Novel Techniques for Interfacial Tension and Contact Angle 
Measurements in Polymer/Carbon Dioxide Systems

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By
Russell A. Baird

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The Ohio State University

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Dissertation Committee:
Professor David L. Tomasko
Professor James F. Rathman

Approved By


Advisor

Department of Chemical Engineering
Abstract

The use of supercritical CO₂ is a leading candidate as a replacement for current foaming agents as they are phased out by the Montreal Protocol. Numerous studies have found that adding CO₂ to polymer melts lowers the viscosity and enhances many foam properties. Despite this, there are many obstacles that need to be cleared, as the traditional foaming agents make much higher quality foams than are currently being made using CO₂. Because of the necessity to create these higher quality foams, work must be done in order to attempt to improve the foams. This work is based on nucleation theory and depends mainly on interfacial tension between the polymer melt and the gas and on the contact angle between the gas, the melt, and the substrate which is usually added to polymer melts.

Literature data is limited when it comes to contact angles with high pressure and high temperature polymer melts. This research attempted to find contact angle measurements for commonly used polymer melt systems and find the conditions that result in the best foaming conditions, based on thermodynamic properties. This was done using a high pressure temperature controlled vessel with plate glass windows to allow observation of the system inside.

Nearly all of the common methods of drop analysis were carried out, as was the capillary rise technique. The drop methods involving a polymer drop in the gas environment led to many problems, resulting from viscosity problems as well as the drop wetting the entire surface. This was an unpredicted phenomenon that showed the glass had a very strong attraction to the polymers. The only method that showed much promise
was the captive bubble method, in which the interfacial tension and contact angle can be measured simultaneously. Because of this, the results were compared to the literature interfacial tensions for polystyrene, and large errors were found. This led to the design of a new apparatus to hopefully minimize any errors that the sides of the apparatus or other bubbles in the system may cause.
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1. Introduction

1.1 Background

Polymer foams have become big business in recent years. Their applications range from simple foam insulation to large filler material in the automobile industry. They are lighter than bulk polymers, while remaining high in mechanical strength. This reduction in weight lowers both cost and processing difficulties, leading to major benefits for those who use foaming. Typically these foams are made though the use of a foaming agent, a gas that will promote the foam properties that are desired. Because of their detrimental effects to the upper atmosphere, the use of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) as foaming agents has ceased in Europe will end in North America in 2010\(^1\).

Supercritical carbon dioxide (CO\(_2\)) is a leading replacement as a foaming agent for many polymer foams. It is environmentally benign, commonly available and therefore inexpensive, and chemically stable. The green chemistry involved makes CO\(_2\) favorable for industry due to its lack of regulation and the minimal environmental impact. It has been used commercially as a solvent and also has been shown to lower viscosity and interfacial tension in polymer systems. The tunable working conditions of supercritical fluids allow the CO\(_2\) to behave with fluid transport properties and gas diffusion properties. Blending work has been done, showing the lowered viscosity and interfacial tension of the supercritical CO\(_2\)/polymer system has enhanced mixing properties\(^2\). The lowering of the interfacial tension was documented by Hongbo Li et al., for polystyrene.
When foaming polymers, it has been found that the addition of small particles allows for the creation of a smaller foam structure. The smaller structure leads to stronger materials and better thermal resistance, all while avoiding the extreme operating conditions necessary for the creation of similar foams from conventional means. It has been hypothesized that the small platelet-like clay particles in use today allow for the creation of nucleation sites. The large surfaces of the clay allow for better contacting of the clay, the polymer matrix, and the gas in use. These extra sites are thought to promote the smaller structure and better mechanical properties in these foams.

