

# Interfacial Effects and the Anomalous Swelling Behavior of Supported Polymeric Thin Films in Supercritical Carbon Dioxide.

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**ABSTRACT:** This work investigates the effects of temperature, initial thickness and material substrate upon sorption and consequent dilation of thin supported polymeric films in supercritical carbon dioxide. High-Pressure Quartz Crystal Microbalance measurements demonstrate that there is an Excess Gibbs Adsorption of carbon dioxide at the polymer/substrate interface, which strongly depends upon temperature, pressure and nature of the solid substrate. This accumulation of carbon dioxide at the submerged surface can explain the “anomalous swelling behavior” observed in polymeric thin films, where a maximum in film thickness with increasing pressure has been found by numerous investigators.

## INTRODUCTION

Well-documented studies on the dynamic properties of polymers at surfaces and interfaces have shown that constrained thin films behave quite differently from bulk films [1-5].

Surfaces undoubtedly dominate the behavior of materials with a small size as a result of their high surface-to-volume ratio and the importance of surface effects on the thickness dependence of the glass transition temperature of thin films as well as the importance of mobility in the vicinity of surfaces and interfaces in understanding properties such as adhesion and friction have been extensively studied over the past decade[1-3], and although relevant as scientific issues per se, they could also have tremendous technological implications in the near future. Moreover, recent experimental results [6, 7] have started to suggest that there is an interesting anomaly in the sorption behavior of thin polymeric films brought in contact with supercritical fluids. Indeed, a maximum in the swelling percentage has been found crossing the critical pressure of the fluid for temperature close to the critical temperature.

However, while there is consistency among different published studies about the experimental evidence of such phenomena [6, 7], the picture that emerges is not yet clear and little in the way of putting forward theoretical basis has been done so far. In this work we review existing theories and present a different interpretation, focused on the interactions between the supercritical phase dissolved in the polymeric matrix and the polymer substrate, suggesting that the very effect that can be used to explain Gibbs Excess Adsorption on hard surfaces could also be responsible of such phenomena.

## **I - MATERIALS AND METHODS - High Pressure Ellipsometry (HPE)**

### **I.1 Materials and Sample Preparation**

PMMA (Mw: 225700, Mw/Mn = 1.06) was purchased from Polymer Source, Inc. Dorval (Montreal, Canada). Toluene (Fisher) was used as solvent to dissolve PMMA.

Silicon wafers (100 mm diameter, a <100> orientation) having  $\approx 1.7$  nm thick native oxide films ( $\text{SiO}_x$ ), GaAs wafers (50 mm diameter, a <100> orientation) having  $\approx 3.0$  nm thick native oxide films ( $\text{GaAs}_x\text{O}_x$ ) and Silicon wafers (50 mm diameter, a <100> orientation) covered with 300nm  $\text{TiN}_2$  were purchased from International Wafer Services (Portola Valley, CA). The wafers were cleaned by soaking in a mixture of JTB-111 alkaline-surfactant, hydrogen peroxide and DI water with a 4.6:1:22.8 volume ratios for 10 minutes and subsequently rinsed with copious amounts of DI water, and dried with nitrogen.

PMMA/Toluene solutions were spin-coated onto silicon wafers using a Headway Research (Model 131-024, Indianapolis, IN) spin coater. The concentrations of the PMMA/Toluene solutions and spin rates were varied to obtain films of different thickness. GaAs wafers were immersed in HCl for 1 minute, then rinsed with copious amounts of DI water, and dried with nitrogen.

### **I.2 Swelling Measurements**

The PMMA films on the silicon wafer substrates were introduced into the chamber and scanned using the ellipsometer described above. The experimental ellipsometric data were fitted using a four-layer model, comprising the silicon substrate, a native oxide layer, a mixed polymer/ $\text{CO}_2$  layer, and a bulk  $\text{CO}_2$  medium. The refractive indices at different wavelengths were adopted from literature values for silicon substrate, the native oxide, and the  $\text{CO}_2$  atmosphere. The fitted parameters for the swelling experiments were the same as those in the calibration scan, with the additional fitting of the refractive index of the swollen PMMA/ $\text{CO}_2$  layer. The refractive index of the swollen PMMA/ $\text{CO}_2$  layer was modelled as a function of wavelength by assuming a Cauchy dispersion relationship.

