

# **SURFACE TENSION VARIATION WITH TEMPERATURE**

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## **Abstract**

Surface tension trends involving temperature, pressure, and temperature with pressure were explained in the terms of the components of the surface tension. In particular, the reduction of surface tension with increasing temperature was consistent with a reduction of segregation between the molecular constituents;

The average of the surface tension values is taken as the equilibrium surface tension when the change in surface tension is less than  $0.0001\text{mJ m}^{-2}\text{s}^{-1}$

**Key Words:** Surface tension variation

## **1.1 Introduction**

Surface tension is one of the most important physicochemical properties for polymeric materials in various engineering processes, such as those involving foaming, suspensions, wetting and blending [1]. In the foaming of polymer melts, the homogeneous nucleation rate When the polymer in carbon dioxide has a lower surface tension than that of the pure polymer, the Gibbs free energy will be reduced by the cubic power of the surface tension, and the nucleation rate will increase exponentially. It is evident that changes in surface tension are crucial to polymer foaming processes, and it is necessary to understand and control such a property in order to optimize such polymer-involved industrial operations [2, 3].

There are many methods to measure surface tension. Among them, the pendant drop method has many advantages because of simplicity and versatility in its setup and principle [4, 5]. The pendant drop method has been used extensively for low molar mass liquids, liquid crystals and polymers. This method relies on the determination of a drop profile of dense liquid in another fluid, and the surface tension of the liquid is obtained from the best fit of the Laplace equation of capillarity to the experimentally determined drop profile [6, 7]. Although the pendant drop

method is theoretically simple, the research to date for determining surface tension of polymers has been limited because of experimental difficulties in handling high viscosity polymer melts under high temperature and high pressure. In fact, there have been only limited surface tension data available for a few select polymers, and the range of experimental conditions, to which polymers are subjected during their measurements, has been rather narrow. All of these shortcomings make the understanding and control of the surface tension of polymers difficult.

The primary objective of this study is to quantify the surface tension of a typical, commercially available polymer, polystyrene, in supercritical carbon dioxide, and to understand its dependence on temperature and pressure in a systematic way. A recently designed high-temperature and high-pressure sample cell is employed in the surface tension measurement to achieve a wide range of experimental conditions. With the collection of a comprehensive set of surface tension data, an empirical equation to approximate the surface tension of polystyrene in supercritical carbon dioxide as a function of temperature and pressure is developed, which provides predictive power for the surface tension variation. Furthermore, trends of the surface tension change with temperature and pressure are elucidated, and in particular, the effect of temperature on surface tension is shown to depend on the value of pressure.

To understand the surface tension behavior further, theoretical analysis of the experimental trends is given using self-consistent field theory (SCFT). It is difficult to achieve numerical accuracy for realistic values of the present system, so only qualitative agreement is sought. In this context, agreement with experiment is found, and three surface tension trends involving temperature and pressure are explained in terms of components of the surface tension. These components can be related to molecular interactions and configurations of polymers and, to some extent, solvents ( $\text{CO}_2$  in the present case). The resulting information provides means to change/ control the surface tension during polymer processing, through chemical and composition design of polymer materials. Specifically, it is found that a reduction in surface tension with increasing temperature is due to an expected increased mixing of chemical constituents upon reducing the segregation parameters between dissimilar constituents (polystyrene and supercritical carbon dioxide) with increasing temperature. A decrease in surface tension with increasing pressure is, however, due to more similar densities between these dissimilar constituents. Related to this, it is found that the slope of surface tension with temperature itself decreases at higher pressures. SCFT shows this to

be due to increased mixing between dissimilar constituents at higher pressure that results from the increased similarity in density. None of these explanations for the experimental trends are found to depend qualitatively on the configurational entropy contribution to the surface tension of the polymer, so these calculations rationalize the use of simple liquid models [4,5] for the quantitative prediction of surface tensions of polymers.

## CHAPTER-II

### 2.Experimental Procedure

#### 2.1.Materials

Polystyrene used was a commercial product (Styron 685D,  $M_n = 120,000$ , polydispersity index=2.6) from Dow Chemical Company. Carbon dioxide used was of chromatographic grade.

#### 2.2. Surface tension measurement

The surface tension of polystyrene in carbon dioxide was measured at temperatures from 170 to 210°C, within a wide range of pressures, from 500 to 2500 psi. To achieve these experimental conditions, a high-temperature and high-pressure sample cell was constructed. Briefly, this optical viewing cell consisted of a cylinder of stainless steel, which was heated by an electrical heater. The inside of the cylinder was hollow, with a diameter of 30 mm and length of 25 mm. Two optical-quality sapphire windows (Meller Optics, Inc.) permitted the illumination and observation of the pendant drop formed by a sample polymer melt. The setup was tested for its accuracy and reproducibility with a range of polymer-gas combinations, and the details of this were described in a recent publication [8].

The technique of Axisymmetric Drop Shape Analysis-Profile(ADSA-P) [9, 10] was used for image analysis and parameter extraction. Surface or interfacial tensions were obtained by fitting the Laplace equation of capillarity to the shape and dimensions of axisymmetric menisci acquired. The value of surface tension was generated as a fitting parameter after a least square algorithm was employed to minimize the difference between experimental drop profile and theoretical ones. During this procedure, the density difference between polystyrene and carbon dioxide was an input parameter [11], which was determined by the Sanchez and Lacombe (S-L) equation of state (EOS).

