamada et al. [11] and is adopted in the present paper. The model is valid for spherical agglomerates in which matrix infiltration is occurring symmetrically, leading to an infiltrated outer shell of constant thickness and a dry core of radius \( R \), as indicated in Fig. 2. The principle of a spherically symmetric infiltration was confirmed experimentally by Bohin et al. using phase contrast microscopy, as shown in Fig. 1 of [23]. It should be emphasized that this model does not require full saturation of the infiltrated layer \( (R < r < a) \). The fraction of
vooids filled with polymer in the infiltrated layer is denoted as $\sigma$. For the sake of simplicity, $\sigma$ is assumed to be uniform over the entire infiltrated layer. The model establishes a relation between the ratio $R/a$ and the time $t$ past since the immersion of the agglomerate in the polymer melt:

$$2 \left( \frac{R}{a} \right)^3 - 3 \left( \frac{R}{a} \right)^2 + 1 = 6\frac{k_w P}{\gamma^2 \mu} t = \Gamma t.$$  \hspace{1cm} (7)

The derivation of Eq. (7) can be found in Appendix A. The use of $k_w$ (effective permeability of the agglomerate to the wetting fluid, i.e., polymer melt) instead of $k$ (agglomerate intrinsic permeability) takes into account the possible presence of air inside the infiltrated region. Residual air reduces the permeability of the agglomerate to the wetting fluid so that the infiltrated layer is only partially saturated ($\sigma < 1$), $k_w$ is smaller than $k$ [24–27].

At the microscopic level, the capillary pressure $P_c$ is different in each pore and is a function of pore geometry and size. In the model, $P_c$ is defined as an average capillary pressure over the air/polymer interface located at $r = R$. Additionally, in the derivation of Eq. (7), $P_c$ is assumed to be constant during the whole infiltration process. For the sake of simplicity, the agglomerate is idealized in this paper as an equivalent capillary of hydraulic radius $r_h$ (ratio of volume to surface of the capillary). Thus, $P_c$ can be replaced in Eq. (7) by the following expression [26]:

$$P_c = \frac{\gamma \cos \theta}{r_h}.$$  \hspace{1cm} (8)

where $\gamma$ is the polymer-air surface tension and $\theta$ is the contact angle of the polymer on calcium carbonate. For $\theta$, the value of the contact angle at equilibrium will be considered, although the contact angle can be higher for advancing liquid fronts [25–28].

The experimental infiltration data (provided in the form of filling factor $s$ as a function of time) need to be related to the ratio $R/a$ so as to allow comparison with the theoretical model. A relationship exists between $s$, $\sigma$ and $R/a$. Indeed, $\sigma$ is defined as the fraction of the porosity of the outer shell ($R < r < a$) which is filled with polymer:

$$\sigma = \frac{4}{3} \frac{V_i}{\pi (a^3 - R^3)(1 - \phi)}.$$  \hspace{1cm} (9)

Combining Eqs. (2) and (9) yields:

$$s = \frac{1}{\sigma} \left( \frac{R}{a} \right)^3.$$  \hspace{1cm} (10)

If the infiltrated layer is fully saturated ($\sigma = 1$), the ratio $R/a$ can be derived from the sole overall filling factor $s$ of the agglomerate. In a first approximation, the infiltrated region will be considered as fully saturated throughout the entire infiltration process. This assumption also implies that $k_w$ can be replaced by $k$ in Eq. (7).

6. Results

The theoretical model developed for infiltration kinetics predicts that the left-hand side of Eq. (7) varies linearly with time, from the immersion of the agglomerate in the polymer melt up to a saturation time when all the pores are filled. The model suggests that the infiltration rate $\Gamma$ is inversely proportional to $a^2$. In order to compare agglomerates of slightly different size, we introduce a characteristic infiltration rate $\Gamma_c$ defined as $(a/a_c)^2 \Gamma$, in which the characteristic radius $a_c$ is approximately the average radius of the agglomerates in the set of experiments under consideration. $\Gamma_c$ represents the slope of the curve $2(R/a)^3 - 3(R/a)^2 + 1$ vs. $(a_c/a)^2 t$ and the saturation time $t_s$ is the inverse of $\Gamma_c$. The experimental curves were fitted to the model. Upon approaching unity, the function $2(R/a)^3 - 3(R/a)^2 + 1$ becomes extremely sensitive to slight experimental scattering of the sedimentation velocity $U(t)$. For this reason, the slopes were determined for values of $2(R/a)^3 - 3(R/a)^2 + 1$ below 0.6. With the exception of one experiment (which will be discussed later), infiltration kinetics follows a linear trend for all the agglomerates we tested. As an example, infiltration kinetics of Calopake F agglomerates is shown in Fig. 3 for PDMS fluids of different viscosity.

