

THE ROLE OF CO₂ IN ENHANCING POLYMER EXTRUSION PROCESSES

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Carbon dioxide is an effective diluent for polymer melts, significantly increasing free volume and thus improving the ability to process materials through reductions in viscosity and interfacial tension. There are many examples in the literature demonstrating the unique capabilities of CO₂ ranging from the production of fine particles to diffusive impregnation and finally continuous blending and extrusion processes. The latter processes are inordinately complex due to the interplay between thermodynamics (solubility, interfacial tension), rheology (viscosity), and heat transfer (temperature gradients). Because of this complexity one must try to match predominantly qualitative experimental results (e.g. SEMs of foam products) with more basic experiments on well-controlled batch systems to reveal the underlying mechanisms in the continuous process. In this talk, we will show the measurements of shear viscosity, interfacial tension for polymer melts under high pressure CO₂, which will provide fundamentals for understanding and design of CO₂ assisted polymer extrusion processes.

Introduction

Supercritical CO₂ is a promising solvent for application in polymer blending and foaming processes. The interfacial tension and viscosity are key parameters in determining the bubble nucleation and growth rate in foaming, as well as droplet break up in blending.^[1-5] While there exists a substantial body of literature on interfacial tension at high temperature (polymer melts with ambient pressure gases) and high pressure (gases with oligomers or polymer solutions), there is relatively little information available on systems of practical interest (i.e. polymer melts) at high temperature and high pressure. Viscosity reduction of polymer melts by carbon dioxide has been well documented in recent years and is easily correlated via shift factor analysis.^[6-13] At the same time little research has been carried out in understanding these CO₂ assisted processes by combining both the interfacial tension and viscosity effects.

The traditional foaming agents, chlorofluorocarbons (CFCs), have been proven to contribute to the destruction of the ozone layer and will be gradually replaced in the near future (2010 in US).^[14-17] Supercritical CO₂ is a promising alternative for polymer foaming because it is environmentally benign, non-combustible, chemically stable and inexpensive. Although basic principles governing the foaming process are understood, the design of a foaming process is still mainly experimental. As a result, researchers are interested in fully understanding the governing parameters in both foam cell nucleation and growth. According to the

homogeneous nucleation theory^[18, 19], the Gibbs free energy for the formation of a nucleus of critical size is given by

$$\Delta G^*_{\text{hom}} = \frac{16p}{3\Delta P^2} \sigma^3 \quad (1)$$

and the homogeneous nucleation rate, is given by

$$N_{\text{hom}} = f_0 C_0 \exp(-\Delta G^*_{\text{hom}}/kT) \quad (2)$$

ΔP can be taken as the pressure change used to supersaturate the polymer and σ is the interfacial tension between polymer and bubble phases. Either a decrease of interfacial tension or an increase of saturation pressure will result in an increase of nucleation rate and the number of bubbles produced. The interfacial tension has a greater influence on the process due to the cubic power in the free energy. Viscosity influences both the pressure profile in an extrusion die and thus the cell growth.

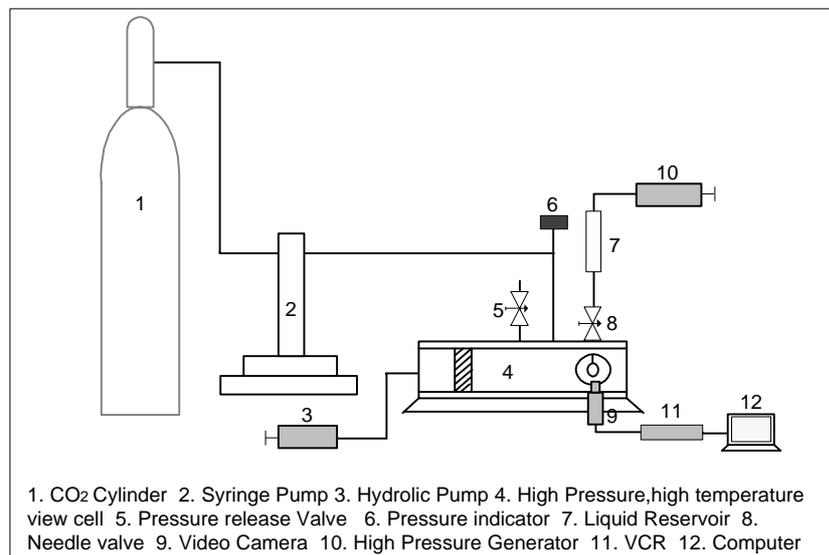
The significance of interfacial tension and viscosity in polymer blending can be described in terms of the Capillary number:

