

Supercritical Washing of Polymers within a Twin Screw Extruder

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Abstract

For some applications, resin purity is critical because contaminants such as residual solvent, monomer, and dimer strongly affect product quality. Volatile contaminants can be removed by devolatilization under vacuum, which can be enhanced through stripping with a medium such as water or alcohol. Some contaminants, however, are difficult to remove by vaporization because they have low vapor pressures or interact strongly with the polymer. For components with low vapor pressures, liquid extraction is a viable alternative to stripping. The drawbacks of injecting conventional solvents like water or alcohol include the addition of a new component which must be volatilized and complications from handling flammable materials. Washing with supercritical fluids can address both of these problems for systems designed to accommodate polymer/SCF separations. SCF extraction has been demonstrated for polypropylene and shows good potential for a number of other applications.

Introduction

The development and optimization of reliable, efficient separation technologies are critical to the production of highly pure polymers. A number of unit operations have been designed to accomplish these separations, and a number of techniques for improving separation performance have been developed as well. Co- and counter-rotating twin screw extruders have been employed for decades as reliable equipment for devolatilizing polymers [1-3].

Direct devolatilization is a staged operation that relies on multiple approaches toward phase equilibrium to achieve a desired product purity [1-3]. These approaches are limited by contaminant volatility, surface area, and diffusion. Volatile vapor pressure, P_1 , follows from the Flory-Huggins model, which predicts the relationship in Equation 1 for low concentrations:

$$P_1 = P_1^0 \varphi_1 e^{1+\chi} \quad (1)$$

where P_1 is the partial pressure of a volatile contaminant; P_1^0 is the ideal vapor pressure of the contaminant; φ_1 is the volume fraction of the contaminant in the polymer matrix; and χ is a dimensionless interaction parameter that accounts for interactions between the contaminant and polymer [2, 3].

When the partial pressure of a contaminant reaches or exceeds the total venting pressure, volatiles will foam even at very low concentrations. This phenomenon is strong contributing factor for efficient devolatilization because is very rapid compared to simple diffusion [2-5].

Typically achieving residual volatile levels below 500 ppm requires either very strong vacuum, very low throughput rates, or both. Carrier substances such as stripping agents can improve devolatilization by (1) reducing the partial pressure, P_1 , over the polymer, thereby shifting the equilibrium concentration of contaminant towards zero; and (2) acting as nucleation aids, enhancing the formation of bubbles which contributes to foam formation and increased surface area for mass transfer [3].

Despite its widespread use, devolatilization with and without the benefit of inert stripping aids is limited by its reliance on volatility for separation. Some contaminants such as monomer, short chain oligomers, and high-boiling solvent can be difficult to remove by boiling alone due to their low vapor pressures and strong polymer interactions, χ . Extraction into a condensed phase offers a solution to this challenging separation.

Extraction with liquids such as water, alcohols, and organic solvents can be incomplete and can complicate separation. Water extraction is inefficient for non-polar contaminants due to their low solubility. Extraction with organic solvents is often effective, but further devolatilization steps are required following the extraction stage in order to remove residual extraction solvent. Supercritical fluids (SCF) offer a solution to all of the problems

An SCF is chosen for suitable compatibility with the polymer and good contaminant solubility. The SCF is highly volatile at low pressures, so it does not require extensive downstream separation. The high vapor pressure of the SCF also contributes to foam formation during the rapid decompression following extraction. SCF extraction can also accelerate the migration of contaminants through diffusion out of the polymer matrix by swelling the polymer [6]. Supercritical carbon dioxide has a solubility in PP around 8 wt% under the conditions studied, which can swell the polymer as much as 20% [6, 7].

Supercritical fluid stripping, which has been studied extensively, still relies on contaminant volatility as the ultimate driving force for separation. The technology described in this article seeks to overcome the limited

volatility of certain contaminated species by washing a polymer stream within a TSE and mechanically separating the SCF-rich phase from the polymer-rich phase above the critical temperature and pressure of the wash medium.

