Rheometric properties of micron-sized CaCO$_3$ suspensions stabilised by a physical polyol/silica gel for polyurethane foams

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Frédéric Pignon
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Abstract This article considers the rheometric properties of mixtures containing a micron-sized mineral filler of calcium carbonate (CaCO$_3$) in a polymer matrix gelled by adding colloidal silica (CS). These mixtures, consisting of a polymer matrix (polymers, catalysts, surfactant) are used to produce polyurethane foams. The suspending phase (polymer matrix/CS) has a yield stress that has been linked to fractal aggregation of the colloidal filler. Suspensions without any colloidal silica (polymer matrix/CaCO$_3$), show aggregation of CaCO$_3$ which is most probably due to the adsorption of catalysts present in the polymer matrix. Beyond a critical CaCO$_3$ volume fraction, a yield stress is detected indicating a 3D connected structure. In the case of suspensions containing colloidal silica (polymer matrix/CaCO$_3$/SC), the yield stress is due to a combination of the fractal network formed by the colloidal silica and aggregation of the micron-sized particles of CaCO$_3$.

Keywords Suspension · Silica · Calcium carbonate · Polyurethane · Foam

Introduction

Understanding the rheological properties of concentrated suspensions of particles in a polymer fluid is essential to optimise the use and ultimate properties of composite materials in industry (Metzner 1985; Malkin 1990). When the suspended particles are more than a micron in size, gravity effects enter into competition with inter-particle or particle-suspending fluid interaction forces. The suspensions may then separate by sedimentation. Depending on the type of application considered, this may need to be avoided. One of the ways of stabilising particles in relation to sedimentation is to gel the suspending phase to give it a viscoplastic behaviour. Evaluating the importance of gravity effects in relation to hydrodynamic and inter-particle forces in the suspension is a key stage in understanding the flow mechanisms of these systems. Other complex types of behaviour may be found. The flow properties at high filler concentrations may lead to unstable flow mechanisms (localisation, cracking) and also properties that depend on the duration and intensity of stress such as thixotropy and yield stresses (Pignon et al. 1997).

Numerous earlier works have dealt generally with suspensions of particles in a viscous fluid, but few have been devoted to suspending matrices with a viscoplastic behaviour. The behaviour of such media with regard to flow initiation is very different from that of a classic suspension in a Newtonian fluid. Although it is involved in numerous applications, few fundamental studies have focussed on this subject.

The aim of this article is to study the rheometric properties of concentrated suspensions of micron-sized calcium carbonate particles. The suspending phase consists of a polymer matrix formed mainly of polyol, a silicone surfactant, catalysts and colloidal silica. Adding this nano-sized filler gels the polyol, leading to
a viscoplastic behaviour in the suspending phase (Saint-Michel et al. 2003) that can keep the micron-sized particles suspended. With regard to industrial applications, these suspensions are used for producing composite polyurethane foams, which pose problems in terms of formulation and preparation. In the case of these mixtures, the influence of the rheometric behaviour of the suspending phase (polyol/colloidal silica) on the rheometric properties of the complete (polyol/colloidal silica/calcium carbonate) system is examined. To do this, the effects of colloidal silica concentration and calcium carbonate concentration on the changes in flow properties (yield stress and viscosity) are evaluated. Initially, rheometric properties under simple shearing of the gelled suspending phase are analysed. The fractal structure of this physical gel is established. Secondly, the rheometric properties of calcium carbonate suspensions in the Newtonian polymer matrix (without colloidal silica) are considered. It will be demonstrated that the catalysts present in the polymer matrix are responsible for aggregation of the calcium carbonate particles. The consequence of this aggregation is the occurrence of a yield stress beyond a critical calcium carbonate volume fraction $\phi_{cc}^\ast$. Thirdly, the complete (polymer matrix/calcium carbonate/colloidal silica) system will be studied. Two silica concentrations were selected to obtain two different yield stress levels of the suspending matrix. The change in flow properties will be analysed as a function of the two structures formed by the colloidal silica and by the calcium carbonate.