$$Ca = \frac{\eta_m \dot{g} R}{\sigma} \quad (3)$$

where η_m is the viscosity of the dispersed polymer phase, \dot{g} is the applied shear rate, R is a length scale and σ is the interfacial or surface tension between immiscible phases. This ratio of viscous to surface forces indicates the relevance of droplet or bubble breakup and coalescence in polymer blending, which in turn determines the domain size in polymer blends. For large capillary number, droplet break-up is the dominant phenomenon ($Ca > 1-10$, depending on the viscosity ratio). When the capillary number is below 0.1 or so, coalescence will dominate. In the region $0.1 < Ca < 10$, both the break-up and coalescence will take place simultaneously^[4].

I- Materials and Methods

For the data presented below, Polystyrene (Dow Chemical, 685D, MW 120,000) and Polypropylene (Huntsman Polymers, P4G2Z-011, Melt Index = 12 g/min) were used as received. Bone dry carbon dioxide (99.9% purity) was from Praxair.



Interfacial tension measurement

A custom high pressure variable volume view cell (Thar Designs) was applied in measuring the interfacial tension for polymer melts and CO₂ using the pendant drop method (Figure 1) The pressure inside the cell is controlled by a syringe pump (ISCO 260D)

Figure 1 Experimental set up for the pendant drop method

operating in constant pressure mode. The temperature inside the cell is controlled by cartridge heaters and a temperature controller with an accuracy of $\pm 0.5^\circ\text{C}$ up to 250°C . A number of threaded ports were drilled to allow the placement of the drop insertion apparatus, CO_2 injection, temperature control, etc. Three flat optical-quality sapphire windows in the cell (1 parallel and 2 perpendicular to the axis of the cylindrical cell) allow back illumination and video imaging of the drop profile.

The ADSA (Axisymmetric drop shape analysis) technique is a well known method of obtaining the interfacial tension. The Bashforth-Adams equation [20] is fit to the drop profile by adjusting the interfacial tension. This equation requires *a priori* knowledge of the density of the drop and the continuous phase. For CO_2 -polymer systems we use a modified BWR equation of state for CO_2 and the Sanchez-Lacombe equation of state for the polymer melt phase saturated with CO_2 .

Viscosity measurement

Our traditional slit die rheometer was modified to incorporate back-pressure control to prevent phase separation during the measurement of CO_2 /polymer solution viscosity. The new design has a slit 2 mm thick and 20 mm wide with three pressure transducers spaced at intervals of 25mm to measure the pressure profile along the die. A flush mounted thermocouple is placed in the melt just after the entrance to the slit and prior to the first pressure transducer in order to monitor the melt temperature. A metered amount of CO_2 was injected into the extruder barrel, controlled by the syringe pump (ISCO 260D). The shear rate was varied by changing screw rotation speed, i.e., the melt flow rate. The shear stress, shear rate, and shear viscosity were calculated using previously described methods [21]. The backpressure was controlled by a metering valve connected to the outlet of the slit die. The high pressure created by the valve keeps the CO_2 dissolved in the polymer matrix without phase separation during the measurement. A constant backpressure of 6.895MPa (1000psi) was maintained at the position of the last pressure transducer for all measurements with different CO_2 concentrations.

II- Interfacial tension for polymer melts under sc CO_2

The effect of CO_2 on the interfacial tension between polystyrene and CO_2 was studied at 200°C , and pressure up to 103 atm as shown in Figure 2. From the experimental results we can see that the interfacial tension decreases rapidly and linearly in the pressure range studied from around 28 to 17 dyn/cm.

For polymer blending, the effect of CO_2 on the interfacial tension between immiscible polymer phases is of most interest. Polystyrene (PS) and polypropylene (PP) saturated with CO_2 was studied at 220°C and pressures up to 165 atm. The dependence of interfacial tension on CO_2 pressure is shown in Figure 3. From the result we see that the interfacial tension decreases rapidly in the pressure range up to 50 atm, and then levels off. There is a greater than 20% decrease of interfacial tension in the pressure range studied.

III- Viscosity for polymer melts under sc CO_2

Figure 4 shows the viscosity of PS melts with different CO_2 concentrations at 180°C measured in the modified rheometer. The results are typical for this system and reinforce the knowledge that viscosity decreases sharply with a relatively small amount of dissolved CO_2 .