The objective of following studies was to identify whether SCF washing could improve the reduction of the outgassing organics contaminating a commercial grade of polypropylene (PP) versus a more traditional inert stripping process.

Experimental

Equipment and Materials

Experiments were conducted in two phases on a 48:1 L/D NFM Welding Engineers TEM-26SS co-rotating twin screw extruder (TSE). The extruder comprised 12 barrel segments, 4 L/D each, outfitted with cast aluminum heaters and cored for water cooling. Both phases of experiments used a K-Tron loss-in-weight feeder positioned over a feed hopper in barrel 1 of the 26mm TSE. A countercurrent flush of nitrogen was injected in the second barrel of the extruder 6D from the feed location to purge oxygen from the system. Strands were extruded through a water bath into a Rieter Primo 100 pelletizer.

Nitrogen and carbon dioxide were supplied by Matheson Tri-Gas in liquid Dewars. These gases were pressurized by a Haskel AGD-14 gas booster, measured by a Micro Motion Coriolis mass flow meter, and regulated using a manual micrometer needle valve. LC/MS grade methanol was purchased from Fisher Scientific (A456-4). Deionized water was produced on-site through a 4-tank ion exchange resin system provided by Culligan. An Eldex piston pump, capable of 10 mL/min at 5000 psi, was used to volumetrically meter methanol and water during Phase 1. A commercially available grade of polypropylene (MFR 28 g/10 min @ 230°C) with low residual outgassing organics (100-150 ppm) was used throughout the study.

In the first phase of experiments, a traditional co-current stripping process was evaluated using nitrogen, carbon dioxide, methanol, and deionized water as stripping media. In the second phase of experiments, supercritical carbon dioxide and nitrogen were compared in a novel co-current SCF washing/stripping process.

Phase 1 (Stripping)

In Phase 1, stripping agent was injected at 1% or 3% of the polymer feed rate 12 D from the feed location. Nitrogen and carbon dioxide were metered through a Micro Motion mass flow meter, and methanol and water were metered through a calibrated Eldex positive displacement pump. At the injection location, the screw was designed to provide gentle mixing to incorporate the stripping agent

into the melt. Four vacuum vents were positioned 8 D apart downstream of the injection point with polymer seals separating them. See Figure 1. The vent pressures were maintained between 3 and 6 torr (absolute).

Phase 2 (SCF Washing)

In Phase 2, SCF was injected at 12 D from the feed location, and SCF effluent was removed under 1200 psig back pressure 12 D downstream of the injection point through an NFM Welding Engineers 0.8" mechanical filter. The mechanical filter is a vertically mounted counter-rotating twin screw extruder designed with tight clearances in order to allow low viscosity materials such as liquids and vapors to be removed from the extruder by pressure flow while retaining solids and high-viscosity polymer melts.

The screw configuration in this set of experiments was designed to provide a melt seal before and after the SCF extraction section. Three kneading sections provided mixing between the SCF injection location and the mechanical filter. A strong melt seal was created under barrel segment 9 using highly restrictive screw elements in order to maintain critical pressure within the extraction zone. One vacuum vent was positioned downstream of the SCF washing section in barrel 11. See Figure 1.

SCF was dosed into the extruder at two different levels, low and high: 32 wt% and 41 wt% for nitrogen and 32 wt% and 48 wt% for carbon dioxide. The high dosing levels were set by the pumping capacity of the Haskel gas booster.