Materials and experimental techniques

Materials

Formulation of suspensions

The suspensions were prepared from a polymer matrix consisting of polyols, a silicone surfactant and catalysts. This polymer matrix is used to prepare polyurethane foams. It consists mainly of two polyols: polypropylene triols supplied by Shell Chemicals. The silicone surfactant, supplied by Air Products, is a PDMS/POE copolymer characterised by NMR spectrometry and mass spectrometry to determine its molecular structure and evaluate its molecular mass. Silicone surfactants are important compounds for formulating polyurethane foams (Snow and Stevens 1999). These surfactants stabilise bubbles during the production process and prevent cells from opening when the foam expands. The two catalysts used are inorganic salts of tin supplied by Air Products. Catalyst A is a dibutyltin dilaurate (DBTDL) while Catalyst B is a $2,2\prime\left[\text{dimethylstannylene} \right]\text{bis(thio)}$ diacetate. They speed up the chain lengthening reaction for preparing polyurethane foams. All the physicochemical data are given in Table 1.

The calcium carbonate, supplied by Provençale SA, consists of crushed angular particles. Its size was determined by measurements carried out on a Malvern laser granulometer. The particle size distributions of the calcium carbonate are shown in Fig. 1. The calcium carbonate is highly polydispersed, with the distribution ranging from 1 $\mu$m to 200 $\mu$m. This distribution is characterised by diameters $D_{10}$, $D_{50}$ and $D_{90}$, representing the diameters for which $x\%$ of the particles by volume have a diameter less than $D_X$. These values as well as the relative densities, specific surface areas and mean diameter are given in Table 2. The absolute density does not take into account the inter-particle spaces. The volume concentration for maximum particle packing ($\phi_{\text{max}}$), where the powder no longer flows, may be estimated from the following expression: $\phi_{\text{max}} = \rho_{\text{app}} / \rho_{\text{abs}}$, in which $\rho_{\text{app}}$ and $\rho_{\text{abs}}$ are the apparent packed density and the absolute density of the calcium carbonate, and $\phi_{\text{max}}$ is of the order of 0.55.

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>Structure</th>
<th>Molar mass (g. mol$^{-1}$)</th>
<th>Hydroxyl number (mg KOH/g)</th>
<th>Viscosity at 25$^\circ$C (Pa. s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyol A</td>
<td></td>
<td>450</td>
<td>380</td>
<td>0.380</td>
</tr>
<tr>
<td>Polyol B</td>
<td></td>
<td>300</td>
<td>570</td>
<td>0.500</td>
</tr>
<tr>
<td>Surfactant</td>
<td></td>
<td>2920</td>
<td>104</td>
<td>0.200</td>
</tr>
<tr>
<td>copolymer PDMS/POE</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst A</td>
<td></td>
<td>631.7</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Catalyst B</td>
<td></td>
<td>751.7</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 1 Physicochemical properties of the chemical compounds used in the polymer matrix. Viscosity of the polymer matrix $\eta = 0.527$ mPa. s at 23 $\pm$ 1 $^\circ$C.

Fig. 1 Particle-size distribution of calcium carbonate C1. The solid line represents the volume fraction. The dotted line represents the cumulative volume.
The components of the polymer matrix (polyol, surfactant, catalysts) were mixed at 600 rpm for 2 min with a Rayneri rotating blade stirrer. The mass concentration of the surfactant (Cs), catalyst (Ccat) and catalyst (Cc) in the polymer matrix (m_matrix) are defined by: $C_{ss} = m_{ss} / m_{matrix}$, $C_{cat} = m_{cat} / m_{matrix}$, $C_{c} = m_{c} / m_{matrix}$ in which $m_{ss}, m_{cat}$ and $m_{c}$ represent respectively the mass of surfactant and catalysts incorporated into the polyol. A volume fraction of colloidal silica ($\phi_{sc}$) is then incorporated into the polymer matrix. The volume fraction of the colloidal silica ($\phi_{sc}$) is defined by: $\phi_{sc} = (V_{sc} / (V_{sc} + V_{matrix}))$ where $V_{sc}$ represents the volume of silica incorporated into the matrix, $V_{matrix}$ represents the total volume of liquid formed by the basic polymer matrix. The dispersion obtained in this way was then mixed with the same stirrer rotating at 1,500 rpm for 10 min, at a temperature of about 20°C.

