

Polymer Thin Film Modeling with Silica Substrate in Presence of Carbon Dioxide

The classical processing and fabrication technologies that produce stable macro- and micro-level polymer structures cannot be used for fabrication of nanostructures because of their length scale dependence on critical properties like Glass Transition Temperature (T_g). Novel methods of fabricating polymers nanostructures without introducing either organic solvents or higher processing temperatures are being explored. One of the methods is the use of subcritical CO_2 as an intermediate processing agent in the polymer. In the presence of CO_2 , there is T_g depression, reduced viscosity and reduced interfacial tension, all of which facilitate processing. However, because many of the underlying molecular level mechanisms are not well understood, fabrication of stable structure is still questionable.

An objective of this research is to develop a molecular dynamics (MD) based multiscale computational model to understand these mechanisms on polymer thin film depending on the film size, free surface, effect of CO_2 and the type of substrate used. The models are being developed based on related experimental work that is going on in other polymer groups at NSEC.

Objective in the period 2007-2008:

1. Free Volume Calculation in Polymer
2. Effect of CO_2 on T_g of bulk Polystyrene
3. Polymer Thin Film Modeling and effect of substrate and free surface on T_g
4. Development of a Coarse Grained Molecular Model

Task Completed and In Progress:

1. Free Volume Calculation and Validation with Positron Annihilation Lifetime Spectroscopy (PALS) Data:

We have successfully characterized T_g using measurements of thermal expansion coefficients and mean squared displacement (msd) from molecular-dynamics simulations. But these methods are more statistical in nature and cannot be used with certainty to study the local structural changes and dynamics at the nanoscale. At the molecular level, free-volume theory has long been proposed to explain the molecular motion and physical behavior of glassy and liquid states. Free-volume theory accurately describes diffusion above and below T_g , based on the presumption that transport is controlled by availability of voids and cavities (free volume) within a system. For our modeling, we have used the trajectory generated from MD to study free-volume characteristics. The microstructural evolution of the system also has been captured and matched with PALS data. PALS is presently the only experimental method for direct detection of local free volume at the atomic level. From PALS, we can

obtain both the mean free volume hole size and free-volume fraction. Focus has been laid on the evolution of cavity (free volume) size and distribution with changing temperatures.

The fractional free volume, fv , is defined as a fraction of free volume V_f and the total volume V_t in the system. A stochastic model has been developed to match with the available PALS data for Polystyrene. The results obtained matched excellently with the PALS data.

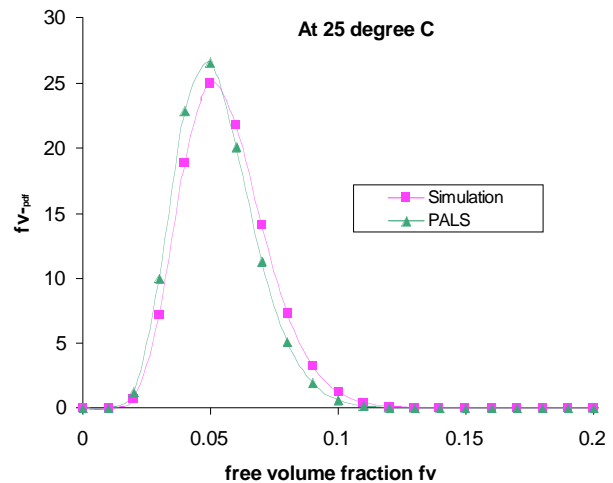


Figure 1. Free Volume Fraction Distribution at 25C and comparison with PALS data

2. Modeling Carbon Dioxide/Polystyrene System

Carbon Dioxide (CO_2) has been modeled using Elementary Physical Model (EPM) potential

$$U(r_{ij}) = \sum_{|i-j| \leq 3} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - 2 \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \sum_k k_\theta (\theta_k - \theta_0)^2 + \frac{q_i \cdot q_j}{4\pi\epsilon_o r_{ij}^2}$$

Elementary Potential Model					
ϵ_{c-c}	28.129 K	σ_{o-o}	3.033 A	l_{c-o}	1.149 A
σ_{c-c}	2.757 A	ϵ_{c-o}	47.588 K	k_θ	1236
ϵ_{o-o}	80.507 K	σ_{c-o}	2.892 A	q_c	+0.6512 e

Table 1. Potential Parameters for Carbon Dioxide

It has been shown experimentally that in the presence of CO_2 , the T_g of PS decreases significantly, as much as $30^\circ C$ for 800psi of pressure. One of the objectives of this project is to model a PS- CO_2 system and study the interactions between polymer and the gas to understand the physics behind this behavior. Also, the cavity analysis algorithm will be applied on it and matched with PALS data as a part of validation.