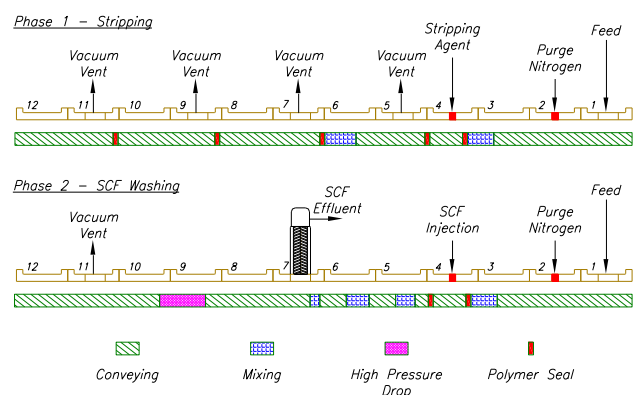


Figure 1. Extruder configurations for experimental phases 1 and 2.

Analysis

PP sample outgassing organic concentration was measured by thermal desorption coupled gas chromatography mass spectroscopy (TD-GC-MS) by a collaborator outside NFM. Outgassing organic values were normalized for pellet surface area, a technique confirmed by the analysis of cryogenically pulverized samples.

Results

Phase 1 (Stripping)

Vacuum devolatilization was evaluated in concert with two gas and two liquid stripping aids: nitrogen, carbon dioxide, methanol, and water. Vacuum devolatilization alone using four vents without any stripping aids achieved an outgassing organic contaminant reduction of 38%. Compared to vacuum alone, nitrogen, carbon dioxide, and water stripping did not improve organic contaminant removal, while stripping with methanol potentially demonstrated some slight improvement. See Figure 2.

Increasing the stripping ratio from 1% to 3% adversely impacted outgassing reduction with nitrogen and showed no effect with carbon dioxide. The behavior was reversed for methanol and water; increasing the dosing level from 1% to 3% improved the outgassing reduction for both.

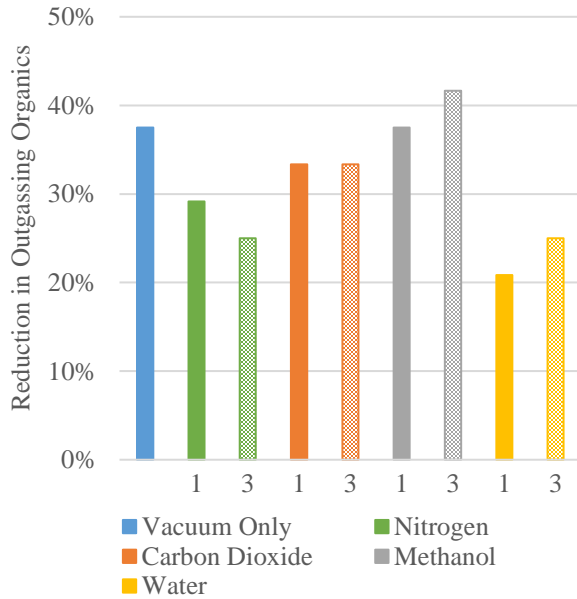


Figure 2. Reduction in outgassing organics by vacuum devolatilization and by stripping with nitrogen, carbon dioxide, methanol, and water. Stripping agents were evaluated at 1% and 3% of the polymer throughput rate.

Phase 2 (SCF Washing)

Supercritical carbon dioxide and nitrogen each significantly reduced the levels of outgassing organics. Nitrogen was more effective than carbon dioxide, reducing the outgassing organic levels by 65% vs 57%. Increasing the SCF ratio from 32 wt% to 41/48 wt% did not significantly improve washing performance for either nitrogen or carbon dioxide SCF. See Figure 3.

Washing with both supercritical carbon dioxide and nitrogen demonstrated significant gains over simple vacuum devolatilization, which reduced outgassing organics by 38%. See Figure 4.

