

Combining Rheology and Spectroscopy for Studying of Polymeric Materials Subjected to High-Pressure Carbon Dioxide

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A rotational viscometer has been adapted to measure the viscosity of liquid polymers and silica suspensions. The viscosity reduction of poly(propyleneglycol) (PPG) with CO₂ was studied. The effect of CO₂ on silica suspensions in PPG proved to be dependent on the surface chemistry of the silica. Suspensions of hydrophilic silica gel under CO₂ atmosphere but the viscosity of suspensions of hydrophobic silica is reduced by CO₂. These rheological data were correlated with information on the associated polymer swelling and concentration of dissolved CO₂ obtained by the spectroscopic approach.

INTRODUCTION

Supercritical fluids are increasingly used for enhanced processing of polymeric materials [1,2], but a detailed understanding of the effects of CO₂ on these materials (including suspensions and pastes) is needed. Number of groups reported effect of high-pressure CO₂ on viscosity of polymers [3-10]. In this new work we used a combined approach (in situ spectroscopy and high-pressure rheology) to study the effects of high-pressure CO₂ on suspensions of solid particles in liquid polymers. Spectroscopy provides molecular level information, whereas rheology reveals changes in macroscopic properties of polymeric materials. In this work, an in-situ infrared spectroscopic methods based on a single reflection diamond attenuated total reflectance infrared (ATR-IR) approach was used [11]. This approach allows simultaneous measurement of polymer swelling and concentration of dissolved CO₂ and also gives insight into molecular interactions. The approach has been used to study polymers that are liquid at room temperature and suspensions of silica particles in liquid polymer.

Rotational viscometers are the most versatile viscometers and are well-suited for studying non-Newtonian fluids. The two main problems associated with their use under high-pressure gases are the magnetic transmission and the headspace required to accommodate the swelling of the polymer. In this work, a modified commercial high-pressure rheology cell was used to study polymers and suspensions of silica particles in polymers subjected to CO₂.

MATERIALS AND METHODS

Samples of fumed silica aerosil 200 and aerosil R805 were supplied by Degussa. Fumed silica is an amorphous, non-porous silica prepared by a flame hydrolysis process. Its primary structure consists of branched aggregates formed by the fusion of primary spherical particles of SiO₂. Aerosil 200 is a hydrophilic silica, with a specific surface area of approximately 200 m²/g and a primary spherical particle size of 12

nm. Aerosil R805 is a partially hydrophobic silica, based on aerosil 200. It is prepared by replacing half of the surface silanols with n-octyl ($-C_8H_{17}$) groups. This was confirmed by FTIR spectroscopic measurements. Aerosil R805 has a specific area of approximately $150 \text{ m}^2/\text{g}$. The continuous phase in our studies was a polypropylene glycol having an average molecular weight $M_w = 2700$ (Aldrich Chemicals), a polydispersity $M_w/M_n < 1.1$ and a density of 1.004 g/cm^3 . Its viscosity was measured to be $563 \text{ mPa}\cdot\text{s}$ at $25 \text{ }^\circ\text{C}$ and $339 \text{ mPa}\cdot\text{s}$ at $35 \text{ }^\circ\text{C}$. Each suspension was prepared by progressively adding the silica to the liquid in a blender.

Concentric cylinder geometries are the most versatile for use in rheometers and are well adapted to the study of non-Newtonian fluids. Rheological experiments were carried out on a Paar Physica high-pressure cell attached to a Paar Physica UDS 200 rheometer. The geometry used consisted of vanes twisted with a 25° angle from the vertical. Some special accessories were developed to adapt it to supercritical fluid studies. The pressure cell allows measurements at pressures up to 150 bar and up to $300 \text{ }^\circ\text{C}$. In the pressure cell, the measurement area is completely sealed against the environment; therefore a magnetic coupling is used to transfer the torque from the instrument motor to the measuring system. Details of the high-pressure cell design used in these measurements are described by Flichy [12].

