Micronization of PET via Freezing of Highly Sheared Emulsions of PET in Saturated Liquid THF

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ABSTRACT

A novel technique for micronizing PET with compressed THF has been developed. PET pellets were introduced to a high pressure vessel along with THF. The vessel was filled halfway with THF along with PET pellets at a loading of up to 8.0 gr PET/100 ml THF. When the vessel was closed and heated to 190 ^oC, the PET melted and was dispersed by intense stirring. No surfactant was required to disperse the PET, and no other organic solvent was identified that was capable of causing this dispersion to form. After mixing the system at 200 ^oC for five minutes, the emulsion was rapidly cooled during agitation, which caused the dispersed droplets to freeze. After cooling to ambient temperature, the THF was easily removed from the particles via decanting and drying; no residual THF remained in the PET. The particle sizes ranged from 2-70 microns. Unlike other SCF-based micronization methods, this method can generate micronized PET at modest pressures (THF vapor pressure at 200 ^oC is ~300 psia), does not require the rapid expansion of supercritical fluids through nozzles, and can be conducted at high loadings of PET in THF.

INTRODUCTION

Commercially, polyethylene terephthalate (PET) is available in the form of resin pellets because it is synthesized by high temperature, vacuum condensation polymerization, Figure 1. Unlike PVC, which can be made by emulsion polymerization, it is not practical to produce micron-sized PET resins.

There are several techniques for preparing small samples of PET particles in the sub-millimeter range. Post-consumer amorphous PET chopped flake was heated in an oven at 250 ^oC for 10 minutes and then cooled to ambient temperature to complete crystallization. The resultant brittle, white flakes were then ground, yielding particles sizes ranging between 2-200 microns [1].

In two US Patents [2,3], Naumann and Lynch concluded that one could dissolve the PET in saturated liquid THF at 190 ^oC because when the solution was flashed to low pressure, PET particles (of unspecified size) were formed. This study was performed in closed high pressure windowless vessels, however.

It is well known that many high boiling point solvents, such as dimethyl sulfoxide, ethylene carbonate, propylene carbonate, and dimethyl phthalate, can dissolve PET at temperatures below the melting point of PET. If these liquid PET-solvent solutions are thermally quenched by cooling, addition of cold solvent, or the addition of an anti-solvent, PET particles will form. The particles will retain a substantial amount of the high boiling point solvent, even after washing with a volatile solvent.

PET powder can also be generated by immersing the PET in liquid nitrogen to enhance its brittleness, followed immediately by crushing. Although suitable for small-scale experiments, this process would be challenging to develop on an industrial scale.

The objective of this work is to produce micron-scale PET powder from PET pellets in a process that could be easily scaled up. Further, it was desired to avoid extremely high operating pressures (>1000 psia) and the rapid expansion of solvents.