## **II - DISCUSSION**

### **II.1 Gibbs Excess Adsorption on bare substrates (hard surfaces).**

Previous studies have examined adsorption of supercritical fluids onto non-swelling hard surfaces. Findenegg [8] showed large surface excesses of ethylene on homogeneous graphitized carbon black surfaces near the critical pressure and critical temperature.

Others have seen large adsorption excesses of compressible fluids onto hard impenetrable surfaces when operating in the proximity of the critical pressure and temperature [9, 10]. At supercritical temperatures, the excess adsorption of ethylene exhibited a pronounced maximum at a pressure slightly less than the pressure where the compressibility of ethylene displayed a maximum. The excess adsorption isotherms were very large and sharp at near critical pressures and at temperatures that were slightly higher than the critical temperature. At higher temperatures the excess adsorption maxima become smaller and much broader in nature, occurring at higher pressures.

Similar behaviors in the supercritical adsorption of  $\text{CO}_2$  on both unmodified and chemically modified silica surfaces as well as on proteins and polysaccharides have also been reported [9, 10].

In all the abovementioned studies the only measurable property is the Gibbs Excess Adsorption ( $\Gamma^{ex}$ ), also called surface excess by many authors, defined in terms of density profiles as

$$\Gamma^{ex} = \int_0^{\infty} (\rho(z) - \rho_{bulk}) dz \approx \int_0^{\delta} (\rho(z) - \rho_{bulk}) dz = \delta(\bar{\rho} - \rho_{bulk})$$

where  $\rho(z)$  is the local density of CO<sub>2</sub> at a distance  $z$  from the substrate,  $\rho_{bulk}$  is the density of the bulk CO<sub>2</sub>,  $\delta$  and 0 represent respectively the concentration gradient upper limit and the substrate surface and  $\bar{\rho}$  is the (average) density of the adsorbed phase, assumed uniform over the gradient length. For many surfaces, the interaction between CO<sub>2</sub> and the surface may be expected to exceed the intermolecular attraction between pure CO<sub>2</sub> molecules, due to the low polarizability per volume of CO<sub>2</sub>.

Since CO<sub>2</sub> is attracted preferentially to the surface,  $\rho(z)$  will be larger than  $\rho_{bulk}$ . In highly CO<sub>2</sub> compressible regimes, the attraction of CO<sub>2</sub> to the surface produces  $\rho(z)$  values with densities approaching those of liquid CO<sub>2</sub>. The pronounced difference between  $\rho(z)$  and  $\rho_{bulk}$  results in large excesses of CO<sub>2</sub> at the surface. As the pressure increases, the bulk density of CO<sub>2</sub> increases markedly, and the excess layer decreases since  $\rho(z)$  becomes closer to  $\rho_{bulk}$ .

Thus the qualitative behavior of  $\Gamma^{ex}$  should exhibit similar trends as that of the isothermal compressibility. For example, near the critical temperature large and sharp excess adsorption maxima are observed near the critical pressure. At higher temperatures, the maxima are smaller and broader and shift to higher pressures.

The excess accumulation on hard surfaces might be studied experimentally with rather different techniques. Using for instance, HPE, QCM and Rubotherm, it is possible to obtain different outcomes of the same phenomenon because of the intrinsic differences among the quantities measured, but they are all consistent once referred to the same physical frame (not shown here for the sake of simplicity).

The layer of carbon dioxide adsorbed onto silicon has a different density with respect to the bulk carbon dioxide, thus having a different refractive index as well (since the refractive index depends on the density). HPE is sensitive enough to “see” the interface adsorbed layer/bulk carbon dioxide and a thickness ( $\delta$ ) can be extracted from the measurements once a convenient choice has been made for the refractive index of the adsorbed phase (the density of this phase changes with distance from the substrate and as expressed by the above equation, an average value will be assumed).

Fig. 1 shows this type of measurements carried out with our apparatus at 35°C and 50°C as well as those published by Sirard et al. at 35°C. The different behavior can be attributed to differences in the choice of the refractive index for the adsorbed phase, as stated before.