The overall shape of the viscosity curve does not change indicating no change in viscoelastic behavior. The effect of CO₂ diminishes as the concentration exceeds 1 weight percent.

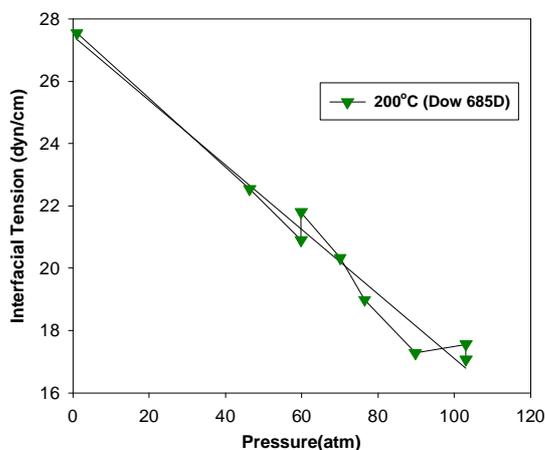


Figure 2. The interfacial tension between PS and high pressure CO₂

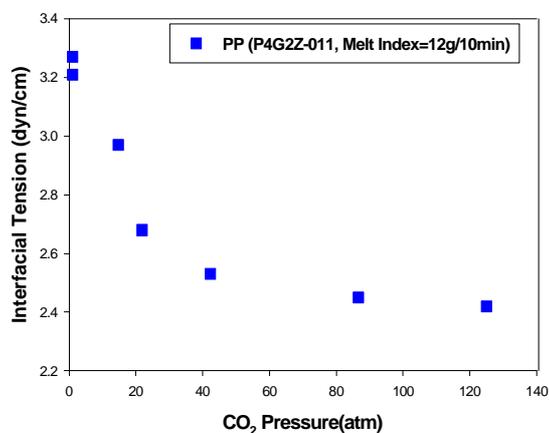


Figure 3. Interfacial tension between PS/PP saturated with CO₂ at 220°C

IV-Role of CO₂ in enhancing polymer extrusion

As discussed above, the Capillary number determines the droplet breakup and coalescence and thus the domain size. Larger Capillary numbers result in smaller domain sizes. From the above data we find that both interfacial tension and viscosity decrease significantly with CO₂ addition. While we have not yet been able to estimate Ca during extrusion (due to unreliable estimates of shear rate), we can corroborate our fundamental measurements with our previous data on polymer blending under the influence of CO₂. Figure 5 shows the morphology development along the length of the extruder for a 50/50 Polymethyl methacrylate (PMMA = black) and PS (white) blend. The domain size of PS is dramatically smaller with CO₂ compared to without indicating a significant increase in the Capillary number and a greater influence of interfacial properties over viscous forces.

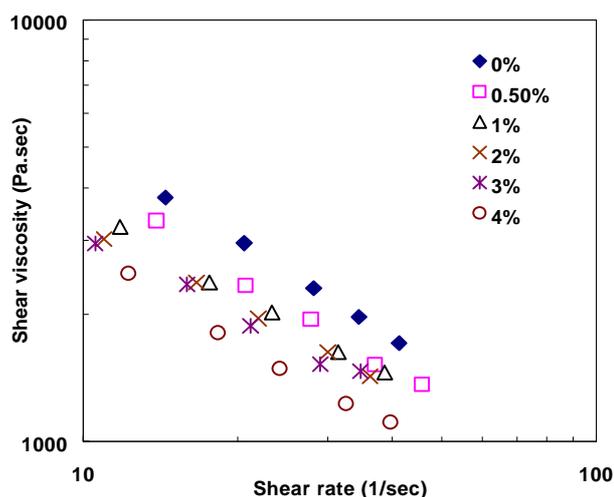


Figure 4. Effect of CO₂ content on the shear viscosity of polystyrene at 180°C

Figure 5 shows estimates of the nucleation rate in PS foaming calculated from the classical nucleation theory. The bar chart is a coarse way of comparing the relative sensitivity of the nucleation rate to a $\pm 1\%$ change about the mean value of four variables. Again we can see a dramatic change in the nucleation rate when the interfacial tension is changed a small amount. This is not a surprise, since as discussed earlier, the interfacial tension has a greater influence cubic power in the free energy. From our experimental results for the interfacial tension

between PS/CO₂, the interfacial tension is decreased from 28dyn/cm to 17dyn/cm, which should result in a dramatic effect on nucleation rate.