RESULTS AND DISCUSSION

Rheology of suspensions of hydrophobic fumed silica in polypropylene glycol under high-pressure CO_2 . The viscosity of 13 % (wt silica/ wt suspension) R805 suspension in PPG was measured for CO_2 pressures up to 55 bar at $25 \text{ }^\circ\text{C}$ and $35 \text{ }^\circ\text{C}$. The steady shear viscosity of the suspension at $25 \text{ }^\circ\text{C}$ under CO_2 pressures up to 45 bar is shown in Figure 1. The viscosity of the suspension is found to decrease significantly with pressure of CO_2 . At least two factors may be expected to play a role in this viscosity reduction. The PPG was previously found to have its viscosity substantially reduced by CO_2 . Furthermore, our spectroscopic studies showed that the suspension swells under CO_2 and that no phase separation occurs. The swelling results in a decrease of the particle volume fraction in the suspension and is bound to have an effect on the rheology. The distortion of the flow curve due to the geometry and the narrow range of shear rates makes it difficult to identify either the shear-thinning region or the shear-thickening region. The relative viscosity of the suspension decreases more with pressure than the relative viscosity of PPG, reflecting the effect of swelling. The swelling of the PPG reduces the volumetric particle concentration, thus affecting the rheology. It was determined from the spectroscopic study that at $25 \text{ }^\circ\text{C}$, the swelling of PPG is ca. 11 % at 20 bar and ca. 23 % at 40 bar.

Rheology of suspensions of hydrophilic fumed silica in polypropylene glycol under high-pressure CO_2 . The viscosity of 13 % (wt silica/ wt suspension) A200 suspension in PPG was measured for CO_2 pressures up to 55 bar at $25 \text{ }^\circ\text{C}$ and $35 \text{ }^\circ\text{C}$. Up to 35 bar at $25 \text{ }^\circ\text{C}$, the trend is qualitatively similar to the one observed for the R805 suspension. The viscosity of the suspension decreases with pressure and the critical shear rate for the onset of shear thickening increases. At 35-40 bar, a noticeable change occurs in the steady-shear flow curve. This can be observed in Figure 2. The low-shear viscosity increases with pressure. As a result of this increase of viscosity, experimental data can be obtained in the region of low shear rate where the torque limit had previously imposed a constraint. As the pressure increases, the flow curve becomes almost linear. It is interesting to note that the effect of CO_2 on the A200

suspension at high pressures is opposite to the effect on the R805 suspension. The suspensions having the same particle concentrations, the only factor explaining this interesting result is the surface chemistry of the silica particles. Hydrogen bonding between the silica particles and PPG is a plausible explanation given the chemical structure of the polymer and the surface of the silica particles.

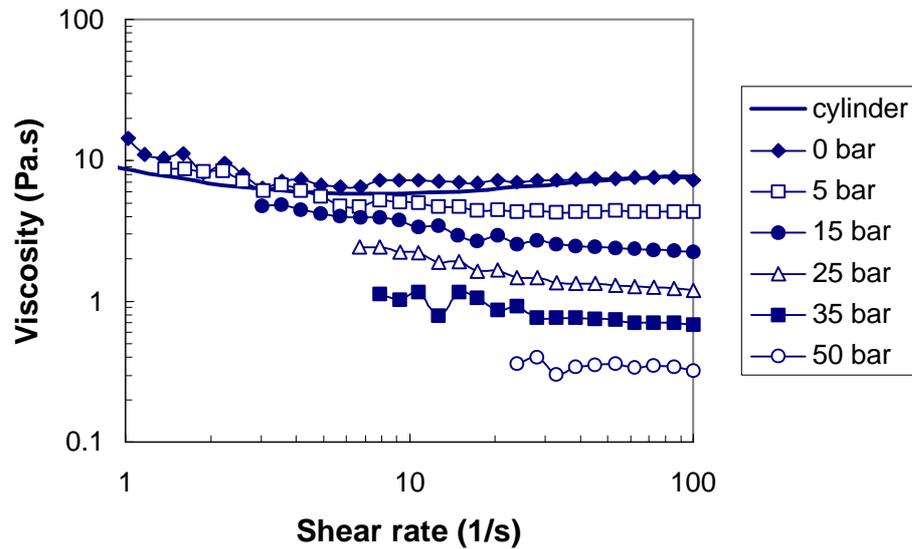


Figure 1. Steady shear viscosity of 13 % R805 suspension under 0, 5, 15, 25, 35 and 50 bar of CO₂ at 35 °C. The data from the concentric cylinder at 0 bar are represented by the solid line.

