Micronization of Polyethylene Terephthalate via Freezing of Highly Sheared Emulsions of Polyethylene Terephthalate in Saturated Liquid Tetrahydrofuran

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ABSTRACT: A novel technique for micronizing polyethylene terephthalate (PET) resin ($\sim$ 3 mm) with saturated liquid tetrahydrofuran (THF) has been developed. PET pellets were introduced to a high-pressure vessel filled halfway with THF at loadings up to $\sim$ 7 wt % PET. When the vessel was closed and heated, the PET pellets exhibited significant melting point depression at 190°C in saturated liquid THF at 17.1 bar. Although other organic solvents were also able to depress the melting point of PET, only THF was able to facilitate the formation of an emulsion of PET-rich liquid droplets in the saturated liquid solvent when the mixture was agitated. In an attempt to generate the smallest possible PET droplets, a high-speed (5000 rpm), close-clearance, radial flow impeller was used to shear and disperse the droplets at $\sim$ 200°C and 20.1 bar. Emulsion was rapidly cooled while mixing. The PET droplets froze at $\sim$ 190°C, and the vessel was then cooled to ambient temperature. The excess liquid THF was decanted, and the PET particles were dried in a vacuum oven to remove residual THF. The PET particle sizes ranged between 2 and 70 μm, with number, area, and volume average diameters of 6, 20, and 30 μm, respectively. A comparison between the PET resin and PET powder properties indicated that the micronization reduced the M_w from 32,700 to 22,800. DSC results suggest that the rapid quench leads to a morphology different from equilibrium, with small somewhat imperfect crystallites, a lower overall degree of crystallinity, and a suppressed ΔC_p at the glass transition. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: poly(ethylene terephthalate); micronization; PET resin; phase behavior; PET processing; intrinsic viscosity

INTRODUCTION

Commercially, polyethylene terephthalate (PET) is available in the form of resin pellets, because it is synthesized by high temperature, vacuum condensation polymerization, and then extruded to produce the final pellet form. Unlike PVC, which can be made by emulsion polymerization, it is not practical to produce PET resins in a micron-scale powder form. Like most plastics, size reduction of PET cannot be accomplished with techniques used for brittle materials, such as jet mills, grinding mills, or impact mills. The PET particles can be made brittle before comminution, however, via immersion of the PET pellets in liquid nitrogen, followed immediately by grinding.[1] Alternately, PET can be heated in an oven to a temperature just above its melting point of $\sim$ 250°C and allowed to slowly cool and crystallize. For example, postconsumer amorphous PET chopped flake was heated in an oven at 250°C for 10 min and then cooled to ambient temperature to complete crystallization. The resultant brittle, white flakes were then ground, yielding particles sizes ranging between 2 and 200 μm.[2] Although these techniques are satisfactory for the generation of lab-scale PET powder samples, neither technique is well-suited for the rapid production of large amounts of micronized PET powder.

It is well known that many high-boiling-point solvents, such as dimethyl sulfoxide (DMSO), ethylene carbonate, propylene carbonate, and dimethyl phthalate, can dissolve PET at temperatures below the melting point of PET. If these PET-solvent solutions are thermally quenched by cooling, addition of cold solvent, or the addition of an antisolvent such as CO_2, PET particles will form. For example, one can dissolve 10 wt % PET in DMSO at 125°C. These transparent solutions can be thermally quenched while being stirred to form PET particles. The resultant PET particles are laden with residual DMSO, however, which cannot be readily removed.

In two US patents,[3,4] it was reported that one could dissolve the PET in saturated ("saturated" with respect to the liquid THF being present in a closed vessel along with a THF vapor phase at the THF vapor pressure) liquid tetrahydrofuran (THF) in a closed vessel at 190°C; when this liquid mixture was flashed through a valve to low pressure, PET particles were produced outside of the vessel. Naumann and Lynch's[2,3] studies were performed with high-pressure windowless vessels, however. It will be demonstrated in this work that PET does *not* dissolve in liquid THF at its vapor pressure, even at temperatures as high as 190°C. The inventors were apparently generating fine PET particles by passing a PET-in-THF emulsion through the valve; the THF-rich liquid droplets formed particles while the THF evaporated.

The objective of this work was to develop a novel lab-scale batch PET micronization technique that could produce PET powder with no residual solvent content using a process that could be readily scaled up to produce tens of kilograms per cycle. Therefore, it was desired that the micronization process did *not* involve the flashing of volatile organic solvents through valves or nozzles, the immersion of PET in cryogenic liquids, mechanical size reduction techniques such as grinding, the use of difficult-to-remove high-boiling-point solvents, or the dissolution of PET in near-critical or supercritical solvents that would require the vessels to be rated to pressures of 100 bar or more.

EXPERIMENTAL

Materials

PET particles (M_n = 21,990, M_w = 32,715, and 3 mm diameter) were obtained from Eastman. Methanol, ethanol, ethyl acetate, acetone, and toluene of at least 99% purity were obtained from SigmaAldrich and used as received. THF (b.p. 66°C), which contained 0.003% water and 110 ppm butylated hydroxytoluene as inhibitor, was used as received from Fisher for the micronization experiments, while anhydrous THF without inhibitor was used as the solvent and working fluid in the phase-behavior experiments.