1.2 Theory

The mechanical process of foaming and homogeneous nucleation has been studied and classic nucleation theory is based on the Gibbs energy of critical nucleus size formation

$$\Delta G_{\text{hom}}^* = \frac{16\pi\gamma^3}{3\Delta P^2}$$  \hspace{1cm} (1)

where $\gamma$ is the interfacial tension between the polymer phase and the bubble and $\Delta P$ is the supersaturation developed in the polymer phase. The rate of nucleation is then

$$N_{\text{hom}} = f_o C_o \exp(-\Delta G_{\text{hom}}^*/kT)$$  \hspace{1cm} (2)

where $f_o$ is the fraction of molecules joining a site, and $C_o$ is the concentration of cites in the matrix. The degree of supersaturation is one tunable property, but increasing pressures has a limited effect and is not as strong as the cubic effect of interfacial tension. Equilibrium interfacial tension is sometimes used in the Gibbs energy expression, but this is not generally agreed upon as the true fundamental result, but because of the lack of means to measure the interfacial tension between the nucleation site and the bulk
polymer, the bulk interfacial tension is used as a means of estimating nucleation rate, and its use is currently the best available method.

Because of the addition of nano-scale particles in the polymer matrix, the homogenous polymer/gas matrix is no longer simply a one phase problem, but becomes a multi-phase problem. This complexity has quite an effect on both the nucleation rate and the Gibbs energy of bubble formation. These sites of three phase contact are thought to lower the energy needed to begin a nucleation site. Young’s theory allows for the balance of the interfacial tensions of the three phases to be calculated. These tensions shape the interface through finding a minimum in energy. Based on these tensions, an angle of incidence between the three phases is set up. This is the contact angle, which Young defines as

$$\cos \theta = (\gamma_{sv} - \gamma_{sl}) / \gamma_{lv}$$  \hspace{1cm} (3)

This equation comes from simple geometry, based on the angle formed between the solid substrate (nanoparticles), the liquid (polymer), and the vapor (CO$_2$).

To account for the contact angle and its lowering effect of the homogeneous nucleation rate a shape factor has been devised. It is based on theory and on the observations of experiments. The lowering effect of the new sites are grouped into the shape factor

$$S(\theta) = (2 + \cos \theta) \times (1 - \cos \theta)^2 / 4$$  \hspace{1cm} (4)

where $\theta$ is the contact angle formed between the three materials in question. The effect of the contact angle is shown below.
This shape factor is then multiplied by the homogeneous Gibbs energy of critical nucleate formation to find the heterogeneous Gibbs energy of critical nucleate formation. This allows the three phases present to all be accounted for in the calculation of the nucleation rate, which now uses the heterogeneous Gibbs energy.

Measuring the interfacial tension is a classical problem with many creative solutions. In Young’s equation, only the contact angle and the vapor-liquid interfacial tensions are available for measurement. The difference in solid-vapor and solid-liquid can then be back calculated. For most applications, differentiating between the two unknowns is not critical, and is usually ignored. Most current methods are based on taking high resolution photographs of system setups which will show either the contact angle or the vapor-liquid interfacial tension, or possibly both. These photos are then analyzed through computer programs to fit the profile correctly.
1.3 Literature Review

Despite the apparent ease of finding interfacial tension and contact angle through optical means, there has been very little work in the polymer melt field. The available data is all centered around high temperature melts at ambient pressures, or room-temperature high pressure on low molecular weight polymers.

Wu et al. was one of the first to use high temperature melts\(^5\). He used many different polymers in his studies, including polyethylene, polyisobutylene, and poly(methyl methacrylate). His work was done through the pendant drop method, in which a drop of critical size is placed on the tip of a thin rod. The drop profile is then analyzed, and based on the profile, the interfacial tension was found. The use of this method became quite universal for polymer melts after his work. Its ease came from the ability to elevate the polymer just above the melting point, form the drop on the rod near this temperature, then lower the temperature until the drop is positioned and ready for measurements. At this point, a heater is used to raise the temperature into the melt range.

The use of the sessile drop technique for polymer melts was first published by Shinozaki et al\(^6\). This technique is also based on a critical drop size, although this time the drop is allowed to free fall to a plate. The drop equilibrates at temperature then a shape profile is recorded, and the interfacial tension is backed out from the profile. Shinozaki used this method for both static and dynamic measurements, although the dynamic measurements are thought to have little physical importance.

