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**THE MASSACHUSETTS  
TOXICS USE REDUCTION INSTITUTE**

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**SUPERCRITICAL CARBON DIOXIDE  
AS A CLEANING SOLVENT**

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University of Massachusetts Lowell

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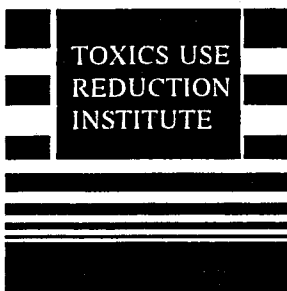
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**The Toxics Use Reduction Institute Research Fellowship Program**

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**The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to governments to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing the Toxics Use Reduction Institute, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854.**

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## **PREFACE**

In 1991 the Toxics Use Reduction Institute established the Research Fellows Program at the University of Massachusetts Lowell (UML). The Research Fellows Program funds toxics use reduction research projects performed by a graduate student and their advisor. The goals of the Research Fellows Program are:

- to develop technologies, materials, processes, and methods for implementing toxics use reduction techniques,
- to develop an understanding of toxics use reduction among UML graduate students and faculty,
- to facilitate the integration of the concept of toxics use reduction into UML research projects,
- to provide UML faculty with "incubator" funding for toxics use reduction related research, and
- to act as a liaison between Massachusetts industries and UML faculty.

The types of projects funded through the Research Fellows Program are technology, methods, and policy research projects. Each final project report is published by the Institute. The opinions and conclusions expressed in this Research Fellow report are those of the authors and not necessarily those of the Toxics Use Reduction Institute.

Supercritical carbon dioxide was chosen for investigation as a primary cleaning fluid due to its low viscosity (0.05 centipoise), high diffusivity, and very low surface tension. Moreover, it is environmentally non-hazardous, non-corrosive, non flammable, readily available, inexpensive and available in high purity grades.

For carbon dioxide, the critical temperature  $T_c$  is  $31^\circ\text{C}$  and critical pressure is also in a practical range at 1050 psi.

A supercritical fluid is actually a highly compressed gas raised above its critical temperature and critical pressure. In a pressure-temperature phase diagram (Fig 1) of carbon dioxide, the liquid-vapor equilibrium line ends abruptly at the critical point, above which the gaseous and liquid states are indistinguishable from each other and a new phase called a supercritical fluid is formed. This new phase exhibits properties common to both gases and liquids and can be regarded as a fourth state of matter.

In supercritical carbon dioxide density changes dramatically with pressure at the critical point. At ambient pressure and at  $31^\circ\text{C}$  the density is  $0.002\text{ g/cm}^3$  while at critical pressure it is  $0.468\text{ g/cm}^3$ , a 234-fold increase in density for a 73.8-fold increase in pressure. Carbon dioxide above its critical pressure has a density and solvating capability comparable to organic solvents. The solvent strength of carbon dioxide varies with pressure for a constant temperature.

Solubility in super critical (SC) solvents can be better understood by examining the Gibbs-Helmholtz equation:

$$\Delta G = \Delta H - T\Delta S$$

Solubilization will occur when the free energy of mixing ( $\Delta G$ ) is negative.

Because the dissolution of polymer is always associated with a large increase in the entropy of mixing ( $\Delta S$ ), the magnitude of the heat of mixing enthalpy ( $\Delta H$ ) determines solubility. According to Hilderbrandt, the heat of mixing can be defined as:

$$\Delta H = v_1 v_2 (\delta_1 - \delta_2)^2$$

where  $\Delta H$  is the energy change due to the making and breaking of secondary bonds,  $v_1$  is the volume fraction of solvent,  $v_2$  is the volume fraction of solute,  $\delta_1$  is the solubility parameter of the solvent, and  $\delta_2$  is the solubility parameter of the solute.

The interaction between  $\text{CO}_2$  in the supercritical region and the polymer has been extensively investigated. However, many fundamental processes that occur in these interactions are not well understood. Therefore, the study of a number of classes of polymeric materials in this region is of utmost importance as this phenomenon is used in several applications such as cleaning. Investigations of the interaction of polymer chains with  $\text{SCF}/\text{CO}_2$  and their effect on the properties of polymeric material can be classified under the following headings.

#### EFFECT OF RATE OF RELEASE OF $\text{CO}_2$ :

Based on preliminary studies, we have found that the rate at which  $\text{CO}_2$  is released, varies inversely with the weight gain for most polymers investigated thus far. Dissolution of  $\text{CO}_2$  in the polymer is responsible for the observed weight gain. The amorphousness of the polymer and the related free volume encourages dissolution of  $\text{CO}_2$  which then acts as a plasticizer, resulting in a lower  $T_g$ . Thus, a polymer such as PMMA which is more amorphous compared to one like PETG (which is less amorphous) shows a relatively higher weight gain and lower  $T_g$ . However, in the case of highly crystalline polymers like HDPE and PP, a small weight gain was noted. Additionally these polymers also showed a small increase in  $T_m$  which is thought to be due to extended chain crystallinity.

#### EFFECT OF PRESSURE AND TEMPERATURE:

Foam formation was observed in PMMA, HIPS, PETG, and ABS at 3000 psi  $\text{SCF}/\text{CO}_2$ , for 1 hr treatment and 1 hr release at 70 °C. For polymers like PMMA and PETG the formation of foam is due to the solubility of  $\text{CO}_2$  in the amorphous region of

the polymers; for ABS and HIPS, it could be due to the solubility of CO<sub>2</sub> butadiene domain. The dissolution of amorphous materials like PMMA, ABS, PVC, CAB, and PETG in SCF/CO<sub>2</sub> was found to be very small, and for the crystalline material PTFE, POM, Nylon 66, PP, HDPE, and LDPE it was found to be negligible.

We found that the glass transition temperature (T<sub>g</sub>) was not a systematic function of applied CO<sub>2</sub> pressure and temperature. By applying the pressure, the gas dissolves into the free volume of the polymeric material, but with the passage of time the gas diffuses out.

Also, DSC thermograms revealed no significant sign of change in melting temperature (T<sub>m</sub>) as a function of CO<sub>2</sub> pressure and temperature with the exception of HDPE.. However, in the case of HDPE, the observed increase in enthalpy might be due to annealing by increasing the pressure and releasing time of SCF/CO<sub>2</sub>.

In addition to the behavior of polymers in SCF/CO<sub>2</sub>, the effect of SCF/CO<sub>2</sub> on adhesives is a matter of concern. These effects may be due to formation of chemical reactions with SCF/CO<sub>2</sub>, to extraction of agents in either the adhesives or the substrate to introduce void formation by dissolving SCF/CO<sub>2</sub> into the polymeric chains, or to extraction of the plasticizer from the polymer chains, producing brittleness in the substrate.

We have begun to investigate the effect of SCF/CO<sub>2</sub> with adhesives and to study the cohesion and adhesion bonding with different polymers which will be reported later.