A volume fraction of calcium carbonate ($\phi_{cc}$) was incorporated: $\phi_{cc} = (V_{carbonate} / (V_{carbonate} + V_{matrix}))$ where $V_{carbonate}$ represents the volume of mineral filler incorporated into the polymer matrix. The suspension was once again mixed at 1,500 rpm for 10 min. Following preliminary tests, these preparation conditions were chosen, as they enable the filler to be completely dispersed. The samples were degassed in vacuum for 24 h in order to eliminate air bubbles introduced into the resin during mixing.

### Table 2 Physicochemical properties of the calcium carbonate used

<table>
<thead>
<tr>
<th>Density (g/cm³)</th>
<th>Apparent packed density (g/cm³)</th>
<th>Specific Surface (m²/g)</th>
<th>D₉₀(μm)</th>
<th>D₅₀(μm)</th>
<th>D₁₀(μm)</th>
<th>Average diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7</td>
<td>1.5</td>
<td>0.4</td>
<td>8.2</td>
<td>44</td>
<td>108.1</td>
<td>52</td>
</tr>
</tbody>
</table>

### Table 3 Physicochemical properties of the colloidal silica used

<table>
<thead>
<tr>
<th>Schematic representation of surface clusters</th>
<th>Average diameter (nm)</th>
<th>Density (g/cm³)</th>
<th>Specific area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12</td>
<td>2</td>
<td>150 ± 25</td>
</tr>
</tbody>
</table>

### Experimental techniques

Rheometric measurements under simple shearing conditions were carried out at a temperature of 23 ± 1°C. These measurements were carried out on a Weissenberg-Carried controlled-speed rotating rheometer. Torsion bar torque sensors were used. The measurements were performed using two different geometries: a Couette configuration (outer radius = 10.75 mm, inner radius = 8.75 mm, height = 40 mm) and a cone/plate configuration hollowed in the centre (outer radius = 25 mm, inner radius = 12.5 mm, angle = 3°). Steady conditions were obtained by imposing a given shear rate until stress equilibrium was reached. Measuring the rheometric properties of suspensions is very complex, and there are many perturbing phenomena that may introduce measurement artefacts. Slip at the interface of the device wall and sample is avoided by increasing the surface roughness of the rheometric devices. By using two measurement configurations, it was possible to check that the observed phenomena were indeed volume properties and not perturbing phenomena such as flow instabilities of the slip or fracturation type (Magnin and Piau 1990). In the cone/plate configuration, the cone was hollowed at the cut-off to prevent particles from becoming stuck (Coussot and Piau 1993). In addition, the cone/plate configuration was used to evaluate perturbing phenomena due to the sedimentation of the mineral fillers. By observing the deformation of a drawn line during the measurements (Magnin and Piau 1990) and analysing the stress response, it was possible to detect sedimentation during the tests. The use of a Couette configuration for low particle concentrations meant that measurement errors could be reduced for suspensions in which sedimentation could occur during the measurement. Measurements were performed to compare the two devices; there was less than 10% difference.

The manner in which the catalyst acts on the calcium carbonate was characterised by performing adsorption measurements. Calcium carbonate was recovered by centrifuging the suspensions. Using a Soxhlet, the powder was then washed with a solvent (acetone/methanol) to extract the free compounds while retaining the adsorbed ones. The powder was dried before being analysed by atomic adsorption. The proportion of tin, which is a characteristic element of the catalysts, was determined (Table 1).

Measurements to characterise the sedimentation of the suspensions were then performed using a Turbiscan...
Results and Discussion

Orders of magnitude of forces

By estimating orders of magnitude for the forces involved, it may be possible to determine what causes the behaviour of the suspensions of interest here.

Firstly, the limiting diameter $D_l$ for which the calcium carbonate particles have a Brownian or sedimentation movement in a Newtonian matrix may be evaluated with the following expression: $D_l = \left(12kT/(\pi(\rho - \rho_f)g)\right)^{1/4}$ in which $\rho$ and $\rho_f$ are the densities of the suspending fluid and particles, $k$ is Boltzmann’s constant, $T$ the temperature and $g$ the gravitational constant. Numerically, for calcium carbonate particles in the polymer matrix with $T = 298\, \text{K}$, $k = 1.38 \times 10^{-23}\, \text{J.K}^{-1}$, $g = 9.81\,\text{m.s}^{-1}$, $\rho_f = 2.700\,\text{kg.m}^{-3}$, $\rho = 1.055\,\text{kg.m}^{-3}$ and the diameter $D_l$ is of the order of 0.5 $\mu$m. The size of the calcium carbonate particles used was distinctly larger than 0.5 $\mu$m (Fig. 1). Particle movement is therefore governed by gravity if the suspending matrix is Newtonian.