Other techniques exist but are usually reserved for particular niches. A “breaking thread” method has been developed by Elemans et al. in the Netherlands for incompatible polymer melt rheology estimations\(^7\). In it, a thread of polymer is extended until it breaks
down into droplets. Based on the rate of this droplet creation, interfacial tension can be calculated. The lack of need for the density of the polymer phases is a critical advantage. Drop spinning is used similarly to the sessile drop method, with centrifugal forces replacing gravity as the external force. A narrow range of viscosities work well for drop spinning, and for this reason, its applications are limited. Bubbles of the vapor for contact angle and interfacial tension measurements are placed below a submerged substrate for the captive bubble method. This method is usually quite difficult in that the substrate must be of the solid wanted for examination, and a way for placing the vapor under the fluid and the substrate is quite difficult. Many other methods exist also, but the list is quite lengthy and descriptions of these methods are not difficult to find. Because of the heated pressure vessel available, many of these methods are not applicable.

High pressure vessels are difficult to make and use. Since most common drop analysis methods involve the use of photographic analysis, a vessel must hold the extreme pressures as well as provide some means of passing light through the vessel in order to photograph the profile. Previously published work has been performed using this method. Harrison et al. measured interfacial tension of polystyrene oligomer in high pressure CO$_2$ at a set temperature$^8$. Because of their setup, they were unable to vary the temperature easily, leading to only the one temperature being used.

The first use of high temperature/high pressure being used for polymer melts came from Hongbo Li et al. His work was the first to combine a large range of pressures and the actual working temperature of the polymer melt. This data was made using polystyrene and poly(methyl methacrylate) in CO$_2$. A pendant drop of sample was prepared and then placed in the heated vessel. Pressure was added and equilibrium was
reached. Soon after, a photograph of the drop was taken and the profile was analyzed. A least squares fit was done to the Bashforth-Adams equation and from this the interfacial tension was found. He saw that the interfacial tension decreased with increasing pressure. The reasons behind this were thought to be from the interaction of the polymers with CO₂, and the increasingly “one phase behavior” exhibited by the system. As more CO₂ dissolves in the polymer, the interfacial tension will decrease as the properties of the polymer become more and more like CO₂.

Although the technique for measuring interfacial tension has been well developed, the contact angle is still needed for estimations of critical nucleus formation rates. Contact angle measurements exist for quite a number of systems, most of which use ambient air as their vapor phase. The reasons for this originate in the methods used to find contact angle. Capillary rise is one of the foremost methods used. The physical background from capillary rise is based on the balance of the upward force, namely interfacial tension, and gravity going downward. Using the force balance, the height of rise can be solved for:

\[ H = \frac{2\gamma \cos(\theta)}{[(\rho_l - \rho_v)gR]} \quad (5) \]

This equation is excellent, as long as the difference in density is known or can be found experimentally. The interfacial tension is usually found using a different method and the contact angle is backed out of the equation. The density of higher pressure gases becomes an experiment in itself for many systems, and for this reason, not much work at high pressure has been done. It is also limited, as the substrate for many systems is difficult to shape into capillary tube.
The other method commonly used is a simple photographic analysis of the sessile or captive drop techniques. This method too requires a base made of the solid substrate wanted for analysis, and this is again very difficult for many systems. A homogeneous plate should be made of the substrate in order to best estimate the true contact angle, as any inconsistencies in the plate surface will result in hysteresis in measurements. This results from the slight differences in surface patterns on the substrate plate. This has been shown by many groups, including Joanny et al. in France.

1.4 Goals of this Thesis

The main goal for this research is to create a technique that can accurately measure the contact angle between polymer substrates, commonly used polymers, and CO₂. Any of the aforementioned techniques, as well as any of the different methods not mentioned, are possibilities. Once a viable technique has been found, the method should be used to construct a means of estimating the rate of critical nucleus formation. This data can then be compared to actual foaming conditions to see if the optimum conditions do indeed yield optimum foams.

2. Experimental

2.1 Equipment and Methods

A heated pressure vessel was used for all experiments. Its setup can be found below. The vessel is labeled as 4. It has a feedback temperature controller (6) which takes the temperature from inside the apparatus, allowing the gas temperature to be controlled. The vessel has two glass plates that allow for a photograph to be taken of any
drop profile inside the vessel. The CO₂ tank is labeled as 1. The pressure inside the vessel is controlled by the syringe pump (2). The pressure is verified by a separate indicator (5).