For agglomerates of similar radius $a_c$, combining Eqs. (7) and (8) yields:

$$\Gamma_c \propto \frac{k}{r_h \mu} \gamma \cos \theta.$$  \hspace{1cm} (11)

In Eq. (11), the first ratio corresponds to agglomerate properties (morphology of powder and packing density), the second ratio characterizes the fluid and $\cos \theta$ depends upon both fluid and powder.

---

![Fig. 3. Infiltration kinetics of Calopake F agglomerates in PDMS ($\phi/ (1 - \phi) = 0.43; a_c = 1.57 \text{ mm}$).](image)
6.1. Influence of powder morphology and agglomerate density

Values of $\Gamma_r$ determined by linear regression are reported in Table 4 for agglomerates of different grades and densities in PDMS 60,000 cSt. These values pertain to agglomerates of radius $a=1.25$ mm. Two experiments were performed for each density. Correlation coefficients are greater than 0.95 for all the agglomerates except for one of the Calofort S agglomerates (0.92). As seen in Table 4, results of infiltration rates are very similar for the two agglomerates tested for each density.

From the results shown in Table 4, it can be concluded that for the ‘high’ density agglomerates $(\phi/(1-\phi)) \approx 0.46$–0.48), infiltration is proceeding faster for Calopake F $(t_u \approx 600$ min) than for Sturcal $(t_u \approx 1000$ min) and Calofort U $(t_u \approx 1400$ min). Agglomerates of Calofort S exhibit, by far, the slowest infiltration $(t_u \approx 4500$ min).

The effect of the stearic acid treatment on infiltration rate appears to be extremely significant. It has been shown in the literature that increasing the extent of stearic acid surface treatment on calcium carbonate resulted in a sharp decrease in the filler surface tension [29,30]. The decrease is more pronounced in the polar component than in the dispersion component. Indeed, the surface of untreated calcium carbonate is very polar while stearic acid molecules are composed of a polar carboxylic head and a long apolar aliphatic tail. The carboxylic group reacts with calcium carbonate: as can be seen in Fig. 4, the value of $\cos \theta$ is predicted to be 1 for both powders. Therefore, Calofort U (untreated) and Calofort S (half a monolayer of stearic acid) are expected to have the same value of $\cos \theta$. This proves that the difference in infiltration rates between Calofort U and Calofort S does not result from differences in wetting angle. The origin of the difference in infiltration rates is still unclear at this stage but it is suspected that the surface treatment could have affected the morphology and packing characteristics of the powder.

The influence of agglomerate density on the infiltration rate can be assessed from the results presented in Table 4. For both Calofort U and Calopake F, infiltration is faster for the lower density agglomerates. Eq. (11) predicts that this behavior can be interpreted in terms of agglomerate intrinsic permeability $k$ and hydraulic radius $r_h$. When the agglomerate density is lowered, the number of pores inside the agglomerate increases or the pore size distribution is shifted towards larger pores or, most probably, both. In any case, the agglomerate intrinsic permeability $k$ is expected to increase. However, if the pore size distribution is shifted toward larger pores, $r_h$ is also expected to increase, which theoretically should lead to a decrease in $\Gamma_r$. Since experimentally $\Gamma_r$ is higher for lower density agglomerates, it can be concluded from the experiments that reducing the agglomerate density has a stronger effect on $k$ than on $r_h$.

In order to estimate $r_h$ for calcium carbonate agglomerates, compacted pellets of calcium carbonate were subjected to mercury porosimetry. (The analyses were performed by P. Le...)