The particles may also be subjected to van der Waals attraction forces. Hamaker’s constant is required to calculated the van der Waals force. This may be determined by Lifschitz’s formula (Gregory 1969)

$$A = \frac{3kT}{4}\left(\varepsilon_1 - \varepsilon_2\right)^2 + \frac{3h\nu_e(n_1^2 - n_2^2)^2}{16\sqrt{(n_1^2 + n_2^2)^3/2}}$$

(1)

$\varepsilon_1$ and $n_1$ are the dielectric constant and refraction index of medium 1, $h$ is Planck’s constant, $\nu_e$ the adsorption frequency, 1 and 2 corresponding to the indices for the calcium carbonate and suspending fluid, i.e. polyol. These parameters are calculated from the material constants given in the CRC Handbook of Chemistry and Physics (Lide 1993) for the calcium carbonate and from the supplier’s data for the polyols. Numerically speaking, for particles of calcium carbonate in polyol $h = 6.62 \times 10^{-34}\,\text{s}^{-1}$, $\nu_e = 3 \times 10^{15}\,\text{Hz}$, $\varepsilon_1 = 6.14$, $n_1 = 1.59$, $\varepsilon_2 = 2.53$, $n_2 = 1.469$ and Hamaker’s constant $A$ is of the order of $4.6 \times 10^{-21}\,\text{J}$. The ratio between van der Waals attraction energy and Brownian energy is of the order of $A/kT = 1.1$. Attraction forces do not appear to be predominant between calcium carbonate particles.

The Péclet number $Pe$, expressing the ratio between shearing energy and Brownian energy, is written as follows $Pe = nD^2\gamma/8kT$. In the case of calcium carbonate particles of diameter $D = 52\,\mu$m dispersed in the polymer matrix of viscosity $\eta = 0.527\,\text{Pa.s}$, $Pe = 3.8 \times 10^7$. In the range of shear rates studied ($10^{-4} - 100\,\text{s}^{-1}$), $Pe >> 1$, shear forces prevail Brownian motion.

For a particle to settle in a yield stress fluid, its mass must be sufficiently great to produce a stress field around it, where the yield stress ($\tau_0$) is exceeded. This phenomenon is normally quantified by a stability criterion defined as the ratio between yield stress effects and gravity effects (Chhabra 1993): $Y_{max} = \tau_0/(\rho - \rho_f)gD$ in which $Y_{max}$ is the value of $Y$ where the sphere remains immobile. It can therefore be used to evaluate the minimum value of the yield stress $\tau_0$ to obtain sphere stability. Several studies have been devoted to determining the value of $Y_{max}$ (Chhabra 1993). Experimentally speaking, the values of $Y_{max}$ are of the order of 0.07 (Chhabra 1993; Jossic and Magnin 2001). Using the characteristic diameters of calcium carbonate grain size distribution (Table 2), particle stability is achieved with $D_{10} = 8.2\,\mu$m, $\tau_0 = 0.009\,\text{Pa}$; $D_{50} = 44\,\mu$m, $\tau_0 = 0.049\,\text{Pa}$; $D_{90} = 108.1\,\mu$m, $\tau_0 = 0.12\,\text{Pa}$ and for $D_{max} = 200\,\mu$m, $\tau_0 = 0.22\,\text{Pa}$.

Flow properties of the polymer matrix/colloidal silica suspending phase

The flow curve for the polymer matrix alone ($\phi_{sc} = 0$) displays a Newtonian behaviour (Fig. 2). When the silica concentration increases, the behaviour of the dispersions diverges considerably from the Newtonian behaviour of the matrix. Above a critical concentration $\phi_{sc}^*$ that may be estimated to be of the order of $\phi_{sc} = 0.5\%$, the flow curves tend towards a low shear-rate stress plateau, characteristic of the occurrence of a yield stress and thus of a viscoplastic behaviour.