## CHAPTER-III

### 3. Results and Discussion

#### 3.1. Surface tension as a function of temperature and pressure

A typical pendant drop image is shown in Figure 1. The surface tension of polystyrene melt in carbon dioxide was measured at five different pressures: 500, 1000, 1500, 2000, and 2500 psi, and five different temperatures: 170, 180, 190, 200, and 210°C. Figure 2 shows the surface tension values as a function of time. The average of the surface tension values is taken as the equilibrium surface tension when the change in surface tension is less than  $0.0001 \text{ mJ m}^{-2} \text{ s}^{-1}$  for 1 hour. Errors are on the order of  $0.01 \text{ mJ m}^{-2}$ . All measurements show that the surface tension reaches its equilibrium value quickly, within 15 minutes. The surface tension values from these experiments show trends of being smaller at higher temperatures and higher pressures, consistent with the data from other studies [11].

From Fig. 2, equilibrium surface tension values of polystyrene in carbon dioxide under various conditions can be obtained by averaging the plateau data points at each condition; the results are shown in Fig. 3. It is apparent that the dependence of surface tension on temperature becomes less with increasing pressure. When the pressure value reaches above  $\sim 2000$  psi, such dependence becomes nil. This implies that increasing temperature is effective at reducing surface tension only when moderate pressure is applied during a polymer process.

The average of the surface tension values is taken as the equilibrium surface tension when the change in surface tension is less than  $0.0001 \text{ mJ m}^{-2} \text{ s}^{-1}$  for 1 hour. Errors are on the order of  $0.01 \text{ mJ m}^{-2}$ . All measurements show that the surface tension reaches its equilibrium value quickly, within 15 minutes. The surface tension values from these experiments show trends of being smaller at higher temperatures and higher pressures, consistent with the data from other studies [12].

## CHAPTER - IV

### SUMMARY AND CONCLUSIONS

A comprehensive set of the surface tension data of polystyrene in supercritical carbon dioxide at various temperatures and pressures was obtained successfully. Based on the obtained data, an empirical equation was developed that predicts the surface tension value at a given temperature and pressure. Within the experimental limits on temperature ( $< \sim 385^{\circ}\text{C}$ ) and pressure ( $< \sim 2153$  psi), the trends of surface tension dependence on temperature and pressure can be quantified with partial derivatives of the empirical equation.

Self-consistent field theory calculations were performed on a model system and surface tension trends involving temperature, pressure, and temperature with pressure were explained in the terms of the components of the surface tension. In particular, the reduction of surface tension with increasing temperature was consistent with a reduction of segregation between the molecular constituents; the reduction of surface tension with increasing pressure was due to increased similarity of density between the polymer (polystyrene) and solvent (supercritical carbon dioxide) constituents; the flattening of the surface tension versus temperature curve with increasing pressure was due to extra mixing between polymer and solvent, which reduces the segregation of the species at high pressures. The extra mixing results from the similar densities of the molecules at high pressures. None of these findings were dependent on the configurational entropy contribution of the polymers to the surface tensions, and so the use of simple liquid models for the prediction of surface tensions is justified. Consideration should be given to the above mechanisms when attempting to engineer surface tension properties.

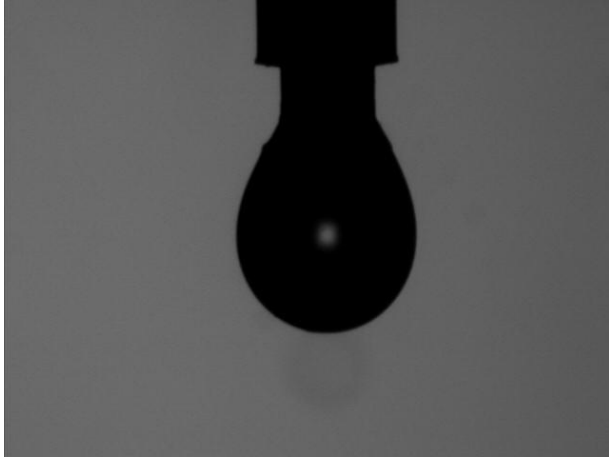


Figure 1. A typical pendant drop image of polystyrene in supercritical carbon dioxide

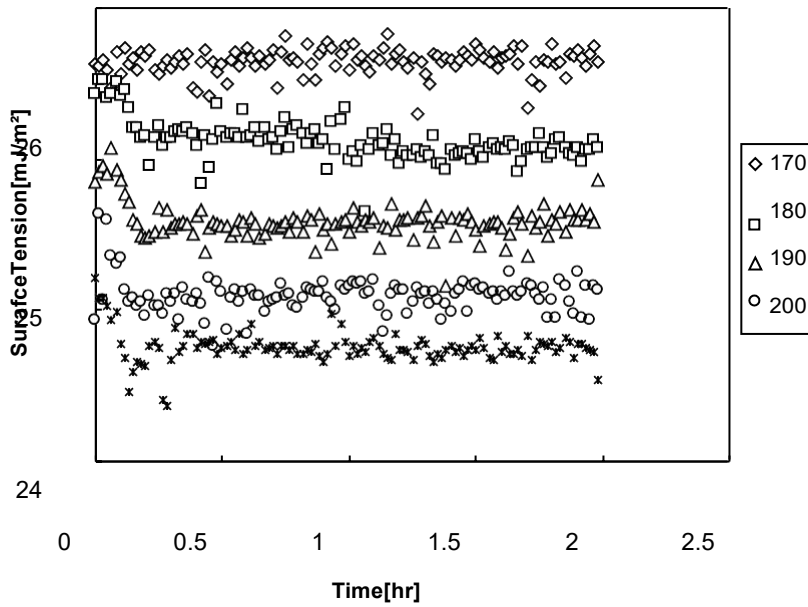


Figure 2. Surface tension of polystyrene in supercritical carbon dioxide at a pressure of 500psi..

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