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Supercritical Solubility of Binders Used in Explosive Formulations
Final Report

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Abstract

The dissolution of polymers in supercritical carbon dioxide was measured using in-situ ultraviolet absorbance. This research was carried out to provide data to support the development of a new process to produce plastic-bonded explosive molding powder. Estane 5703, the polymer used to bind PBX 9501, was insoluble at the tested conditions.

The dissolution of Kraton FG 1901 was tested at 27 to 100 °C and 29 to 65 MPa. Only a small fraction of this polymer dissolved, and the quantity that dissolved increased with the polymer sample size. The tested polymer was polydisperse, and it is thought that the lowest molecular weight fraction of the polymer preferentially dissolved. Based on this observation, dissolution of the polymer prior to molding powder synthesis is recommended to obtain a uniform molding powder product.

The dissolution of nearly monodisperse samples of polyethylacrylate were tested at 27 to 90 °C and 10 to 65 MPa. The resulting solutions were very dilute, on the order of 100 mg/liter, and the solutions did not reach saturation during the 90 hour test period. The slow approach to saturation indicates that mass transfer rates may significantly affect process performance.

Background

Plastic-bonded explosives (PBX's) are components of DOE weapons systems. A PBX consists of a granular explosive that is bonded with a polymer. Molding powder (actually a granular material), containing both the explosive and the binder, is pressed in a mold to make a solid block of PBX.

Molding powders are typically made using the slurry process^{1,2}. The explosive powder is slurried in water, and a lacquer consisting of the binder dissolved in an organic solvent, such as methyl ethyl ketone, is added to the slurry. A combination of heat, air sweep, and a slight vacuum is used to remove most of the solvent. The binder coats the particles, which agglomerates. The slurry is filtered, and the solids are dried to form molding powder.

About a gallon of waste water, contaminated with solvent and explosives, is produced for every pound of molding powder. This research grew from a desire to eliminate the wastewater produced during molding powder production, and to also avoid the safety hazards associated with flammable, and often toxic, organic solvents.

Many studies have shown that conventional solvents can sometimes be replaced with supercritical fluids, especially supercritical carbon dioxide. McHugh and co-workers undertook numerous studies of polymer dissolution in supercritical carbon dioxide. In one of these studies³, they showed that Flourel, a commercial fluoropolymer and a potential binder polymer, is soluble in carbon dioxide, especially when acetone is used as a co-solvent.

Los Alamos Collaboration and Concurrent Work

Robert Bishop, at Los Alamos National Laboratory, investigated process concepts that could be used to coat HMX, an explosive, with a binder dissolved in supercritical carbon dioxide⁴. His most successful configuration included a high pressure tank that

contained the binder polymer. High pressure carbon dioxide flowed through the tank, and the resulting solution was sprayed into a bed of HMX particles. The particle bed was at atmospheric pressure. Bishop tested a few polymers, and found that Flourel was the most soluble of the polymers that he tested.

The University of Wyoming work was intended to provide process data that could be used to support the development of a supercritical fluid-based molding powder process. Unfortunately, the work at Los Alamos ended shortly after Bishop successfully demonstrated his process concept. Almost no process optimization was attempted, and the experimental molding powders were never pressed and tested to determine their properties. The University of Wyoming research will be valuable if process development resumes.

Experimental Approach

Two experimental techniques are commonly used for measuring solubility in supercritical fluids. The first technique, which was proposed for this research, is an extractive technique. Supercritical carbon flows through a bed of the solute. The resulting solution is depressurized, causing the solute to precipitate. This precipitate is weighed to determine the quantity that dissolved at high pressure.

Discussions with Bishop at Los Alamos showed that it would be difficult to obtain highly accurate data for these polymers using this approach. In Bishop's system, the spray nozzle frequently clogged and much of the sprayed polymer was lost because of entrainment by the carbon dioxide leaving the bed of explosives. The other common approach, cloud point measurement, was well-established, but the cost of the equipment was too much for the limited budget of this research project. Consequently, a new approach was taken. Figure 1 is a conceptual drawing of the test cell. The polymer sample is sealed in the small, high pressure vessel. The vessel is then mounted in an oven and heated to the experimental temperature. The vessel is then pressurized with carbon dioxide to the experimental pressure.

Dissolution of the polymer, during the course of the experiment, is measured using a fiber optic UV spectrophotometer. The polymer dissolves in the supercritical carbon dioxide, and diffuses through the stagnant fluid to the space between the measurement windows. The chief advantage of this technique is that measures both solubility of the polymer (based on steady state absorbance values), and diffusion coefficients (from the absorbance versus time data). This is also a relatively simple experiment. There are very few moving parts, which minimizes the potential for mechanical failure.

This experimental technique is limited to polymers with ultraviolet chromophores, and transparent solvents. This eliminated some of the potentially interesting polymer/solvent systems, such as Fluorel/carbon dioxide.

Many of the experiments lasted 90 hours. Maintaining tight seals, to avoid significant pressure loss, was a continuing challenge. Many of the experiments were repeated because of pressure loss. The o-rings that were used to seal the vessel windows tended to shift when the vessel was pressurized, and this affected the calibration of the spectrophotometer. This effect was partially offset by taking a reference spectrum just after the vessel was pressurized.

Figure 1. Conceptual drawing of high pressure vessel used in this research.

In latter experiments, run by graduate student Julie Wallace^{5,6}, a sample cup was added to the vessel. The sample cup had a porous lid that permitted polymer to diffuse out of the cup, but largely prevented precipitation of polymer back into the cup when the pressure was released. The weight change of the cup, before and after the experiment, provided an additional measure of polymer solubility.