Figure 2.1-1. Experimental Setup

A control valve (3) is placed to allow for easy pressure relief. The CDC camera (8) captures the images and saves them to a VCR (9). Any images wanted are then saved by the computer (10) for later analysis.

2.2 Experimental Setup and Procedure

Given the apparent ease of using the sessile drop analysis method, it was carried out first. A sample of Dow Styron 685D polystyrene was prepared in the vacuum oven for 24 hours at 200°C. The temperature used is higher than the melting point and the vacuum oven should remove any moisture or volatile contaminants from the polystyrene. The difficulty in preparing a substrate plate was avoided by opting to use a glass plate as a substrate. Due to the similarity of glass and talc, the common polymer additive today,
this should provide at least some insight into the actual system used today. The glass was placed under acetone and also placed in a vacuum oven for 24 hours. A thin rod was used to pull molten polystyrene. Once a drop was formed, it was allowed to fall to the glass surface. Although a “critical drop size” is required, there are no specific means of determining a “critical drop”. In order to best estimate a drop, different amounts of polystyrene were put on the rod tip. A short time interval until the drop fell was seen in drops that were above the critical drop size. If the drop would not fall in any time, it was below the critical drop size. Based on this, it became clear when a drop was near the critical size.

Once plated, the drop was placed in the apparatus. The apparatus was heated to the proper temperature and filled with CO₂. The vessel was pressurized and vented three times to ensure a nearly complete CO₂ atmosphere. Once this process is finished, the pressure is set at the requisite pressure. The syringe pump and the pressure indicator are used to keep the wanted pressure. This is very important because the pressure will change quite a bit as the apparatus heats. Based on the work by Hongbo Li et al., an accurate estimate of the time needed for equilibrium in both CO₂ and temperature can be made by simply checking the rate of change between the two previous interfacial tension determinations. Once there is an acceptable deviation in the measurements, it is acceptable to say steady state data is being taken.

In addition to the sessile drop method, a capillary method was also examined. This was done using a similar sample preparation. A small beaker and capillary were cleaned thoroughly and placed in the vacuum oven. Again glass was used for the substrate in the system. The polymer used for the capillary method was an oligimer of
poly(dimethyl siloxane). A sample of proper volume was placed in the vacuum oven for the requisite 24 hours in a hope to remove volatiles. One of the most difficult steps in the arrangement of the capillary rise setup results from the requirement that the tube be perfectly vertical. This is simply solved by using the captured image and its geometry to correct the angle of the capillary. Similarly the equilibrium is to be waited for. This is done just as before, except the height of rise is used for comparison to the previous image.

The captive bubble technique was the last method to be used. It was quite difficult to achieve the desired setup. A perfectly level plate of substrate is required, so again glass was used. The difficulty was constructing an apparatus that held the fluid, was able to allow for the CO$_2$ bubble to be placed below the substrate, and still be stable enough to take the pressure and be able to be leveled. Since there was no simple means of constructing such an apparatus, plans were drawn up and it was fabricated by the Ohio State Glassblowing Shop. The plans for this apparatus can be seen in the Appendix. For all experiments using the fabricated glass box the following experimental set up was run: The glass box was submerged in an appropriate solvent for the polymer last used for 24 hours. The solvent was then flushed out until no visible polymer remained. At this point, the box was again soaked, this time in acetone. It was then put in the vacuum oven for 24 hours. The polymer used was added after the box had cooled. This was done using a glass dropper until the box section was full. All the bubbles were allowed to flow out of the polymer at this point at an appropriate temperature depending on the polymer. The box is then overfilled to ensure no unwanted air enters the box. At this point the box is ready to be filled with gas.
The difficulty in injecting CO$_2$ into the polymer under the glass plate was quite simple to bypass. This was done using a bent syringe. The needle was turned at a 90° angle and the syringe body, being plastic, was melted to a gas inlet from the syringe pump. This assured all the gas in the bubble was CO$_2$. The pump slowly fed gas into the box until a proper bubble size was reached.

A pendant drop method was also attempted, using a similar process as the work by Hongbo Li. His work is cited and his methods can be viewed.

All image analysis was done using the axisymmetric drop shape analysis (ADSA). A MATLAB script is used to fit the drop profile using least squares to the theoretical profile made from the Bashforth-Adams equation.

