MELT GLYCOLYSIS OF POLY(ETHYLENE TEREPHTHALATE) USING CO_2-ASSISTED EXTRUSION

Joan D. Patterson, Saad A. Khan and George W. Roberts
Chemical & Biomolecular Engineering, North Carolina State University, Raleigh, NC USA

Abstract

A single-step, extrusion-based process to depolymerize poly(ethylene terephthalate) (PET) is being investigated. The depolymerization is effected by reacting ethylene glycol (EG) with the high molecular weight polymer (glycolysis). The ethylene glycol causes chain scission by attacking the ester linkages along the polymer backbone. The objective is to recover purified low molecular weight oligomers of bis(hydroxyethyl) terephthalate (BHET) for repolymerization. The process has two novel features: 1) the use of a twin-screw extruder to convey the polymer and to continuously create the fresh surface that is required for the depolymerizing agent to penetrate into the polymer, and 2) the use of supercritical carbon dioxide (scCO$_2$) as a processing aid. Results of glycolysis experiments on a Leistritz 34 mm counter-rotating twin-screw extruder have been characterized by substantially faster depolymerization rates than typical batch glycolysis reactions, shortening reaction times from hours to minutes. Oligomers with number-average degrees of polymerization (DP_n) as low as 13 (M_n = 2,500) can be produced continuously from the starting bottle-grade PET resin (DP_n = 102 and M_n = 20,000) in residence times of just 10 minutes. By changing operating conditions, e.g. feed rate and EG:PET ratio, the DP of the final product can be controlled at essentially atmospheric pressure.

Keywords: depolymerization, glycolysis, PET, reactive extrusion, carbon dioxide

Introduction

The recycling of poly(ethylene terephthalate) (PET) has become increasingly important due to its high level of consumption worldwide, primarily by the packaging industry for use in making beverage containers. However, the majority of recycled PET does not go back into the bottle market. In the United States, for example, just 2.7% of all post-consumer PET bottles that were collected for recycling went back into bottles in 2004.[1] Meanwhile, demand for PET bottles continues to increase as applications broaden from water and soda bottles to beer, milk and other specialty containers. In general, PET that is recycled into beverage containers must be chemically recycled. More specifically, the recycling process must include a step where PET is chemically degraded into its originating monomers or oligomers which are then purified for repolymerization. This research is concerned with the chemical recycling of PET via glycolysis. This process involves a partial to full depolymerization where the polymer is contacted with ethylene glycol (EG), causing chain scission and producing low molecular-weight oligomers of bishydroxyethyl terephthalate (BHET). The majority of glycolysis research and practice has involved batch reactions in solution which suffer from slow reaction rates and the inefficiencies of discontinuous operation.[2]

This work investigates a single-step, extrusion-based depolymerization of PET by glycolysis. The process has two novel features: 1) the use of a twin-screw extruder (TSE) as a depolymerization reactor, and 2) the use of supercritical carbon dioxide (scCO$_2$) as a processing aid. The continuous operation of a TSE provides improved economics. In addition, the extruder itself presents an ideal environment for PET glycolysis as it provides high levels of mixing and a continuously refreshed polymer surface for reaction with EG. Our preliminary results have shown residence times on the order of minutes in an extruder (versus hours for batch).[3] These findings are supported by Colomines *et al.* who used a twin-screw extruder for glycolysis of PET via oligoester diols to study polyurethane formulations.[4] Compared to earlier work studying the batch formation of such glycosylates, Colomines saw batch reaction times of 2 hours drop to extruder residence times of 2-4 minutes. [5]

The TSE has an additional advantage in that it can sustain pressures high enough for injection of scCO$_2$ which can easily be removed from the product and recycled to the process. Supercritical CO$_2$ acts as a plasticizer for the polymer and it has been shown to significantly reduce polymer melt viscosities by an order of magnitude or more with as little as 2-4 wt.% CO$_2$ fed.[6] The presence of scCO$_2$ also increases the diffusivity of EG into the polymer, increasing reaction rates and lowering overall reaction times. This claim has been substantiated by preliminary results which show that doubling the CO$_2$ feed rate to the system results in a doubling of the reaction rate.[3] The CO$_2$ can also remove volatile organics, unreacted EG and some monomer from the system, helping to purify the reaction products. Work done by Praxair using our twin-screw extrusion system has demonstrated the ability of scCO$_2$ to remove lindane and toluene from PET in amounts greater than 95%. [7]

Experimental

Materials
Bottle-grade (CB12) virgin PET resin used in this study was donated by Voridian (Weight-average molecular weight, M_w = 55,000, PDI = 2.8). Ethylene glycol (purity > 99%) from Acros Organics was used as received.