Table 4

<table>
<thead>
<tr>
<th>Powder</th>
<th>$\phi/(1-\phi)$</th>
<th>$10^4 \Gamma_r$ $(\text{min}^{-1})$</th>
<th>Average $t_u = 1/\Gamma_r$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calofort U</td>
<td>0.46</td>
<td>6.5</td>
<td>1400</td>
</tr>
<tr>
<td>Calofort U</td>
<td>0.36</td>
<td>12</td>
<td>120</td>
</tr>
<tr>
<td>Calopake F</td>
<td>0.46</td>
<td>16.7</td>
<td>16.4</td>
</tr>
<tr>
<td>Calopake F</td>
<td>0.40</td>
<td>22.5</td>
<td>20.7</td>
</tr>
<tr>
<td>Sturcal H</td>
<td>0.46</td>
<td>10.4</td>
<td>10.6</td>
</tr>
<tr>
<td>Calofort S</td>
<td>0.48</td>
<td>2.5</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 5

<table>
<thead>
<tr>
<th>Powder</th>
<th>Median pore radius ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calofort U</td>
<td>0.15</td>
</tr>
<tr>
<td>Calopake F</td>
<td>0.4</td>
</tr>
<tr>
<td>Sturcal H</td>
<td>0.6</td>
</tr>
</tbody>
</table>
formed for us at Rhodia Research Center in Aubervilliers, France). These pellets were identical to the ones from which the spherical agglomerates were cut. Thus it is expected that the values obtained for the compacted pellets also characterize the spherical agglomerates. Results have been reported in Table 5. The median pore radius that is obtained with this technique (around 0.5 μm) can be considered as an estimation for the hydraulic radius \( r_h \). With \( r_h = 0.5 \) μm and \( y = 20 \) mJ m\(^{-2}\) (PDMS), Eq. (8) yields a capillary pressure \( P_c \) of 40,000 Pa. Using Eq. (7), the ratio \( \beta = a/\sqrt{k} \) can be assessed from the capillary pressure, the fluid viscosity \( \mu \) (60 Pa s), and the value of \( t_c \) determined experimentally:

\[
\frac{a}{\sqrt{k}} = \left( \frac{P_c}{6 \mu t_c} \right)^{1/2},
\]

\( t_c \) is roughly 1000 min for the untreated calcium carbonate agglomerates of reduced density 0.36–0.46; hence, \( \beta \) is found to be approximately 15,000. This result implies that \( \sqrt{k} \) is of the order of 0.1 μm. This value is two orders of magnitude lower than the value previously reported (30 μm) which was obtained from sedimentation of completely filled Calopake F agglomerates. We believe that this may be due to a difference in permeability between the surface and the bulk of the agglomerate. As stated earlier, the region of the agglomerate that can be drained by viscous flow extends approximately to a depth \( \sqrt{k} \) beneath the agglomerate surface. Therefore, assessing permeability through sedimentation velocity amounts to probe only the shell immediately underneath the agglomerate surface. It is easily conceivable that the immediate outer shell of the agglomerate is less dense and more permeable than the bulk. The value of \( \sqrt{k} \) derived from infiltration kinetics, on the other hand, characterizes the bulk and is found to be much lower.

### 6.2. Influence of polymer viscosity and chemistry

Fig. 3 shows the kinetics of infiltration of PDMS fluids of different viscosities into Calopake F agglomerates characterized by a reduced density \( \phi/(1-\phi) = 0.43 \). Correlation coefficients are greater than 0.98 for all the agglomerates. As expected, increasing matrix viscosity is retarding infiltration. Values of the infiltration rate \( \Gamma_c \) are plotted in Fig. 5 as a function of the inverse of the fluid viscosity \( \mu \). Eq. (11) predicts a linear relationship between \( \Gamma_c \) and \( 1/\mu \) and agreement of the experimental data with the model (solid line) is good.

Values of the infiltration rate \( \Gamma_c \) measured in various polymers are summarized in Table 6a–b for Calopake F agglomerates and Table 7 for Calofort S agglomerates, along with polymer properties and values of \( \cos \theta \). It can be inferred from Fig. 4 that PDMS, EP and SBR spontaneously spread on untreated calcium carbonate powders such as Calopake F since their surface energies are all below the critical surface energy for wetting about 45 mJ m\(^{-2}\). Values of \( \cos \theta \) for Calofort S are extrapolated from Fig. 4.

For a given type of agglomerate, the rate of fluid infiltration is predicted to be proportional to the quantity \( 1/\mu \gamma \cos \theta/\mu \) which is mentioned in the tables for the purpose of comparison with \( \Gamma_c \). However, for each of the three comparisons proposed, infiltration rates cannot be solely explained by the quantity \( \gamma \cos \theta/\mu \). This leads to the conclusion that some of the assumptions made in the derivation of Eq. (7) may not be valid.