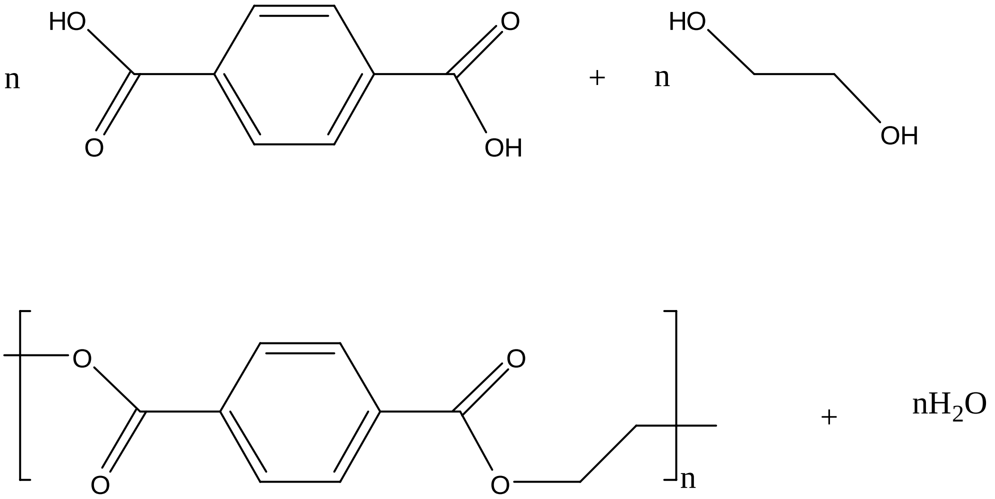

Figure 1: Condensation polymerization of PET

MATERIALS

PET particles (21990 Mn and 32715 Mw, Tmelt ~ 250 ^{o}C) were obtained from Eastman. Tetrahydrofuran (99+%, b.p. 66 ^{o}C), which contained small amounts of water and BHT, was used as received from SigmaAldrich. Other solvents of at least 99% purity included methanol, ethanol, ethyl acetate, acetone and toluene, all obtained from SigmaAldrich.

APPARATUS

A 50 ml high pressure microreactor (Autoclave Engineers) with an ID of 0.97” fitted with an external electric heating jacket and an inner coil for water cooling was used for most particle generation experiments. The impeller was capable of spinning at up to 5000 rpm, and a 0.82” diameter radial flow impeller with 6 square blades was positioned 1/3 of the way from the bottom of the reactor. The maximum tip speed of the impeller was 215”/sec, and the maximum shear rate in the 0.075” gap between the impeller tip and reactor wall was 2870/sec.

A 2-liter windowed, heated, agitated vessel with an internal cooling coil, in the laboratory of Dr. Badie Morsi of the University of Pittsburgh, was also available. Although not capable of generating the tip speed or shear rate in the microreactor, this windowed vessel allowed us to visually verify whether the PET was unaffected, molten, dispersed or dissolved in saturated liquid THF at elevated temperature (up to 225 ^{o}C).

A high pressure, high temperature, windowed phase behaviour apparatus was also employed at Clemson University. This apparatus was used to determine the cloud point pressure of 5wt% PET in compressed liquid THF.

THF-PET PHASE BEHAVIOR

Our initial task was to verify if PET could be readily dissolved in compressed liquid solvents with relatively low normal boiling points. We combined PET pellets with organic solvents such as methanol, ethanol, ethyl acetate, acetone, toluene and THF. PET was not soluble in any of these saturated liquid solvents at ~200 ^{o}C, including THF. This was further verified by determining the cloud point pressure of 5wt% PET-95%THF solutions, Figure 2. These pressure values greatly exceed the vapor pressure of THF (Tc = 267 ^{o}C, Pc = 51.3 bar). These results clearly indicate that compressed liquid THF can dissolve PET. Although saturated liquid THF can lower the melting point of PET from 250 oC to ~190 ^{o}C, saturated liquid THF cannot dissolve PET..