Sample Analysis
Oligomeric products were collected at the extruder outlet and analyzed by intrinsic viscosity (IV) measurement with a Rheotek RPV-1 Polymer Viscometer. The measurements were done at 25°C in a 60:40 (vol.) mixture of phenol/tetrachloroethane (Harrell Industries). Values of the number-average molecular weight, M_n, were calculated from the measured IV using a correlation from the literature.[8]

Twin-Screw Extrusion System
A schematic of the extrusion system configuration can be seen in Figure 1. The main component in this system is a Leistritz 30/34mm counter-rotating twin-screw extruder (TSE). Feeding to the TSE is a Randcastle vertical 1" single-screw Microtruder, in series. Barrel sections 2 and 3 of the TSE are configured with ports for the injection of CO$_2$ and EG, respectively. These are fed to the system using Isco 260-D continuous flow syringe pumps. In the experiments discussed here, EG was fed in varying weight ratios to the PET feed rate at atmospheric pressure, without the presence of CO$_2$. The TSE speed was kept constant at 150

rpm while the single-screw speed, or feed rate, was varied. The barrel temperature of the TSE was held at 260°C for all runs.
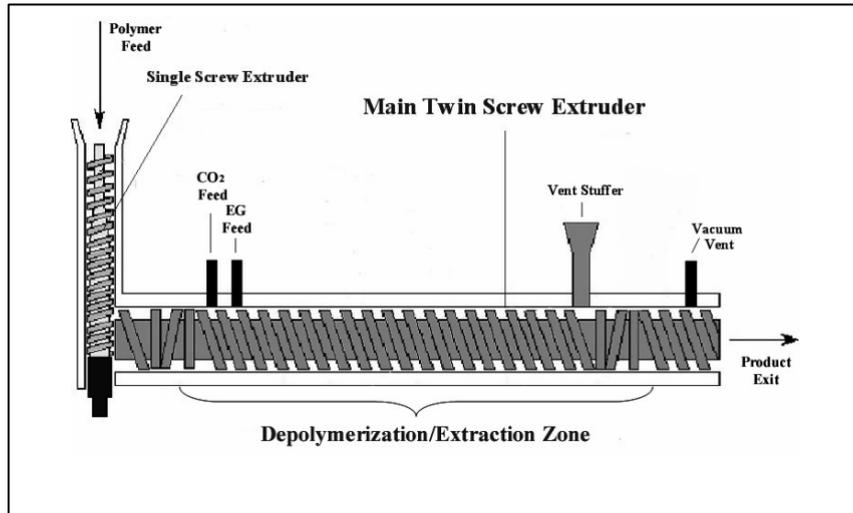
**Figure 1**. Schematic of the twin-screw extrusion system at NCSU.

Results and Discussion

The twin-screw extrusion system is a very effective means of depolymerizing PET via glycolysis. Figure 2 shows the change in the intrinsic viscosity of the glycolyzed PET over time, running at a fixed EG:PET (w/w) feed ratio. Compared to the IV of the virgin PET resin, shown by the dashed line (IV=0.83), the IV of the products at both of the feed ratios shown decreased by more than 75%. The plot also shows the behavior of the glycolysis reaction over time at fixed operating conditions. The extruder reached steady-state within 10 minutes (about one residence time) and was able to produce a uniform product over time. Increasing the feed ratio of EG:PET (w/w) increased the extent of depolymerization.
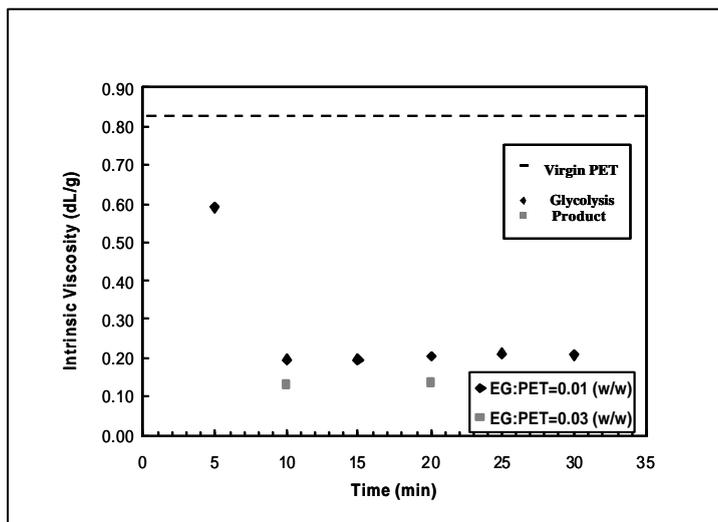
Figure 2.Continuous glycolysis results, 260 °C, 1 atm.