The assumption that \( \Delta P_e \) (excess air pressure in the dry core of the agglomerate relative to atmospheric pressure) can be neglected compared to \( P_c \) (capillary pressure) is questionable particularly in the case of the experiments conducted in the SBR. Infiltration kinetics of the Calopake

### Table 6

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \mu(25^\circ C) ) (Pa s)</th>
<th>( \gamma(25^\circ C) ) (mJ m(^{-2}))</th>
<th>( \cos \theta )</th>
<th>( \gamma \cos \theta/\mu ) (mm s(^{-1}))</th>
<th>( 10^4 \Gamma_c ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>150</td>
<td>20</td>
<td>1</td>
<td>0.13</td>
<td>5.6</td>
</tr>
<tr>
<td>EP</td>
<td>200</td>
<td>31</td>
<td>1</td>
<td>0.16</td>
<td>3.2</td>
</tr>
</tbody>
</table>

### Table 7

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \mu(25^\circ C) ) (Pa s)</th>
<th>( \gamma(25^\circ C) ) (mJ m(^{-2}))</th>
<th>( \cos \theta )</th>
<th>( \gamma \cos \theta/\mu ) (mm s(^{-1}))</th>
<th>( 10^4 \Gamma_c ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>60</td>
<td>20</td>
<td>1</td>
<td>0.33</td>
<td>1.8</td>
</tr>
<tr>
<td>SBR</td>
<td>15</td>
<td>34</td>
<td>0.75(^a)</td>
<td>1.7</td>
<td>2.7(^b)</td>
</tr>
</tbody>
</table>

\(^a\)Approximated from Fig. 4.

\(^b\)Calculated assuming \( \Omega = 1 \).
F agglomerate tested in SBR does not exhibit a linear trend over the whole infiltration process but only during the initial stage (first 100 min from which a value of \( \Gamma_c \) could be calculated). Infiltration then slows down, indicating that air pressure inside the agglomerate might be rising and partly counterbalancing capillary pressure. In the case of Calofort S, \( \Omega \) was not measured in SBR because the agglomerate broke into halves before complete filling could be reached. This phenomena can be attributed to compression of air inside the agglomerate voids (the volume of which is reduced as polymer infiltrates the agglomerate). This is corroborated by the fact that no air bubble was seen to escape from the Calofort S agglomerate during the course of the experiment.

Additionally, the issue of the level of saturation in the infiltrated layer has to be addressed more closely. For Calopake F agglomerates, it can be extrapolated from the infiltration results that the degree of saturation of the infiltrated layer has to be addressed more closely. For values of \( \sigma \) higher than 0.8, \( \sigma_c \) is within a 10% margin of \( \sigma \), provided \( \sigma_c \) is below 0.25 which is most probable. In the following, \( \sigma_c \) will be identified with \( \sigma \), and \( n \) will be arbitrarily set equal to 3.5.

Under the hypothesis that \( \sigma \) is equal to 1 for PDMS, one can estimate \( \sigma \) in the case of EP or SBR. In Eq. (7), the effective permeability of the polymer, \( k_w \), is replaced by \( k \) for PDMS and by \( k \sigma ^{3.5} \) for EP or SBR. Combining Eqs. (7) and (8) with \( \cos \theta = 1 \) yields:

\[
\frac{\Gamma_c}{\Gamma_c, \text{PDMS}} = \frac{3.5 \gamma}{\gamma, \text{PDMS}} \frac{k_{\text{PDMS}}}{\mu} \frac{1}{\mu},
\]

where the parameters without subscript refer to EP or SBR. The determination of \( R/a \) from experimental data using Eq. (10) also involves the parameter \( \sigma \). The experimental value of the infiltration rate \( \Gamma_c \) is therefore a function of \( \sigma \). Thus, \( \sigma \) can be adjusted such that \( \Gamma_c \) verifies both Eqs. (10) and (15) with the values summarized in Table 6a for EP and Table 6b for SBR. Using this procedure, the degree of saturation of the infiltrated layer \( \sigma \) is found to be approximately 0.89 in the case of EP and 0.93 in the case of SBR, provided \( \sigma \) is equal to 1 for PDMS.