The yield stress level increases with the increase in the volume fraction of colloidal silica following a law of the type $\sigma_0 \approx \phi_{sc}^{0.7 \pm 0.3}$. In our previous work (Saint-Michel et al. 2003), radiation scattering measurements (SANS, Fig. 2 Steady-state flow curves for colloidal silica suspensions. Influence of silica concentration ($\phi_{sc}$). $\phi_{sc} = 0\%$, $C_s = 0.7\%$, $C_{ca} = 0.56\%$, $C_{eb} = 0.28\%$, $T = 23 \pm 1\,^\circ\text{C}$)
SALS) revealed that the structure of colloidal silica dispersions corresponds to a fractal particle arrangement ($D = 1.8 \pm 0.1$) in the polyol, up to a scale of a few microns (Fig. 3). The yield stress and elastic modulus of hydrophobic silica dispersions follow a volume fraction scaling law of the type: $\sigma_0 \approx \phi^{2.9 \pm 0.3}_v$ and $G' \approx \phi^{4.1 \pm 0.4}_v$.

Correlations between theoretical scaling laws (Piau et al., 1999) and experimental laws have also been corroborated. These results showed that the mechanical properties (plasticity and elasticity) of colloidal silica dispersions are governed mainly by the fractal structure at large length scales, as already observed in other types of colloidal dispersions (Pignon et al. 1997) One of the most likely methods of inter-particle connection is that resulting from octyl chains grafted on to the surface of the hydrophobic colloidal silica (Table 3).

**Flow properties of suspensions in a Newtonian polymer matrix**

The flow curves of suspensions containing different volume fractions of calcium carbonate ($\phi_{cc}$) in the Newtonian polymer matrix ($\phi_{sc} = 0$) are represented on Fig. 4. The behaviour of the suspensions diverges significantly from the Newtonian behaviour of the polymer matrix when the carbonate concentration increases. At $\phi_{cc} = 4.3\%$ of calcium carbonate, the suspension is still Newtonian. At a concentration of $\phi_{cc} = 14.3\%$, the behaviour is of the shear-thinning type. At $\phi_{cc} = 28\%$, the curves tend towards a distinct stress plateau that reveals the existence of a yield stress and hence a connected network of CaCO$_3$. This yield stress increases with the increase in calcium carbonate. The critical concentration at which a yield stress occurs is situated below 28%. The critical concentration $\phi_{cc}^*$ is close to 20%, as suggested by the measurement points at the lowest shear rates (Fig. 4). Beyond the yield stress, the suspensions flow according to a viscous shear-thinning law.

**Flow properties of suspensions in a viscoplastic suspending phase**

The flow curves for mixes containing a concentration of colloidal silica $\phi_{sc} = 0.5\%$ and $\phi_{sc} = 1.1\%$ for various calcium carbonate concentrations ($\phi_{cc}$) are represented respectively in Figs. 5 and 6.

The flow curves of suspensions containing a concentration of colloidal silica $\phi_{sc} = 0.5\%$ (Fig. 5) display a yield stress. In the absence of calcium carbonate ($\phi_{cc} = 0$), a yield stress exists. The flow curve tends towards a...
plateau near low shear rates. A yield stress clearly appears with low calcium carbonate concentrations, and increases with the CaCO₃ concentration. Yield-stress behaviour with shear-thinning behaviour is kept for all CaCO₃ concentrations.

In the case of the flow curves for suspensions containing a colloidal silica concentration \( \phi_{sc} = 1.1\% \) of colloidal silica, a yield stress is observed regardless of the calcium carbonate concentration \( \phi_{cc} \) (Fig. 6). Yield-stress behaviour with shear-thinning behaviour is kept for all CaCO₃ concentrations.

**Variation in rheological parameters**

Several empirical relations have been proposed to adjust flow curves for yield stress materials. Here, the Herschel–Bulkley viscoplastic model (Macosko 1994) was calibrated with the measurement points:

\[
\tau = \tau_0 + K\dot{\gamma}^n
\]

\( \tau \) represents the shear stress, \( \tau_0 \) the yield stress, \( K \) the consistency, \( \dot{\gamma} \) the shear rate and \( n \) the shear-thinning index. Interpolations in this model are represented by the dotted curves (Figs. 4, 5, 6). The model is satisfactory over the entire range of shearing explored and for all the suspensions concerned.