Figure 2.2-1. Captive bubble technique setup

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3. Results and Discussion

3.1 Sessile Drop Method

The sessile drop method was first attempted using polystyrene. Due to its interfacial tension data being already available, the contact angle was the only data to be gathered. Since the program used was able to produce both the interfacial tension and contact angle for the same photographs, the interfacial tension data gathered was to be compared to the literature values for polystyrene and CO₂. Following the plan of waiting for equilibrium became quite tedious and difficult, as the glass was completely wetted. The initial trials were at the working temperature of 200°C and a CO₂ pressure of 1000 PSI. Since the drop wetted at elevated pressure, the pressure was then dropped to atmospheric. This was done to test whether the CO₂ interaction in the polymer changed the interaction with the glass. The only observed change was the time span needed for wetting to complete. As the drop wets completely the surface below, the contact angle goes to 180°, meaning that the interfacial tension in the homogeneous system is the interfacial tension in the heterogeneous system. This is thought to not be an accurate estimation, given that the foaming properties are much better with the addition of the third phase. The actual contact angle is thought to lie somewhere along the path followed by the wetting drop, but it is not physically possible to place where on this curve it lies using this experimental method. Since there has been little work done on this method and polymer melts, PDMS was also used to see if this was a unique phenomena resulting from the system used. The PDMS also wet the plate. The time frame needed to wet was
much less, and this is thought to result from the much lower viscosity of PDMS when compared to polystyrene.

The contact angle change is governed by at least three variables that are complex and difficult to separate. The first is the heat transfer into the polymer. As the drop is heated, the viscosity is lowered, and because of the geometry of the drop, the unsteady nature is difficult to model. In addition to the rate of heating, the amount of CO₂ absorbed also is unsteady in nature and shows a viscosity changing effect. The lowering of the viscosity allows more gas to enter the matrix at a higher rate, all while the drop continues to spread. The interfacial tension between the gas and the polymer matrix is lowering as the gas is absorbed. This is easy to observe in the proper system, but with the motion of the drop and the dynamic nature of the system, the interfacial tension is nearly impossible to discern from the moving drop. Given that dynamic contact angles and interfacial tensions have no physical importance in extrusion foaming, it is almost meaningless to record the data.

2. Same drop at 4 hours
3.2 Pendant Drop Method

Given the difficulty that the sessile drop method ran into during the experiments, it became apparent that there would need to be different techniques used in order to accurately measure the contact angle. The most promising method for doing this would be the capillary rise method, but given the time scale estimated for the highly viscous polystyrene to rise, PDMS was to be used. The lower viscosity would allow us to check the technique to make sure that it would work before investing the amount of time needed to press the polystyrene up the capillary.

In order for the height of the capillary rise to correlate the contact angle, the interfacial tension of the gas/polymer interface would need to be known. Since no one had previously done this work using PDMS and CO₂ under high pressure, it was decided to proceed using the pendant drop method. This method was used quite successfully for polystyrene and poly(methyl methacrylate). A similar procedure was to be used with the hope of achieving interfacial tension data.

PDMS is much less viscous when compared to polystyrene, and because of this, the ease of forming a pendant drop disappeared. The runny and non-adherence of the drop made critical drop formation nearly impossible. After many trials and attempts, drops were formed at the end of the metal rods, only to drop off at any point in time once setup in the apparatus. The critical drop size became an unachievable goal. Any vibrations at all gave the drop enough energy to escape from the rod, even when it was obvious that the critical size had not been approached. The data taken from the sub-critical drop showed very little coherence to the trends previously encountered with the other polymer systems and with the predicted trends that any CO₂-interacting polymer
would show. This is a result of the fitting program taking a drop below the critical drop size and attempting to stretch its parameters into a critical drop shape. The program is not capable of such a stretch and was not made with the intention of such. Because of this, the pendant drop method for a lower viscosity polymer under pressure is not thought to be an applicable system for finding the interfacial tension. The thinning of the drop was seen occurring regardless of pressure of CO₂, so this phenomenon is not a plasticization effect. Given the difficulty encountered both here and using the sessile drop method, it becomes easy to see why there is no high pressure interfacial tension data for PDMS and other lower viscosity polymers.