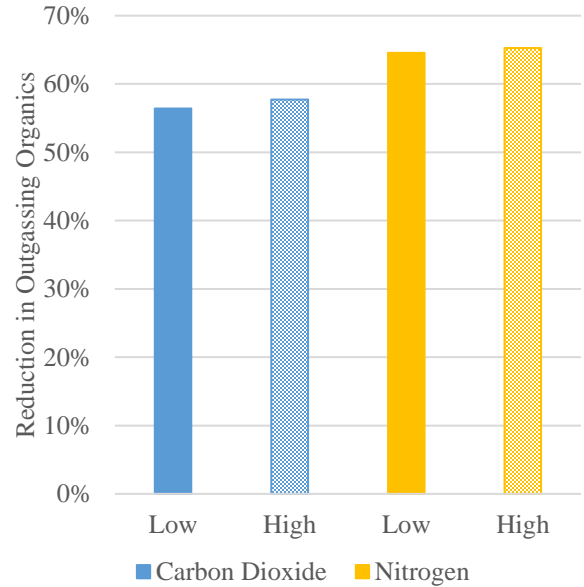


Figure 3. Reduction in outgassing organics by SCF washing with carbon dioxide and nitrogen. Both fluids were evaluated at low and high levels.

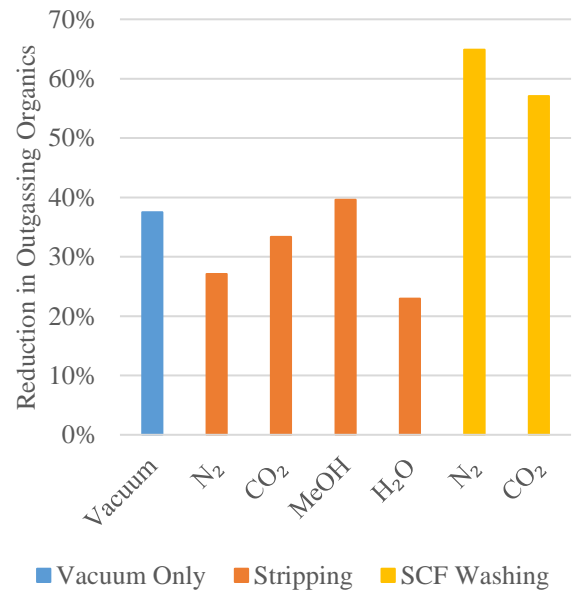


Figure 4. Comparison between outgassing organic reduction using stripping and SCF washing.

Discussion and Conclusions

The polypropylene used in these experiments was selected for its relatively low level of residual organic

volatiles. These organics were known to comprise a range of short chain oligomers, some of which have very low vapor pressures. Around 38% of these outgassing organics could be removed by vacuum devolatilization alone, but the remaining 62% was more difficult.

Conventional stripping was ineffective, if not counterproductive, compared to simple vacuum for all but one of the stripping media studied. Methanol was likely more successfully dissolved into the polymer melt than water, nitrogen, or carbon dioxide under the processing conditions. This would have resulted in enhanced foam formation. Stripping performance with water was the worst of all media evaluated. This could be attributed to the poor compatibility of PP and water, and the high latent heat of water, which will result in melt cooling on boiling.

The modest gains in outgassing organic reduction from 1% to 3% stripping ratio for methanol and water is likely due to proportionally enhanced foaming and/or surface area expansion due to boiling.

Supercritical fluid washing performed very well compared to vacuum alone and traditional stripping. Vacuum devolatilization was able to remove 38% of outgassing organics in four vent stages. These components likely had the highest vapor pressures, leaving behind higher molecular weight oligomers. With only one vacuum stage, SCF extraction was able to improve the reduction of outgassing organics by an additional 30%. Some of this improvement can be attributed to the rapid expansion of dissolved nitrogen/carbon dioxide during decompression out of the extraction zone [6].

From these studies, traditional stripping techniques were not well-suited for improving the devolatilization performance of a twin screw extruder for high-purity PP. SCF extraction, however, enhanced organic contaminant removal by more than 70% versus vacuum alone. This technology shows promise for a number of applications including the removal of monomer, oligomers, and high-boiling solvent, which have been difficult in the past to separate via devolatilization alone.

References

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