

Supercritical Carbon Dioxide and Adhesives

The emission of volatile organic compounds (VOCs) is hazardous to both the workers who use them and the environment. They have been implicated in a large number of health conditions, as well as damage to the ecosystem from air, water, and soil pollution¹. One kilogram of VOCs can be responsible for the generation of 2.3 to 3.0 kilograms of greenhouse gasses if directly released to the atmosphere; if incinerated in a natural gas furnace, up to 18 kg of greenhouse gasses can be released per kilogram of VOC². To this end, there has been an effort to reduce the emission of VOCs in industrial processes. One such process is the spraying of adhesives. The goal of this work is to replace a portion of the solvent used in the spraying process with carbon dioxide. This work is modelled after the UNICARB[®] process, which was developed for the spraying of paints.

The first step in the improvement of the spraying process is the reformulation of conventional sprayed adhesives. These conventional adhesives are made up of three major components; they are polymer, slow-evaporating solvent, and fast-evaporating diluent. The reformulated mixtures typically have all of their fast solvent, which is a VOC, replaced with carbon dioxide. This project has two parts: First, the phase behavior of the reformulated adhesives is mapped out with various concentrations of carbon dioxide and solvent. The viscosity and other properties also are measured. In the second part, the binding properties of the reformulated mixture are tested to insure proper material performance.

The phase behavior is probed in an apparatus that was provided by Union Carbide. It is an improvement on a design originally published by McHugh³. The key piece of equipment is a sample cell embedded with electric heating elements. The pressure is controlled with a hydraulic pump and a piston. A viewing port, camera and light source are built in for visual observation of the phase transitions. The cell typically is filled with the test formulation, allowed to sit for 6-12 hours to equilibrate, and then the pressure is changed at a fixed temperature to find the phase boundaries. Similar to the UNICARB[®] process, it is desirable for the operating line to start in a single-phase liquid region, as shown in Figure 1. Then, as the pressure is dropped, the mixture should go through a two-phase liquid-liquid region, cross a three-phase liquid-liquid-vapor line, and enter another two-phase liquid-vapor region. This progression of phase transitions insures a rapid vaporization of the carbon dioxide, and improves the spraying process by inducing a more uniform atomization.

It is interesting that the material properties of these new formulations are improved. Lap shear results for a variety of adhesive formulations are shown in Figure 2. The first column is

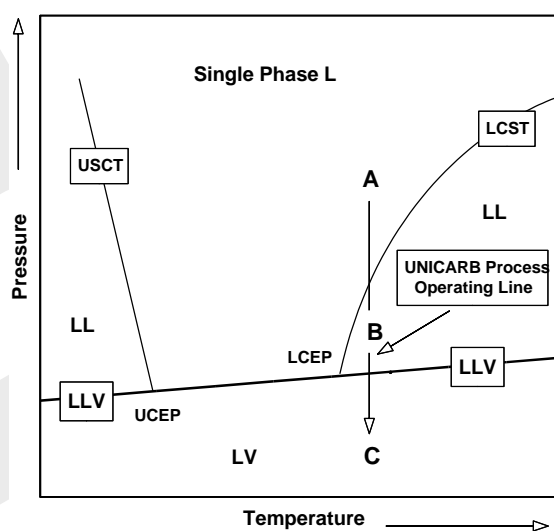


Figure 1: Phase diagram for a mixture of polymer, solvent, and carbon dioxide. The UNICARB[®] operating line is labelled.

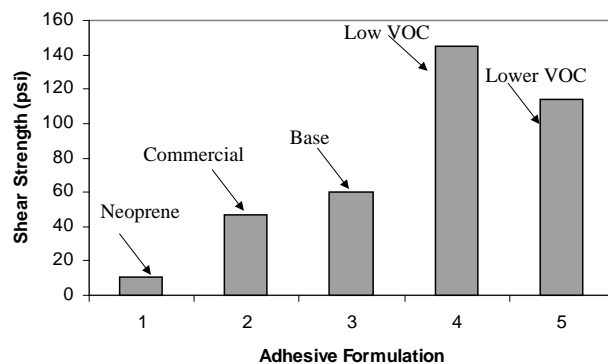


Figure 2: Data on material properties of reformulated adhesives from lap shear testing.

neoprene in toluene, the second is a commercial neoprene based contact adhesive, the third is the same commercial product without hexane, and the last two are low VOC neoprene based formulations developed in this study. The last adhesive has a 20% lower toluene content than the low VOC formulation, and both low VOC formulations contain no hexane.

Future work will include new formulations focussing on long term performance and additional applications for the adhesives currently being studied. Additional work is planned for the investigation of structural adhesive applications and opportunities for zero VOC emissions.

¹National Research Council, Division of Medical Sciences, Assembly of Life Sciences. In *Vapor-Phase Organic Pollutants*; National Academy of Sciences: Washington, D.C., 1976, pp 236-270.

²Nielsen, K. A.; Busby, D. C.; Glancy, C. W.; Hoy, K. L.; Kuo, A. C.; Lee, C. Supercritical Fluid Spray Application Technology: A Pollution Prevention Technology for the Future. In *Proceedings of the Seventeenth Water-Borne and Higher-Solids Coatings Symposium*; Storey, R. F.; Thames, S. F., Eds.; University of Southern Mississippi: Hattiesburg, MS, 1990; pp 218-239.

³McHugh, M. A.; Guckes, T. L. *Macromolecules* **1985**, 18, 674.