Figures 3.2-1 and 3.2-2. 1. The profile of a pendant drop of polystyrene as seen by the computer. 2. A drop of polystyrene as photographed at 200°C in CO₂ the atmosphere.
3.3 Capillary Rise Method

The motivation for using the pendant drop was to be able to solve for the contact angle based on the rise in the capillary tube method. This was done because for a lower viscosity polymer, the rise would not take a long time and would be easy to equilibrate. Given the selection of lower viscosity polymers, it was found that almost no interfacial tension data was available with an elevated pressure using CO₂. Using the pendant drop led to more problems than it solved.

Despite this, the capillary rise method was tested. Both polystyrene and PDMS were used, although only the polystyrene data could be equated into contact angle because of the known interfacial tensions. The contact angle in this case is the angle formed by the edges of the meniscus and the glass tube.

![Capillary tube diagram](image)

**Figure 3.3-1. Capillary tube diagram**

Using the PDMS, it became obvious that the technique would work properly. The time span needed was very workable, with the polymer climbing the tube before any amount of pressure was seen by the system. The interaction between the glass and the
polymer is highly evident, as the meniscus has a very low bottom relative the height of the climb of the polymer on the wall. With something as difficult as measuring the exact height of the PDMS climb, the resolution with the camera begins to be of importance.

![Image of polymer climb](image)

**Figures 3.3-2, 3.3-3. 1. Initial placement of capillary in polymer. 2. Initial rise of polymer.**

The resolution is surely not high enough to base the contact angle on the image, but the height of the bottom of the meniscus is quite easy to differentiate, and with the known outside diameter of the capillary tube, a relative comparison could be made to estimate the height. Based on this success and the lack of interfacial tension data necessary to estimate the contact angle, the polystyrene trials were attempted.

The equation for the height is based on not only interfacial tension data and contact angle, but also the difference in densities of the two phases. This is where the polystyrene system ran into trouble. Had the polystyrene formed a homogeneous phase, the density of the CO₂ swollen polymer could have been either experimentally measured or calculated using a complex equation of state. The gas density would have also been a simple equation of state calculation. The problem resulted again from the very high
viscosity of the polystyrene melt. Polymer beads were heated in a vacuum oven with the hope of removing all bubbles from the melt. Even under vacuum above the melting point for a week, the polystyrene never formed a single homogeneous phase. There were bubbles in everything, including the polymer that began to rise in the centered capillary. This lack of a homogeneous phase prevented the equations governing capillary rise to hold, and the resulting rise and calculations led to shape factors greater than one, a physically meaningless result. This process was therefore eliminated as a candidate for determining the contact angle for the polystyrene CO$_2$ system.

3.4 Captive Bubble Method

As described in the experimental design section, a glass box was made for the purpose of attempting the captive bubble method. Unlike any of the previous methods, this method concentrated on placing a bubble of gas under the substrate and filling the surrounding area with polymer. This is similar to the filling of the capillary in that a homogeneous polymer phase must be constructed. Although not governing the profile observed of the bubble, this too became quite difficult for the polystyrene system and its enormously high viscosity. The bubbles that were resulting however, were fairly minimal compared to the size of the CO$_2$ bubble that can be injected for measurements.

In addition, the captive bubble technique allows the interfacial tension to be measured as the contact angle is being measured. This allows for comparison between the observed interfacial tension and the literature values. The magnitude of the difference between this technique and the pendant drop method is quite large using the glass box as manufactured, but because of flaws and oversights in design, a newly designed box will
hopefully shore up the problems encountered. In particular, the flaws result from the glass substrate plate being too small in comparison with the distance to each of the walls. The wall effects the shape of the bubble even though the bubble is visually not in contact with the wall. This effect was quite unexpected and hopefully can be fixed in the future.

For the PDMS system, similar results followed. The polymer was much easier to work with and remove the bubbles from, but because the wall effect was encountered in the polystyrene, it was assumed that it too was present here. For this reason, both the contact angle and the interfacial tensions measured were rejected.