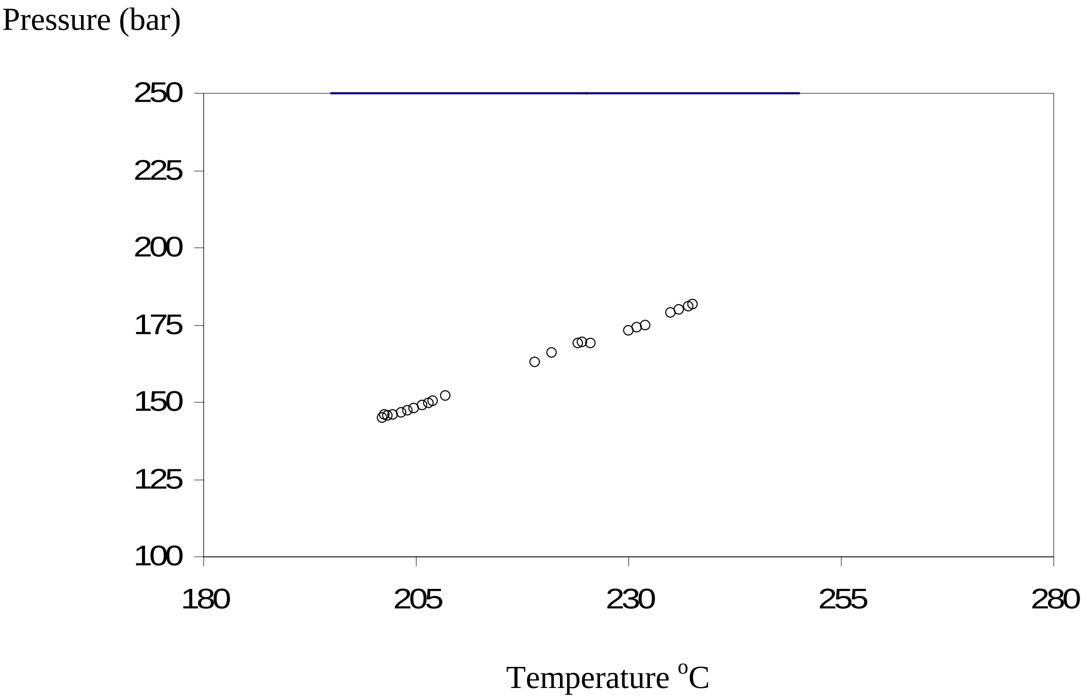

Figure 2. Cloud point pressure of 5wt% PET in THF between 240-240 ^{o}C; a single phase exists above the curve; a PET-rich liquid phase formed as pressure was reduced to the pressure indicated by the data. Data provided by Dr. Mark Thies of Clemson University.

FREEZING OF EMULSIONS OF PET IN SATURATED LIQUID THF

It was desired to develop a process that would operate at much lower pressures than those illustrated in Figure 2, therefore the phase behavior of PET in THF was re-examined in the windowed vessel at the University of Pittsburgh. Three-phase LLV equilibria (polymer-rich liquid, THF-rich liquid, THF-rich vapor) was observed for several organic solvents at pressures quite close to the vapor pressure of the solvent. Only in the case of THF, however, did the molten PET-rich liquid readily disperse with mixing; all others solvents yielded a high-viscosity PET-rich liquid that clung to the sides and bottom of the windowed vessel. The dispersion had the appearance of an emulsion of small droplets of PET in THF, even though no surfactant had been introduced to the system. We have not measured the interfacial tension between these phases to determine if the THF caused a significant reduction in the IFT between the two liquid phases. Although we did determine that the molecular weight of the PET was reduced due to processing in PET, there was no indication that a surfactant-like compound had formed.

It appears that although the prior reports of Naumann were incorrect regarding the dissolution of PET in saturated liquid THF. His flash devolatilization technique nonetheless generated PET particles because he apparently flashed this dispersion of PET droplets in THF, thereby forming particles.

EXPERIMENTAL PROCEDURE

We did not want to flash the THF to form particles, however, because this would have necessitated the incorporation a THF vapor condensation and recovery system. Therefore we filled the vessel half-way with liquid THF and PET particles and flushed the vapor space with nitrogen. Due to the expansion of the liquid THF phase in a closed vessel, the liquid level of THF rises from 50% to 80% as the reactor temperature rises to 225 ^{o}C. It was deemed undesirable for the saturated liquid THF to fill the vessel because further heating of the compressed liquid THF could lead to substantial pressure increases. We then heated the system. The PET melted at 190 ^{o}C and was easily dispersed in saturated liquid THF at ~200 ^{o}C and ~300 psia. The emulsion was then agitated at 5000 rpm with the close-clearance, high speed radial impeller for 5-10 minutes. While the impeller was still stirring, the heater was turned off and cooling water was displaced through the cooling coil with the microreactor. The dispersed PET droplets froze at ~190 ^{o}C, and the system was further cooled and agitated until the temperature was ~150 ^{o}C. The system was then cooled to ambient temperature at a low impeller speed of ~1000 rpm. The mixture of liquid THF and micronized PET particles was then drained from the microreactor.