The values of \( \tau_0 \), determined by calibrating this relation as a function of the volume fraction of calcium carbonate and colloidal silica are represented in Fig. 7.

The viscous effects of these suspensions are evaluated via the change in stress at a high shear rate (Fig. 8). The change in consistency \( K \) and shear-thinning index \( n \) are given respectively on Figs. 9 and 10. These results will be discussed below.

**Origin of yield stress for polymer matrix/CaCO₃ suspensions**

Let us now consider the suspensions in a non-gelled matrix (\( \phi_{sc} = 0 \)). The rheometric measurements revealed the occurrence of a yield stress and its increase with the addition of calcium carbonate in the polymer matrix (Fig. 4). It is not uncommon to find viscoplastic behaviour referred to in the literature with regard to suspensions of calcium carbonate particles in a polymer melt such as polypropylene or polystyrene (Suetsum and White 1983; Mayadunne et al. 1996; Wang and Wang 1999). When the particle volume concentration approaches the maximum packing volume fraction, a yield stress may be observed owing to the increase in contacts between particles (Mayadunne et al. 1996). In the case of the suspensions studied here, the maximum packing volume concentration for the dried powder \( \phi_{max} = 55\% \). In addition, sedimentation measurements showed a maximum packing volume concentration for a suspension of calcium carbonate of 61%. However, the
occurrence of a yield stress was detected above a critical calcium carbonate volume fraction $\phi_{cc}$ of about 20%. This value is distinctly lower than the two maximum packing volume concentrations for the dry powder (55%) and for the suspension (61%). Particle packing is not the pertinent criterion for explaining the origin of the yield stress.

The reason why this yield stress exists was sought by examining the possible effects of the silicone surfactant and catalysts present in the polymer matrix on the rheometric behaviour of suspensions containing $\phi_{cc} = 46.2\%$ (Fig. 11). The surfactant did not have any effect on the rheometric behaviour of the suspensions. A shear-thinning behaviour without any yield stress was observed. Figure 11 shows that adding catalysts A and B at concentrations $C_{ca}$ and $C_{cb}$ leads to the occurrence of a yield stress. The rheometric measurements may be corroborated by sedimentation observations.

The sedimentation study, involving two different rest times (4 and 15 days) revealed different kinetics of sedimentation. After 4 days, the volume of sediment in the calcium carbonate suspension not containing catalysts had not changed significantly. Two distinct zones were observed in the tube: a wide and very opaque one at the bottom of the tube, corresponding to rapid sedimentation of the largest particles, and a second, opaque transition zone where the finest particles were settling slowly. In contrast, in the case of the calcium carbonate suspension containing catalysts, the kinetics of sedimentation were different. Sedimentation occurred over a much longer period (15 days). Two distinct zones could again be observed. The first one was wide and very opaque, and the second translucent, located at the tube surface. The calcium carbonate particles had therefore settled all at once, a clear sign of strong interaction between all of them.

The way in which the catalysts acted on the calcium carbonate particles was characterised by carrying out adsorption measurements. The results of these analyses (Table 4) for a suspension containing catalyst A show the presence of tin at the surface of the calcium carbonate. The catalyst is a polymer of the tin salt type (Table 1); its structure suggests that it consists of a hydrophobic part ($\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ alkyl chains) and a more hydrophilic part (tin surrounded by oxygen atoms).

<table>
<thead>
<tr>
<th>Table 4 Results of analyses by atomic adsorption of calcium carbonate powders. Suspensions containing $\phi_{cc} = 46.2%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspensions</td>
</tr>
<tr>
<td>Tin adsorption ($\mu$g/g of CaCO$_3$)</td>
</tr>
</tbody>
</table>

Fig. 9 Change in consistency $K$ as a function of the volume fraction of calcium carbonate ($\phi_{cc}$) and colloidal silica ($\phi_{sc}$). $C_s = 0.7\%, \, C_{ca} = 0.56\%, \, C_{cb} = 0.28\%$, $T = 23 \pm 1\, ^\circ\text{C}$