In the preceding calculations, the determination of the filling factor \( s(t) \) involves the parameter \( \Omega \). As previously, \( \Omega \) is replaced in the calculation by its value at long times (Table 3). Indeed, when \( k \) is replaced by \( k \sigma ^{3.5} \) in Eq. (5) [33], the resulting value of \( \Omega \) is a very weak function of \( \sigma \) for \( \beta \) greater than 25 and \( \sigma \) greater than 0.8 (both conditions are met by our agglomerates). It can be shown that between \( \sigma = 0.8 \) and \( \sigma = 1 \), \( \Omega \) changes by less than 1.5%, which justifies the use of \( \Omega \) values determined for completely filled agglomerates.

### 7. Conclusions

The infiltration kinetics of calcium carbonate agglomerates by liquid polymers was shown to obey a theoretical model based on Darcy’s law. This model correctly predicted the effects of agglomerate size and polymer viscosity. Reducing the agglomerate radius, polymer viscosity or agglomerate density led to higher infiltration rates. The stearic acid surface treatment was observed to have a dramatic influence on infiltration kinetics. Infiltration was much slower for the surface-coated powder than for the untreated powders. Experiments carried out with fluids of different chemical nature (EP and SBR) enlightened the possibility of air entrapment inside the agglomerate or less than complete saturation of the infiltrated layer.

### Acknowledgements

The authors are grateful to Rhodia for financial support of this work.

### Appendix A

Darcy’s law relates the velocity of a liquid infiltrating a porous medium to the pressure gradient \( dP / dr \) inside the liquid phase:

\[
u_r = -\frac{k_w}{\mu} \frac{dP}{dr},
\]

in which \( k_w \) is the effective permeability of the agglomerate to the wetting fluid (polymer melt). The volumetric flow rate \( q_r \) of infiltrating fluid is given by:

\[
q_r = -4\pi r^2 (1 - \phi) \sigma u_r.
\]

Under the assumption that the agglomerate porosity \( (1 - \phi) \) is uniform and that the degree of saturation \( \sigma \) is constant over the whole infiltrated layer and since the fluid is incompressible, \( q_r \) is independent of \( r \). Integration of Eq. (A1) over \( r \) leads to:

\[
P_l(a) - P_l(R) = \frac{q_r \mu}{4\pi (1 - \phi) \sigma k_w} \left( \frac{1}{R} - \frac{1}{a} \right).
\]
For an agglomerate located at a distance $h$ from the surface of the liquid:

$$P_l(a) = P_0 + \rho gh,$$

(A4)

where $P_0$ is the atmospheric pressure. $P_l(R)$ can be expressed from the capillary pressure $P_c$, i.e., the pressure difference across the liquid/gas interface inside the agglomerate:

$$P_c = P_g - P_l(R),$$

(A5)

in which $P_g$ stands for the air pressure inside the dry core. Hence:

$$P_l(a) - P_l(R) = P_c - (P_g - P_0) + \rho gh$$

$$= P_c - \Delta P_g + \rho gh.$$  

(A6)

In formula (A6), $\Delta P_g$ is the excess air pressure in the dry core relative to atmospheric pressure. In our experiments, air bubbles are released from the agglomerate during the course of infiltration. Therefore, it is assumed that the air pressure inside the dry core does not rise sufficiently to oppose the capillary pressure term significantly. In a first approximation, $\Delta P_g$ is neglected compared to $P_c$. Since the mean agglomerate pore radius is very small (about 0.5 $\mu$m as shown in Table 5), the capillary pressure calculated from Eq. (8) is around 40,000 Pa. The hydrostatic term $\rho gh$ (500 Pa on average in our experiments) can therefore be neglected compared to the capillary pressure term $P_c$. The volumetric flow rate can be related to the advance of the dry/wet interface:

$$q_i = -4\pi R^2 \frac{dR}{dt} (1 - \phi) \sigma.$$  

(A7)

If the capillary pressure is the only pressure term retained, combining Eqs. (A3), (A6) and (A7) leads to:

$$P_c \frac{dt}{dR} = -\frac{\mu}{k_w} \left( \frac{1}{R} - \frac{1}{a} \right) R^2 dR.$$  

(A8)

Under the assumption that $P_c$ is constant during the whole infiltration process, integration of Eq. (A8) yields Eq. (7).

References