## II.2 Gibbs Excess Adsorption at the buried polymer/substrate interface.

Sirard et al. [6] were the first to discover an interesting maximum in swelling percentage of a thin PMMA film (ranging from 88 to 321nm) at pressures around the CO<sub>2</sub> critical pressure at 35°C using High-Pressure Ellipsometry. They tried to explain this phenomenon in terms of phase separation within the sample driven by the carbon dioxide isothermal compressibility. The latter quantity experiences a maximum around the critical pressure as well and it is well-known that the compressibility of the system might play an important role when it comes to phase stability. However, their explanation is somehow questionable since it fails to explain why the same behaviour cannot be seen in bulk films and because they invoked the compressibility of carbon dioxide alone (external phase) which is quite different from that of the polymer-CO<sub>2</sub> system.

Using Neutron reflectivity and exploring different polymers, Koga et al. [7], found the same behaviour for much thinner films [from 20 to 100nm]. Their explanations dealt with the so-called “Ridge of density fluctuations in supercritical fluids”. Indeed, this quantity depends upon the isothermal compressibility of the fluid and thus has a very similar behaviour. They suggested then that across the critical pressure, the swelling percentage would be density fluctuations dependent, whereas elsewhere it would be bulk density dependent.

Their idea, as well as that of the first group, cannot explain why this maximum has been seen only with thin films because it does not consider at all the size of the sample.

Moreover, both groups seem to be focusing on the external phase overlooking the importance of the polymeric phase.

As already discussed the other well-studied quantity that has the same qualitative behaviour of the isothermal compressibility is the Gibbs Excess adsorption.

Our fundamental hypothesis is that an excess accumulation of carbon dioxide can be found at the buried surface as result of stabilization induced by the molecular interactions between carbon dioxide and the solid substrate. This hypothesis has been successfully demonstrated by our group using a Quartz Crystal Microbalance setup and a regression procedure (not shown here) and it has been found that the amount of carbon dioxide accumulated at the submerged polymer/substrate interface matches within experimental error the amount of carbon dioxide adsorbed onto the bare substrate (also not shown here).

This “extra” carbon dioxide will very likely influence the swelling of the polymeric phase coated onto the substrate but the molecular nature of this effect will not be treated here, only its extent.

Experimental tests aimed at showing the effects of temperature, material substrate and initial thickness on the maximum were carried out. Indeed, carbon dioxide Gibbs Excess Adsorption on bare substrates changes dramatically with temperature (disrupting effect) and becomes smaller moving from TiN, to SiO<sub>x</sub> and to GaAs, due to the rather different surface forces that can stabilize a carbon dioxide wetting layer on these substrates. As for the thickness influence upon the anomaly, it is intuitive to expect a decreasing importance of surface effects for thicker films, even though, as we shall see, this has not been the case.

In figure 2, dilation isotherms are shown as swelling percentage vs. pressure for a 87-nm thick film spun onto silicon at three different temperatures: 27°C, 35 °C and 50 °C. Full symbols represent sorption runs while open symbols are the corresponding desorption runs.

It is clear from this figure that increasing the temperature the maximum becomes smaller and broader and shifts to higher pressures. These pressures can be easily located using the vapor-liquid pressure line for temperature below the critical temperature (27°C) and the so-called “Ridge of density fluctuations” for the two temperatures above the critical temperature [7].

It is interesting to note how the anomaly can barely be seen at the highest temperature, sign this of a clear disruptive effect of temperature. Indeed, the higher the temperature the higher the system “bulk” energy ( $kT$ ), which in turns allows to reduce the stabilizing effect of the substrate thus reducing the amount of adsorbed carbon dioxide as can be seen by looking at the Gibbs Excess Adsorption for bare substrates at different temperatures (fig.1).

In figure 3, the effect of the abovementioned substrates on the swelling percentage vs. pressure is shown at 35°C for 87nm thick films.

Clearly the size of the maximum is affected by the different substrate and the film coated on TiN has the highest value as could be expected by looking at the Hamaker coefficients  $A_{CO_2-PMMA-TiN_2} > A_{CO_2-PMMA-SiO_x} \square A_{CO_2-PMMA-GaAs}$  (neglecting all interactions but van der Waals forces) calculated using the Lifshitz theory of interactions is a medium from the information about refractive indices retrieved from HPE (not shown).