Fig. 10 Change in shear-thinning index $n$ as a function of the volume fraction of calcium carbonate ($\phi_{cc}$) and colloidal silica ($\phi_{sc}$). $C_s = 0.7\%, \, C_{ca} = 0.56\%, \, C_{cb} = 0.28\%$, $T = 23 \pm 1\, ^\circ\text{C}$

Fig. 11 Steady-state flow curves for suspensions containing $\phi_{cc}=46.2\%$ of calcium carbonate. Influence of catalysts and surfactant. $T = 23 \pm 1\, ^\circ\text{C}$
Two mechanisms may explain the aggregation of the calcium carbonate particles. First, aggregation may be due to bridging by adsorption of the catalyst on two particles. However, this mechanism has been demonstrated for molecules with a carbonate chain length of the same order of magnitude as the particle radius (i.e. nano-sized particles). In view of the carbonate chain length of tin salts and size of the calcium carbonate particles, this mechanism can be ruled out. Second, the tin salt may be adsorbed via hydrophilic bridges between the hydrophilic surface of the calcium carbonate and hydrophilic groups of the compound. The calcium carbonate particles surrounded by tin salt possess a hydrophobic layer due to the presence of the alkyl chains of the catalyst, which are oriented towards the suspending fluid (polyol). Interaction may then take place between the hydrophobic alkyl chains of two neighbouring particles, causing them to aggregate. This phenomenon was observed by Charney (1999) in a study of talc particles in an aqueous solution, via adsorption of a polyoxyethylene/polyoxypropylene (POE/POP) copolymer. It is this mechanism of interaction between the alkyl chains of the catalysts that appears to be the most likely cause of aggregation of the system. Above $\phi_{cc}^*$, aggregation between all the calcium carbonate particles is sufficient to form a connected 3D structure characterised by a yield stress (Fig. 12). An increase in $\phi_{cc}$ reinforces this structure and consequently raises the yield stress.

**Origin of yield stress in CaCO$_3$/colloidal silica suspensions**

Adding colloidal silica to the polymer matrix thus leads to the formation of a fractal particle structure, which causes the formation of a yield stress. Adding calcium carbonate to the polymer matrix beyond a critical concentration $\phi_{cc}^*$ also leads to the formation of an aggregated particle structure under the effect of catalyst adsorption.

Figure 7 shows that the yield stress rises with the colloidal silica and calcium carbonate concentration. At a constant volume fraction $\phi_{cc}$, adding colloidal silica raises the yield stress of the suspension. In addition, the more the calcium carbonate volume fraction increases, the less the colloidal silica has any effect. This results in convergence of the curves for volume fractions $\phi_{cc} > 60\%$. This value corresponds to the carbonate particle stacking value (Mayadunne et al. 1996). At low calcium carbonate concentrations, the yield stress is governed by the structure formed by the colloidal silica particles. At high calcium carbonate concentrations, it is governed by the structure generated by the calcium carbonate particles.

In the case of suspensions with $\phi_{cc} = 0.5\%$ (hence close to the critical concentration at which a connected fractal network of silica occurs), there is a rapid increase in the yield stress right from low CaCO$_3$ concentrations. For the CaCO$_3$ particles to be stabilised, the silica network must be able to develop a sufficient yield stress. Applying relation (10) shows that for $\phi_{nc} = 1.1\%$ all the particles are stabilised. For $\phi_{nc} = 0.5\%$, the largest particles are not stabilised by the gelled matrix, which does not develop a sufficient yield stress. In contrast, the increase in CaCO$_3$ concentration creates a connected network that helps to stabilise the large CaCO$_3$ particles.

On the basis of these observations, it is possible to propose an explanation for the structure formed by calcium carbonate suspensions in the polymer matrix.
gelled by colloidal silica. This is presented in Fig. 12. Above a critical colloidal silica concentration $\phi_{cc}^*$, a fractal structure is created by the silica network. With low calcium carbonate concentrations, the hardly aggregated particles are kept in suspension in the meshes formed by the fractal network of colloidal silica particles. Around $\phi_{cc}^*$, the aggregated calcium carbonate particles are sufficiently interconnected to form a 3D structure, leading to the occurrence of a yield stress. This structure coexists with that generated by the colloidal silica. These two interlinked structures govern the mechanical properties of the suspension. At high calcium carbonate concentrations, the calcium carbonate particle packing in the suspension is such that the yield stress level is governed primarily by the structure formed by the calcium carbonate particles.