If dry PET was desired, the PET particles were permitted to settle overnight, and the excess THF was decanted. The wet PET particles were then placed in a vacuum oven overnight, yielding dry PET particles. About 90-95% of the PET was recovered in each run, with most of the loss of PET attributable to particles solidifying on the walls of the microreactor vessel and impeller. These dry particles agglomerated, however, and were difficult to suspend in a non-volatile liquid. If it was desired to suspend the PET particles in a non-volatile solvent (rather than THF), the liquid (e.g. DMSO) was added to the THF-PET particle mixture, and the mixture was heated at ~65 ^{o}C for several hours to drive off the THF. This yielded a suspension of fine PET particles in the liquid DMSO.

RESULTS

Micronized PET was successfully obtained for loadings as high as 8gr PET/100 ml THF. This degree of loading is much greater than that associated with rapid expansion processes that yield particles. Higher loadings in this process led some of the molten PET forming puddles at the bottom of the vessel that could not be dispersed. At the end of the experiment, a substantial portion of the PET was found in this large piece of PET at the bottom of the vessel.

Best results were obtained with the greatest stirring (5000 rpm) and the smallest gap between the impeller and the reactor wall. For example, replacing the 0.82” diameter impeller with a 0.74” diameter impeller and/or conducting the experiment at markedly lower rpm (e.g. 2500 rpm) led to larger particle sizes.

Although the bulk of the PET particles were formed by the freezing of the emulsified PET droplets, a small amount of the PET particles were formed by the traces of dissolved PET coming out of solution. This was qualitatively noted by the THF-rich liquid phase of the emulsion becoming slightly cloudy as the vessel was cooled.

The PET particles sizes ranged from 2 – 70 microns, as illustrated in the number distribution shown below in Figure 3. This data was obtained with a Hockmeyer Particle Analysis System (HPAS-2000) with with MicroPart (rel 2.0) Software.