If the anomalous behavior depended on either mixture isothermal compressibility or density fluctuations the above result could not be explained.

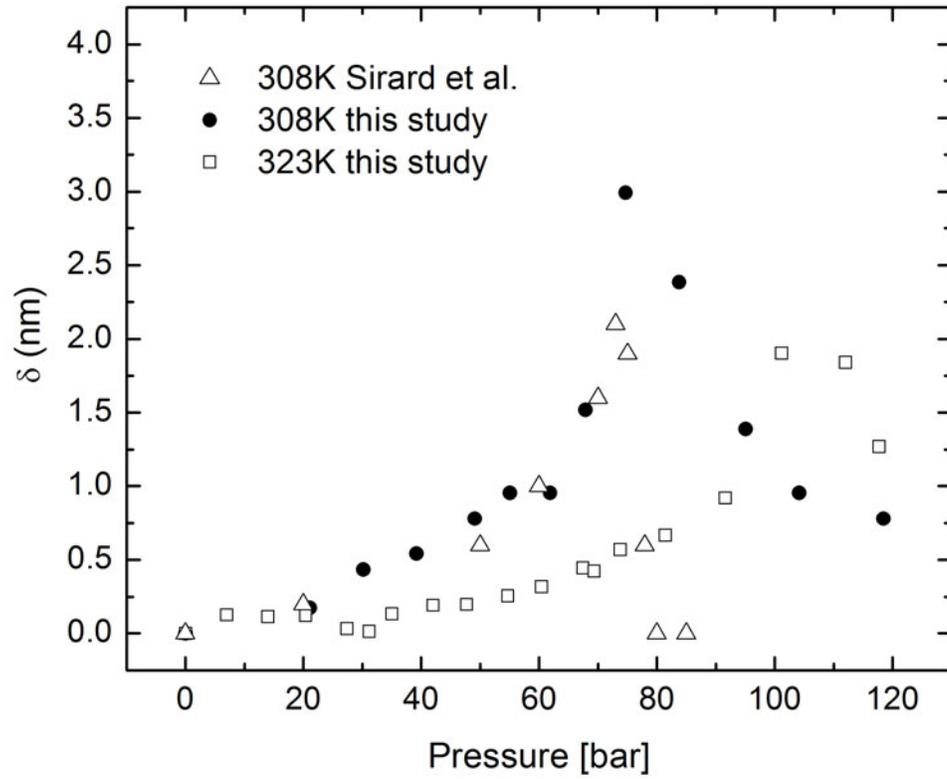
Our approach, on the other hand, focusing on a different physical quantity,  $\Gamma^{ex}$ , strongly related to the solvent-substrate interaction is able to predict such a behavior.

As last variable examined we left the most unclear of all, i.e. the effect of the initial thickness. From the above discussion one can infer that the only effect that the thickness would have upon the anomaly is to reduce it. As the thickness increases the maximum should decrease until, eventually, smoothly vanish for initial thicknesses approaching the bulk threshold value (which incidentally no one knows for sure where is located). By looking at fig. 4, it would then be very disappointing to notice that the behavior is exactly the opposite of what intuitively expected!