Selection of Solvent and Polymers

Organic solvents were not considered because of safety concerns. These solvents could have been safely handled in this research, but a combination of explosives and flammable gasses is unacceptably dangerous. Some non-flammable solvents, such as Freons, were not considered because of their environmental impact, while others, such as xenon, were not considered because of cost. This limited the choice of solvent to carbon dioxide and carbon dioxide/water mixtures.

Graduate student Joseph Kolnik carried out a series of preliminary experiments⁷ with polymers that are used, or could be used, in PBX formulations. He found that carbon dioxide swelled Estane 5703, the polymer used in PBX 9501, but that the polymer was essentially insoluble in carbon dioxide. This confirmed Bishop's results with the same polymer. Kel-F 800, the polymer used in PBX 9502, was not an ultraviolet absorber, so it was not an appropriate choice for the experimental technique used in this research. Preliminary experiments were also carried out with Kraton 1650, Kraton FG 1901, and polyethylacrylate. Kraton FG 1901 had the greatest solubility, so this polymer

was chosen for further study by Kolnik. For reasons that are discussed later, Wallace investigated the solubility of polyethyl acrylate.

Kraton FG Studies

Kolnik measured the solubility of Kraton FG in carbon dioxide at 27, 50, 90, and 100 °C, and at 29, 35, 42, 56, and 65 MPa (a total of 25 combinations of temperature and pressure). The highest apparent solubility, 830 mg/liter, occurred at 90 °C and 65 MPa. The apparent solubility, however, varied with the amount of polymer loaded into the sample cell. As shown in Figure 2, only a small fraction of the polymer dissolved, and, except for one data point, the quantity of dissolved polymer increased with an increase in polymer loaded into the sample cell. The solubility of a pure, solid sample should not be a function of the quantity of solid present, so this data suggests that the dissolved material consists a relatively high solubility component in an impure sample. Most polymers are polydisperse, meaning that the polymer contains a wide range of polymer molecular weights. A possible explanation for the data shown in Figure 2 is that only the lowest molecular weight polymers dissolved.

Because of this finding, the Kraton FG data is only qualitatively correct, at best. Consequently, this data was not submitted for publication. A practical result of this work is that it shows that a process based on continuous polymer dissolution, such as the process tested by Bishop, may yield an inconsistent product. Early in the dissolution process, the solution would contain a relatively high concentration of low molecular weight polymer. Later in the process, the solution would contain a lower concentration of higher molecular weight polymer. To obtain greater molding powder consistency, the polymer solution should be formed before the coating process begins.

Figure 2. Measured solution absorbance at 70 °C and 45 MPa as a function of the quantity of Kraton FG polymer loaded into the sample cell. The percentage numbers attached to each data point indicate the percentage of the polymer sample that dissolved.

Polyethylacrylate Studies

The results shown in Figure 2 prompted us to confine our studies to polymer samples that are nearly monodisperse (the sample contains a very narrow range of polymer molecular weights). We lack the ability to prepare these samples, and the availability of commercially available samples is limited, so this led to the selection of polyethylacrylate for further studies. Table 1 shows the properties of the polyethylacrylate samples that were used. A perfectly monodisperse sample would have a polydispersity index equal to one. As previously described, a sample cup was added so that absorbance data could be compared to sample cup weight loss data.

Table 1: Properties of tested polyethylacrylate samples.

<u>Sample</u>	<u>Molecular Weight</u>	<u>Polydispersity Index</u>
1	5,500	1.06
2	23,500	1.07

Figure 3 shows absorbtivity versus time data for sample 1. The concentrations shown in the legend are from the sample cup weight loss data. Both of these experiments show that the solubility of polyethylacrylate in carbon dioxide is very low at the tested conditions. A very large quantity of supercritical carbon dioxide would be required in a molding powder process that uses these solutions. Higher concentrations are possible at

Figure 3. Absorbance versus time data for polyethylacrylate sample 1 dissolved in carbon dioxide (0.8 g/cm^3 density). The concentration data shown in the legend are based on the sample cup weight loss data.

higher solvent pressures. The solution was not saturated after 90 hours, which shows that mass transfer rates may have a significant impact on the process. A few experiments were run for longer times, but it was difficult to maintain a tight seal on the sample cell for longer periods of time.

Wallace mapped the solubility of sample 1 between 40 °C and 90 °C, and between 10 MPa and 65 MPa. At 90 °C and 65 MPa, the seals consistently leaked, so no data was collected at this condition. At the lower temperatures and pressures, the solubility was close to the experimental error, but reproducible data were obtained at higher pressures and temperatures. She also tested the solubility of sample 2 with a subset of experimental conditions.

Conclusions

The dissolution of polymers in supercritical carbon dioxide was measured, using in-situ ultraviolet spectroscopy. These experiments were carried out to provide data for a new process for the production of plastic bonded explosive molding powder. Estane 5703, the polymer used in PBX 9501, was insoluble at the tested conditions. Only a small fraction of the Kraton FG 1901 samples dissolved, and the quantity that dissolved increased with increased sample loading. This result may be due to the relatively high solubility of the lower molecular weight polymer fraction.

Experiments with nearly monodisperse polyethylacrylate showed that this material has low solubility at the tested conditions. The solutions were not saturated after 90 hours, which suggests that mass transfer rates may affect the molding powder process.

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