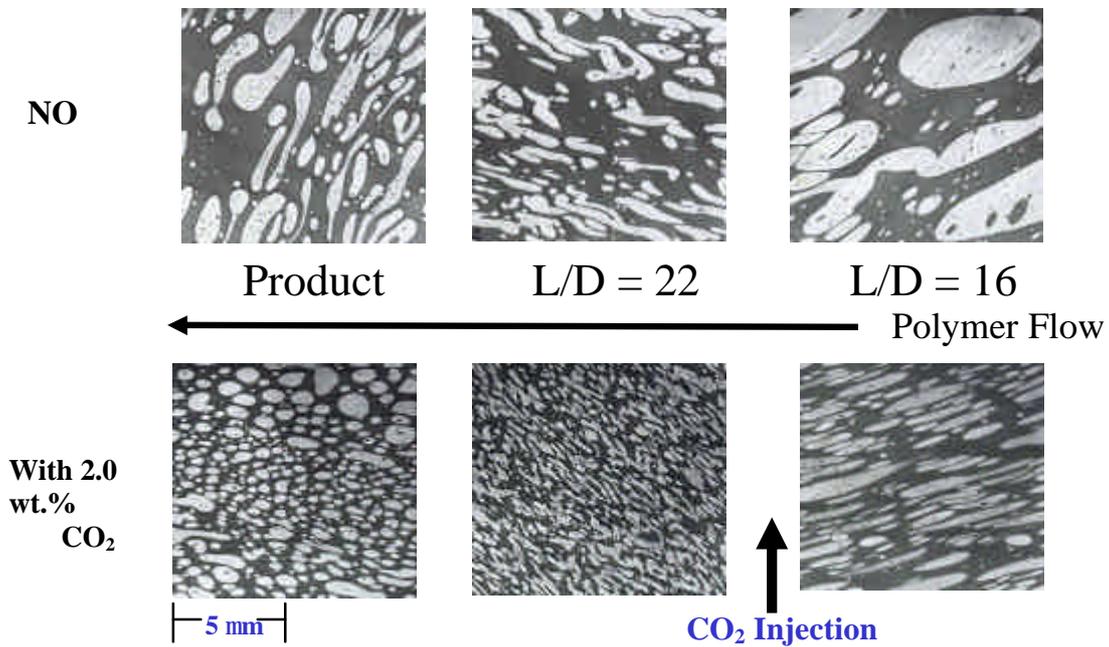


Figure 4. Morphology development (PMMA/PS) along the extruder length with and without CO₂ (Figure from reference [22])

Conclusion

The pendant drop method was used to measure the interfacial tensions for polymer melts under high pressure CO₂ conditions in a high pressure and high temperature view cell. The interfacial tension between PS and CO₂ was measured in the pressure up to 103 atm and 200 °C, and was depressed dramatically from 28 to 17 dyne/cm. The interfacial tension between PS and PP saturated with high pressure CO₂ was studied at 220°C and pressures up to 165 atm and was depressed by more than 20%. The viscosity reduction of polystyrene was measured via a slit die rheometer with backpressure control and the results are consistent with previous studies. The viscosity decreases sharply when only a small amount of CO₂ is dissolved in the melt and the effect diminishes at higher concentrations. Comparison with experimental blending results and calculated nucleation rate shows the relative importance of interfacial tension in CO₂ assisted polymer processing.

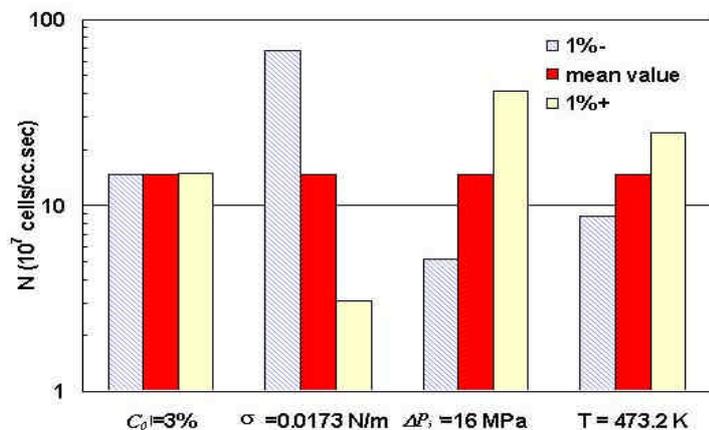


Figure 5. Nucleation rate calculated from the classical nucleation theory

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