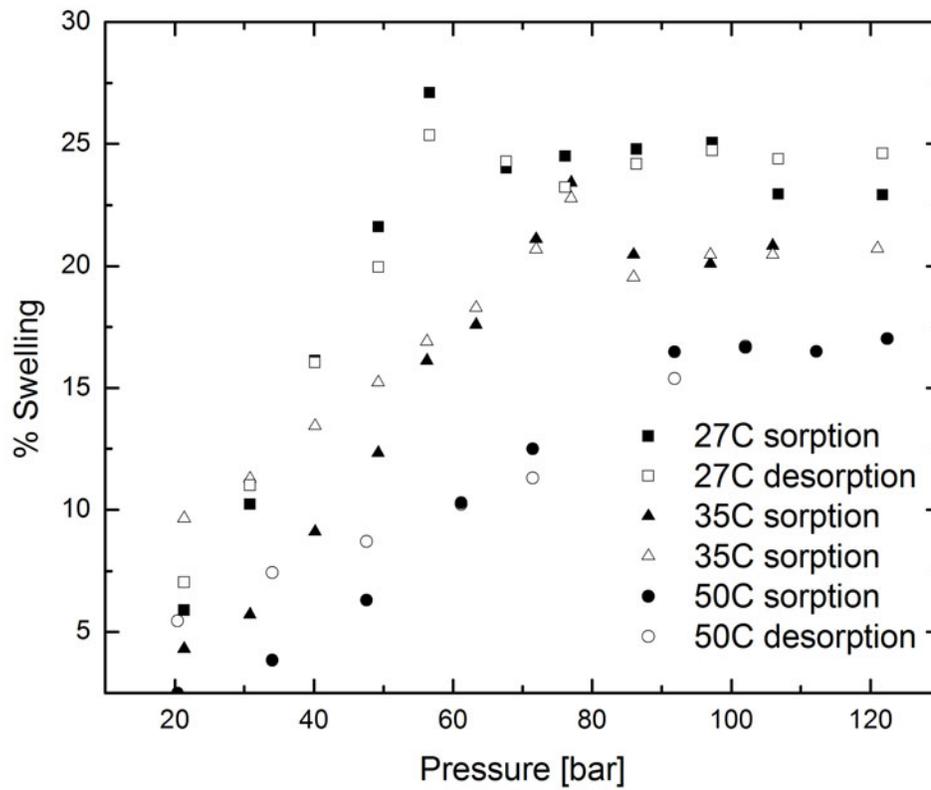
The figure presents data collected using HPE at 35°C at three different initial thicknesses: 87nm, 180nm and 420nm. As clear from the graph, the higher the initial thickness the higher the size of the maximum. This feature, pointed out first by this work, is totally unexpected and unintuitive and none of the so far proposed theories, included the one presented here, are currently able to explain such important experimental finding.

## CONCLUSIONS

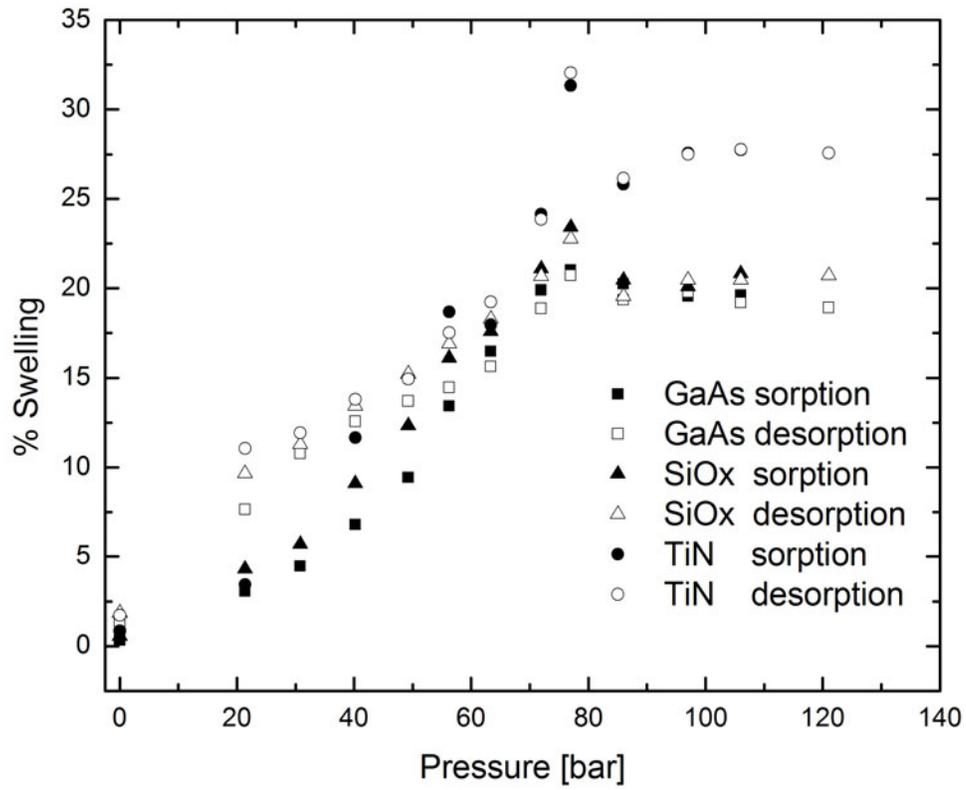
The role of surfaces in the anomalous swelling behaviour of thin polymeric films brought in contact with supercritical carbon dioxide has been investigated through the use of High-Pressure Ellipsometry technique applied to the PMMA-CO<sub>2</sub> system. The importance of substrate-CO<sub>2</sub> interactions in explaining the complex phenomenon has been found by trying three very different substrates: GaAs, SiO<sub>2</sub> and TiN as shown in picture 3. None of the previous theories could explain such behaviour. The authors believe that the same principles responsible for the wetting of bare substrate by carbon dioxide could be the cause of such phenomena for buried surfaces. Further experimental and theoretical attempts aimed at consolidating our hypothesis as well as at further investigating the effect of initial thickness are currently in progress.