Viscous effects

Figure 8 shows the stresses at a shear rate of 100 s$^{-1}$ plotted for all the suspensions. The stresses are rendered dimensionless at the same shear rate of the suspending phase. At this shear rate, viscous forces predominate over colloidal forces and plasticity effects. Comparing Figs. 8 and 9 shows that the colloidal silica concentration has little influence on the stress level at high shear rates, in contrast to what is observed with regard to the yield stress (Fig. 7).

The connected fractal network of silica at rest fragments under shearing. Under heavy shearing, the matrix gelled by the silica at rest behaves as a diluted dispersion of silica aggregates. Indeed, if it is assumed that the silica aggregates are about a micron in size (Fig. 3), the Peclet number (Eq. 9) is of the order of $3 \times 10^4$. It therefore seems that the volume occupied by the calcium carbonate and the state of the structure imposed by shearing govern the flow properties of the suspensions at high shear rates. This effect is confirmed by Figs. 9 and 10.

The change in consistency $K$ as a function of the calcium carbonate and colloidal silica concentration also produces two characteristic domains (Fig. 9). Below $\phi_{cc}^*$, the values of $K$ increase with the addition of colloidal silica. Above $\phi_{cc}^*$, the values of $K$ are hardly affected by the addition of colloidal silica. This demonstrates that the viscous behaviour of the suspensions is dominated by the structure formed by the calcium carbonate particles during shearing.

When the suspension does not contain colloidal silica, the behaviour index $n$ falls considerably as a function of the volume fraction, which is characteristic of strong shear-thinning (Fig. 10). Two different evolutions may be observed, with the break occurring above the critical volume fraction $\phi_{cc}^*$ corresponding to the concentration where a yield stress is detected (Fig. 7). These two states can also be observed in the suspensions gelled by silica. The index $n$ increases as long as the CaCO$_3$ concentration is below the critical concentration $\phi_{cc}^*$. Above this concentration, the values of the index $n$ decrease and join those obtained without any colloidal silica.

This examination of viscous effects clearly demonstrates the existence of two characteristic calcium carbonate concentration $\phi_{cc}$ domains. These are separated by a critical concentration $\phi_{cc}^*$. When $\phi_{cc} > \phi_{cc}^*$, these viscous effects are governed by the colloidal silica. Adding colloidal silica leads to a reduction in shear-thinning. When $\phi_{cc} < \phi_{cc}^*$, these viscous effects are governed by the calcium carbonate, leading to an increase in shear-thinning. These observations confirm those made in the study of the yield stress.

Conclusions

This study looked at the rheometric properties of mixtures containing micron-sized particles of calcium carbonate in a polymer matrix gelled by the addition of colloidal silica. These mixtures, consisting of a polymer matrix (polyols, catalysts, surfactant), are used to produce polyurethane foams. The rheometric behaviour of the suspending phase was modelled over a range running from Newtonian (without any colloidal silica) to viscoplastic, by increasing the colloidal silica concentration.

In the case of suspensions without any colloidal silica (polymer matrix/calcium carbonate), it was established that the calcium carbonate forms aggregates. This aggregation is very likely due to particle attraction via adsorption of the catalysts present in the polymer matrix. Above a critical concentration $\phi_{cc}^*$, a yield stress is detected; this is characteristic of a connected network.

In the case of suspensions containing colloidal silica (polymer matrix/calcium carbonate/colloidal silica), the origin of the yield stress is a combination of the fractal network formed by the colloidal silica and aggregation of the micron-sized particles of calcium carbonate.

An examination of flow properties at high shear rates clearly showed the existence of two characteristic calcium carbonate concentration $\phi_{cc}$ domains. Below a calcium carbonate fraction $\phi_{cc}$ the rheometric behaviour is governed by the fractal network formed by the colloidal silica in the polyol. Above $\phi_{cc} > \phi_{cc}^*$, the rheometric behaviour is governed mainly by the structure formed by interactions between the calcium carbonate particles.

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References