3. Polymer Thin Film Modeling and effect of substrate and free surface on T_g

A “three layer” model (Silica-Polystyrene-CO₂) has been developed to study thin film at atomistic scale. The three-layer model includes the pressure-inducing gas (CO₂) at the top of a Silica-Polystyrene layer. The advantage of using gas as a pressure-inducing agent is that it also facilitates a realistic free surface model for simulation. Different pressure on the polymer system is attained by changing the volume of gas occupied.

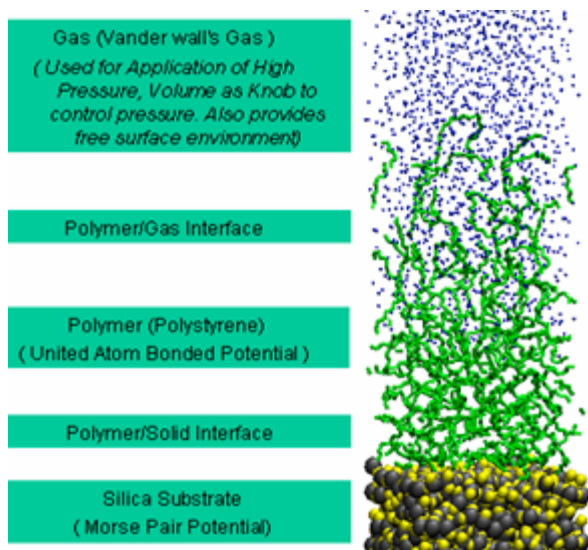


Figure 2. The “Three Layer” model for polymer thin film

Force fields for PS-Silica interface are scarce, and study of the nature of interfacial interactions is an active area of research. Currently, we assume the interfacial interaction to be non-bonded, but if required (based on new suggested experimental observation), the model can incorporate phenomena like hydrogen bonding as well.

4. Development of a Coarse Grained Molecular Model

A coarse-grained (CG) model is obtained by replacing a group of chemically connected atoms with an effective particle and deriving a coarse-grained interaction potential for this new system, which reproduces the structure and dynamics at the desired length and time scale. For Polystyrene, the side chain has been lumped into an effective backbone bead because the polymer chain has just three constraints: the bonds, the angular restraint and the dihedral restraint.

The implementation of a coarse graining procedure is underway. The probability distribution functions are unknown functions of CG bond length, bending angle and dihedral angle. This probability function is used to obtain the potential of mean force and in turn the potential energy functions of the model.

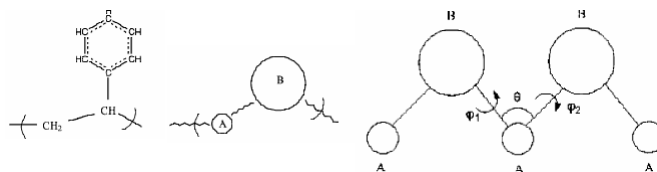


Figure 3. From atomistic to “meso” scale modeling

Collaborations and Future Outcome:

a. PALS and MD Simulation: The calculation of free volume for the PS-CO₂ system is underway. The experimental data for this system has been obtained from the Supercritical Fluids group led by Dr. Lee at NSEC. A joint paper is underway for this work [2].

Dr. Jean’s group at the University of Missouri-Kansas City, in collaboration with Dr. Lee’s group at Ohio State, have done experiments on free volume measurements on thin film and shown a gradient in mean cavity size across thickness. The trajectory information obtained by MD simulation on the “three layer” thin film model will be used to capture this gradient in cavity distribution. This is expected to lead to another publication [3].

b. Coarse Graining and MD Simulation: Dr. Kusaka’s group at NSEC is developing a 2 parameter coarse-grained model for the PS-CO₂ system based on polymer density functional theory. One of the future tasks is to match the energetic and other physical properties with the MD-based calculations. It is expected to result in one publication [4]

Publications:

1. A. Srivastava, S. Ghosh, Simulation study of Glass Transition of Polystyrene and Validation with Free Volume Theories (to be submitted)
2. A. Srivastava, S. Ghosh, C. Alleman, J. Yang and L.J. Lee. Effect of high pressure CO₂ on Glass Transition temperature and free volume distribution of Polystyrene. (to be submitted)
3. A. Srivastava, S. Ghosh, J. Yang, L.J. Lee and Y C Jean. An computational-experimental study of glass transition temperature variation in thin films (in preparation)
4. A Srivastava, S. Ghosh, J. Yang, I. Kusaka and M Talreja. Atomistic Coarse Grained model for Polystyrene based on Polymer Density Function theory. (in preparation)