Figure 3 shows the influence of EG:PET (w/w) feed ratio and PET feed rate. Again, increasing the EG:PET ratio leads to an increase in the extent of glycolysis. Increasing the feed rate, or shortening the residence time, has the effect of decreasing the extent of depolymerization, as expected. At the highest EG:PET ratio and longest reaction time, the product obtained has an IV of 0.11, corresponding to a decrease in molecular weight (M_n) from 20,000 to 2,500 and a decrease in the degree of polymerization (DP_n) from 102 to just 13. If we assume that the equilibrium constant for this reaction is on the order of 1, common for such polycondensation reactions, we see that at the longest residence time (feed rate = 55 g/min), the final DP_n of the product comes very close to the predicted DP_n that would be reached at equilibrium for all EG:PET feed ratios. As we decrease the amount of time available for reaction, we move further away from the equilibrium DP_n. This suggests that in order to operate at higher feed rates and still achieve low DP products, there is a need to increase the reaction rate.
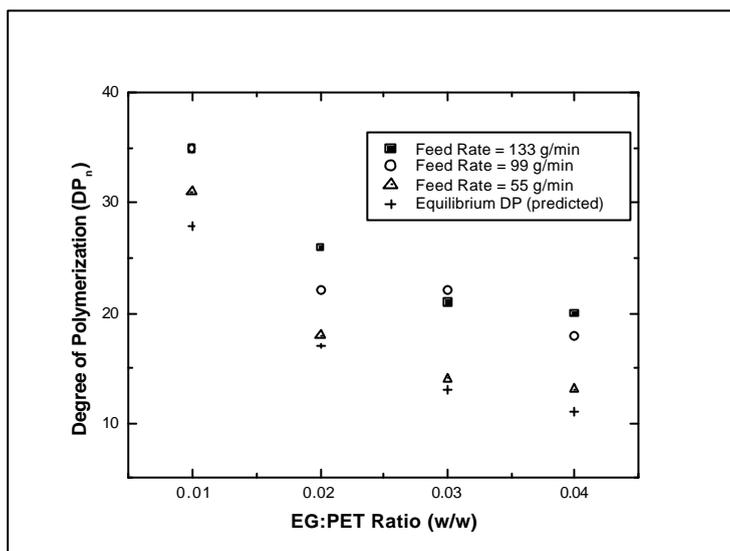
Figure 3.Varying feed rate and EG:PET ratio, 260°C, 1 atm.

Conclusions

We present a novel process for the depolymerization of PET in $scCO_2$. Results clearly show that using an extruder as a reactor for the glycolysis of PET is a highly effective means of depolymerizing the polymer. In a residence time of just 10 minutes, we are able to reduce the IV more than 85%, from 0.83 to 0.11, with a final DP_n of 13. Without pressurizing the extruder, we see that increasing the residence time (by decreasing the feed rate of PET) or increasing the EG:PET ratio leads to an increase in conversion. Using supercritical CO_2 in the system should increase the reaction rates, allowing for the production of equally low molecular weight oligomers at higher throughputs.

This research could play a large role in reducing the millions of pounds of waste PET that are generated annually, resulting in a significant environmental and economic impact. Furthermore, this approach should be applicable to any step-growth polymer, including nylons and polycarbonates.

Acknowledgements

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