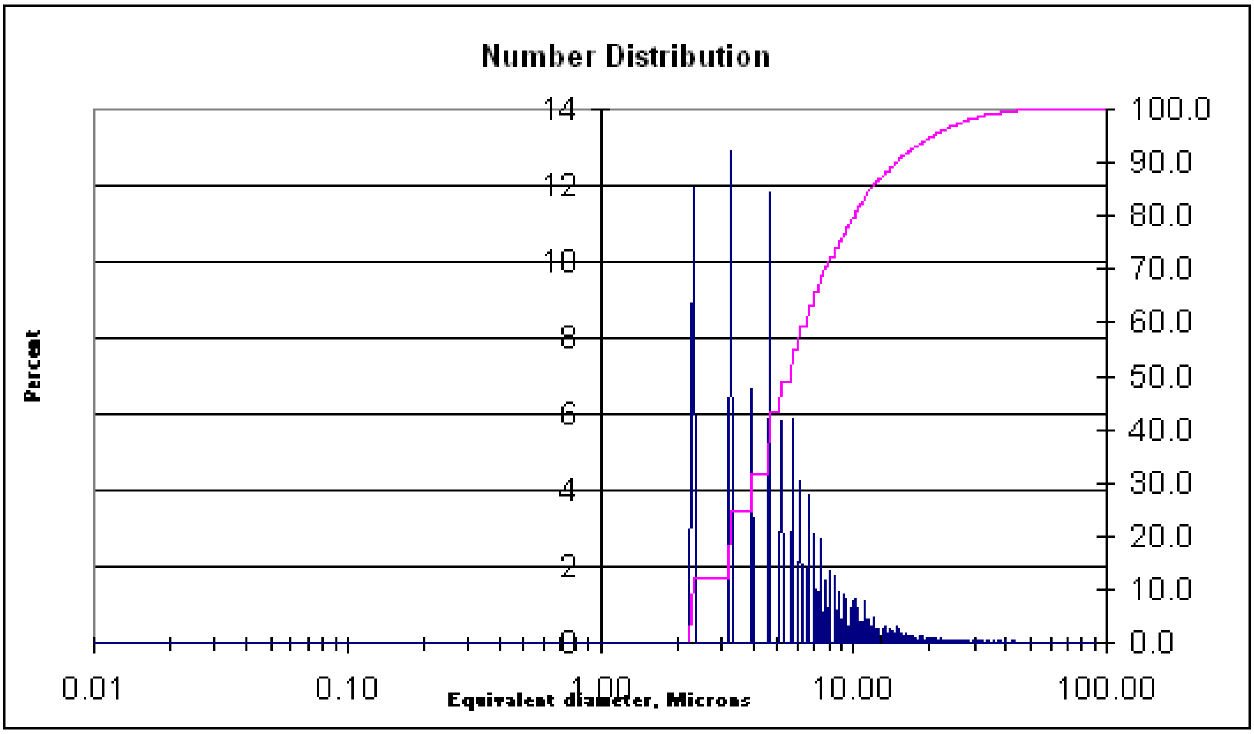

Figure 3. PET particle size distribution

TEM images of some of the smaller particles are provided in Figure 4 below.

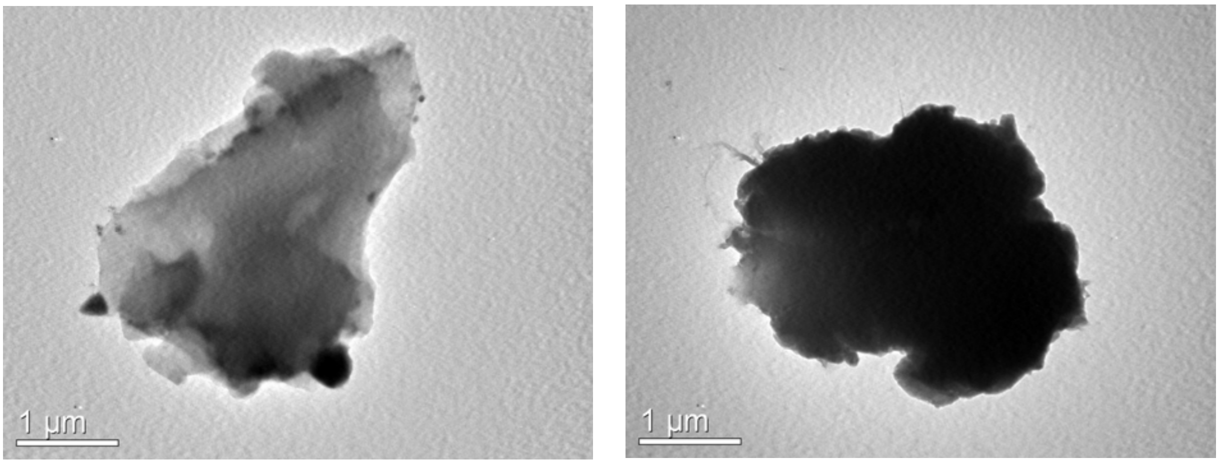

Figure 4. TEM images of small PET particles

PET molecular weight before and after micronization was determined by ASTM D4603 method; intrinsic viscosity provided by Polyhedron Laboratories. The Mn and Mw of the PET were 21990 Mn and 32715 Mw for the pellets, and 15969 Mn and 22787 Mw for the PET micronized powder.

CONCLUSION

A new method for micronizing PET has been developed. An emulsion of PET in saturated liquid THF at 200 ^{o}C was stirred at a very high shear rate and then rapidly cooled during agitation. The PET droplets solidified, yielding micron-scale PET particles. PET particle sizes ranged from 2-70 microns, and the number average molecular weight of the PET was reduced from 21990 to 15969 by this process. Future work will be directed at modifications that may lead to smaller particle sizes.

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