4. Conclusions

Contact angle measurements present a difficult problem. When looking at the simple governing equations and the thermodynamics behind the process, it seems that the physical system worked with has very few complications beyond the pressures and temperatures that are needed. The heated pressure vessel, tapped to allow for a rod to be placed for the pendant seems to alleviate any problems that would be encountered following the standard methods for determination. The exhaustive literature search that yielded almost no data for contact angles in polymer systems showed that this was not the case. Even a simple desktop experiment without any heating or pressure resulted in almost no usable data, as the experimental design that works so well for so many systems fails for the polymer system.

There are many reasons why this is so. Of particular interest is the affinity of the polymer toward the glass surface. Although typically falling somewhere between hydrophobic and hydrophilic, the glass surface was found to be very attractive toward the
polymer, regardless of the conditions around it. This provides some interesting insight into the physical process of the formation of critical nucleate sites. The lowering of the energy at the interface of the three materials promotes the growth of bubbles. This validates the work by Zeng et al., showing an improvement in foam formation and final characteristics.

The higher working viscosities of polymer melts also makes the systems tested quite different than the usual systems. Although the increased viscosity should make the system less complicated to work with, in that the viscosity can be set with the temperature used, it presents more problems than it solves. The “workability” of the system is quite limited, as it is quite difficult to form the proper shape and control the drops as the viscosity changes so much over a small temperature range. The narrow range of critical drop size makes the pendant drop method very limited as the viscosity on the system changes, as the critical drop size depends on temperature and viscosity.

5. Recommendations & Future Work

With the promising early results seen from using the captive bubble technique, it is best that the next step is to properly design the captive bubble chamber. Its design, along with the previous original design, is included in the appendix. Once the new chamber is constructed, more trials with the polystyrene/CO₂ system should be done in order to compare the interfacial tension taken from these trials to the data from the pendant drop method. If the interfacial tension compares well with the literature method, the contact angle measurements taken at the varying temperatures and pressures can be recorded as actual values. As the processing pressures and temperatures are all done,
there should be some type of maximum that exists for the system. Once a maximum is
detected, experiments using foam extrusion and batch foaming should be run using a
substrate similar to the glass. This again would validate the results for the best conditions
to achieve the optimum contact angle.

Since there is little or no literature data on the PDMS/CO₂ system, there is almost
no way to compare any data that is taken with the captive bubble to other results or other
methods. Perhaps the only way to validate any data that results from the captive bubble
is to compare this to the predicted height of rise in the capillary method. With a contact
angle and interfacial tension known, the height of rise can be solved for. If the predicted
height of rise is equal to the actual height under the same working conditions, and
assuming identical glass properties, it would be safe to assume the data taken from the
captive bubble were actual thermo-physical properties of the material.

Once this method has been established and proven to be accurate, the possibilities
of it are quite limitless. The number of foaming polymers and their applications are
growing, and this method will allow some quantitative means of finding the best foaming
conditions. Any number of gasses could be used, depending on the application. Most
importantly, the substrate surface can be changed. Glass can be made hydrophobic or
hydrophilic, depending on the surface treatment. These treatments can be done to the
glass plate used as the substrate, to correlate the interactions between the polymer
systems and many different materials. In addition, the altered design allows for the
insertion of any type of material into the glass box. With this arrangement and the
advances in surface chemistry, any type of substrate can be created and shaped to fit into
the box, better simulating the actual interaction in the polymer melts being foamed.
6. References


Appendix

The captive bubble apparatus design

The height of the apparatus was .75” with a glass plate affixed .5” from the bottom. The total length of the apparatus is 1”. It has no top and the affixed glass plate does not completely cover the opening, leaving a space for the needle to inset CO2. The first drawing shows how this would work. The needle is bent to allow the drop to release to the bottom of the glass plate. The dark fill is the polymer in the apparatus.

As mentioned above, this design did not allow for enough area for the bubble to not interact with the walls of the apparatus. Because of this, a new design has been made, with the intention of removing any error that may result from the walls. In addition, the new design will make it much easier to remove any bubbles that are present in the system that are not part of the experiment. The current design makes it quite difficult to do so.
Improved Captive Bubble Apparatus

The apparatus will be only slightly larger, but will only attach at the front and back, not on the sides. This makes the system much easier to work with and distance the bubble.