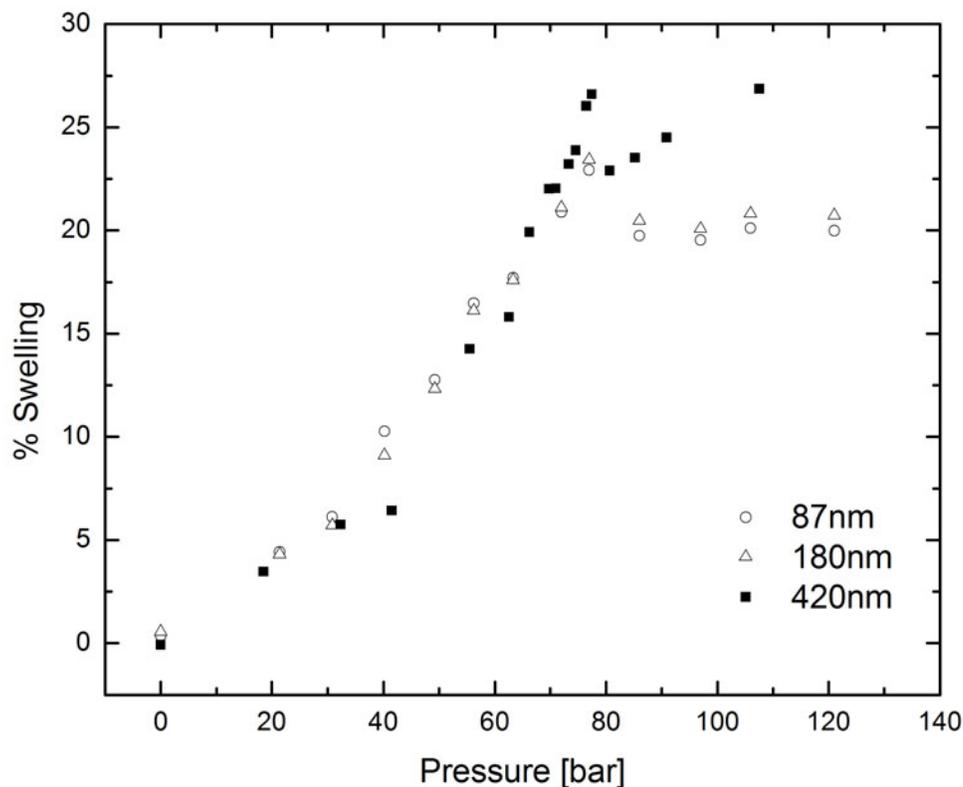
**Figure 1. HPE measurements of carbon dioxide wetting layer on bare silicon at different pressures and two temperatures (308K, 323K).**



**Figure 2. Swelling isotherms at three different temperatures, same initial film thickness (87 nm), same substrate (silicon).**



**Figure 3. Same initial thickness (87nm) and same temperature (308K), three different materials for the substrate.**



**Figure 4. Same substrate (Silicon) and same temperature (308K) different initial thicknesses.**

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