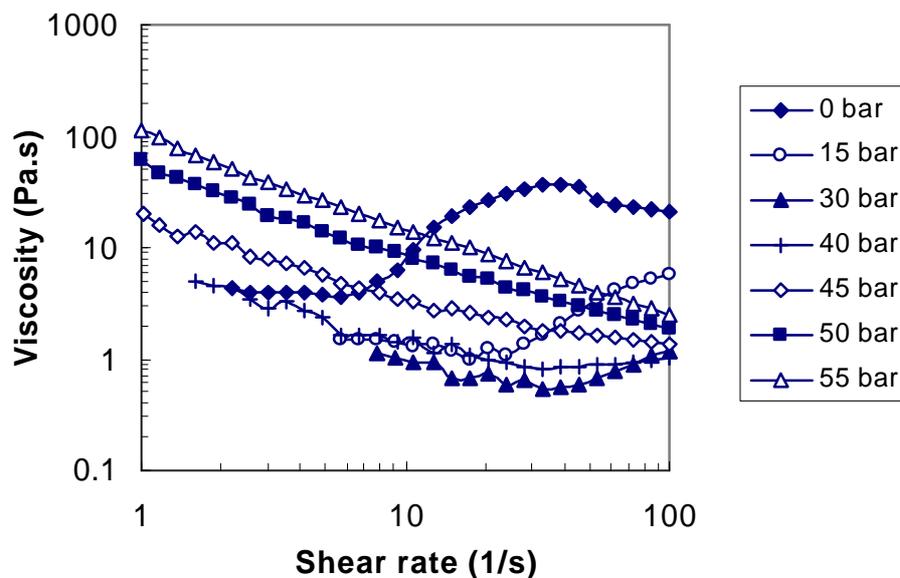


Figure 2. Steady shear viscosity of 13 % A200 suspension at 25 °C under CO₂ pressures up to 55 bar.

CONCLUSIONS

This study illustrates the potential of supercritical fluids and high-pressure gases for the viscosity reduction of polymer-particle systems. The effect of high pressure CO₂ on the rheology of PPG and suspensions of hydrophobic and hydrophilic fumed silica in PPG was measured. CO₂ was found to have a significant effect on the viscosity of PPG. Three factors were found to affect the viscosity of the suspensions: the viscosity of the continuous phase, the suspension swelling (which reduces the volumetric particle concentration) and the chemical interactions between the particles and the gas saturated fluid. The latter were found to play an important role, which demonstrates that understanding the chemistry of the system may play an important role in predicting the effect of high-pressure gases on the viscosity of filled polymer systems. The hydrophobic R805 suspension showed an apparent Newtonian plateau at moderate shear rates. A simple analysis showed that in this region the changes in viscosity could be interpreted in terms of the change in polymer-solvent viscosity and the effect of polymer swelling on the particle volume fraction. Data for the A200 system showed a change in the physico-chemical behaviour of the suspension at around 35-40 bar. Below this pressure, the suspension showed a reduction in viscosity with increasing CO₂ pressure. Above 40 bar, the suspension formed a gel, which became stronger with increasing CO₂ pressure and increasing mass fraction of absorbed CO₂. The approach presented in this work shows promise for studying the effects of high-pressure and supercritical CO₂ on various polymer-particle systems. The effect of CO₂ on the viscosity of such systems has many implications. For example, reduction of the viscosity of the polymer binder phase of ceramic pastes may result in lower extrusion pressures, reducing the residual stresses and improving the precision of the forming process. Therefore, high-pressure CO₂ may be beneficially used in processing of polymer-based pastes, and other particle-filled polymeric materials.

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