

612h Anomalous Swelling of Thin Films with CO₂

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What has become obvious in the last year or so is that we do not have a clear understanding of why thin polymer films appear to anomalously “swell” in CO₂ under certain conditions. This is an important problem within the context of using CO₂ as a processing solvent in microelectronic applications. One potential adverse effect would be the de-lamination of the film from the substrate. We would like to provide a definitive answer to this problem by using a combination of Sanchez-Lacombe Equation of State and interfacial tension theory. We will investigate the following hypothesis: The anomalous swelling is NOT caused by an increase of solubility of CO₂ in the polymer film. Our position, based on a thermodynamics argument, is that CO₂ becomes less soluble in a polymer when CO₂ becomes more compressible. One explanation is that in the very compressible region of CO₂, the expulsion of CO₂ is not uniform within the thin film. The presence of the substrate could act as an attractive and nucleating surface for the accumulation of CO₂ at the polymer/substrate interface. The accretion of relative low density CO₂ at the interface would increase the overall film thickness (volume expansion). This effect would not be a significant percentage wise in a thick film, but it would be in a thin film. We plan to use compressible model of a CO₂/polymer (PDMS and PMMA) and calculate the affect of an attractive surface on the distribution of CO₂ within the film. Under conditions where CO₂ is very compressible, it is expected that the bulk solubility of the CO₂ in the film will decrease; the expulsion of the solvent will not be uniform and a CO₂ rich layer will form at the substrate-film interface. This is the hypothesis that we wish to check by carrying out this calculation.