Apparatus: High-pressure vessels

A variable-volume, windowed, high-pressure phase-behavior apparatus was used solely to determine the pressure required to dissolve 1 wt % PET in compressed liquid THF (i.e., cloud point pressure) via the synthetic method. (The synthetic method is a nonsampling technique in which specified amounts of PET and THF are introduced to a variable-volume vessel, and the temperature and pressure of the mix-ture are isothermally increased via compression until a single fluid phase occurs. The sample volume is then slowly expanded until a "cloud" of liquid droplets appears; the pressure at which this phase transition occurs is the cloud point pressure.) Particle generation experiments were not conducted with this vessel. This apparatus was capable of operating at temperatures up to 240°C. A magnetic stir bar was sufficient to facilitate the complete dissolution of PET in compressed liquid THF. Before cloud-point experiments, the Eastman PET pellets were dried at 170°C under vacuum overnight. The phase-behavior apparatus used in this work has been described in detail elsewhere.[5] The main components of the apparatus include a variable-volume (30-mL maximum volume) view cell based on the design of McHugh and coworkers[6] and a syringe pump (Isco, Model 500HP), which is connected to one end of the view cell and uses THF as the working fluid to compress/depressurize the PET-in-THF polymer solution on the other (sample) side of the piston. The view cell is located in a nitrogen-purged isothermal bath. A boroscope setup is used for observing the polymer solution inside the cell. For a typical cloud-point experiment (i.e., liquid–liquid transition) of a 1.0 wt % PET solution in THF, the cell was purged with nitrogen gas and then charged with 0.159 g of dried PET and 15.830 g of THF to an accuracy of ±0.0005 g. The mixture was then compressed to ∼ 240 bar with the THF working fluid as delivered from the syringe pump. The cell was heated from ambient conditions under continuous mixing using a magnetic stir bar at ∼ 0.6°C/min until a homogeneous, transparent solution of THF and polymer was obtained. PET started to melt at ∼ 180°C and was completely dissolved in THF at ∼ 190°C. As the temperature approached ∼ 175°C, the heating rate was reduced to ∼ 0.2°C/min for cloud-point measurements. To determine cloud-point pressures, the pressure was slowly decreased (i.e., 1.4 bar/min when approaching the cloud-point pressure) during continuous mixing until the clear solution became hazy. The cloud-point pressures, which were measured at temperatures as high as ∼ 240°C, were used to determine the very high-pressure requirements associated with a process that would require the complete dissolution of PET in the THF.

A 4-L, 12.10-cm internal diameter, windowed (Jerguson sight windows), heated, agitated, Autoclave Engineers vessel capable of operating at temperatures up to 220°C[7–9] was used for lower pressure observations of multiple-phase mixtures of PET and THF. This vessel facilitated visual determination of whether the PET was in the form of resin, powder, molten polymer, or dispersed droplets in saturated liquid THF at temperatures as high as ∼ 210°C. The reactor is equipped with four baffles located

symmetrically and an agitator with a six-flat blade impeller (Rushton turbine) with 5.05-cm diameter rotating at ∼ 1200 rpm. A stainless steel cooling coil for water surrounds the rotating impeller. A thermowell provided with a K-type Chromel-Alumel thermocouple is used to monitor the liquid temperature, and two K-type thermocouples are used to measure the gas temperature and the heating-jacket temperature. A 0–500 psia pressure transducer from Setra model 280E is located at the top of the reactor to measure the total pressure. The reactor is heated by four heating rods placed in an aluminum casing fitted around the stainless steel reactor. This vessel was primarily used to determine the appropriate operating conditions for the windowless, extremely high-shear microreactor in which powder generation experiments were conducted.

The 50-mL high-pressure microreactor (Autoclave Engineers) with an ID of 2.464 cm fitted with an external electric heating jacket and an inner coil for water cooling was used for most particle generation experiments, as the shear rates attainable in this vessel far exceeded those attainable in the 4-L phase behavior cell. The impeller was capable of spinning at up to 5000 rpm, and a 2.083-cm diameter radial-flow impeller with six square blades was positioned one-third of the way from the bottom of the reactor. The maximum tip speed of the impeller was 5.46 m/s, and the maximum shear rate in the 0.188 cm gap between the impeller tip and reactor wall was 2870/s. Because of the high-shear rates attainable in this 50-mL vessel, it was used to shear the molten PET droplets as the vessel was cooled, thereby minimizing the particle size of the PET powder that formed as the PET droplets solidified. Because the 50-mL vessel is windowless, the temperature and pressure operating conditions had to be previously established with the 4-L phase behavior vessel. Detailed particle size analysis was conducted only for the micronized PET samples made with this apparatus. The effect of particle loading was also established with this microreactor.

Particle size distribution

The particle size distribution of the micronized PET was determined with a Hockmeyer Particle Analysis System, HPAS-2000. The PET powder was mixed with a nonvolatile organic carrier liquid (e.g., aromatic 100), and the resultant paste was smeared on a glass microscope slide. The HPAS-2000 uses a standard light microscope fitted with a black-and-white or color digital camera and a black-and-white or color capture card to capture live video of the sample on the slide within the visible wavelength of light. A series of live images of the particles are analyzed using MicroPart, HPAS-2000 software, to obtain statistical information regarding mean particle size and frequency distribution by number, area, and volume. The software monitors the mean particle size versus the number of images used to generate the histogram. As more images are accumulated, the mean particle size is determined. The results are presented in terms of number, area, and volume distributions.

Molecular weight determination

Molecular weight analysis was provided by Polyhedron Laboratories. Weight–average and number–average molecular weight of the PET pellets and PET powder was obtained by correlating them to intrinsic viscosity using these relations[10]:

$$\eta = 3.72 \times 10^{-4}(M_n)^{0.73}$$
$$\eta = 4.68 \times 10^{-4}(M_w)^{0.68}$$

where M_n is number–average molecular weight, M_w is weight–average molecular weight, and η is intrinsic viscosity and is obtained using ASTM D4603-03 Standard Test Method for determining inherent viscosity of PET by glass capillary viscometer.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was done on a thin section of a PET pellet and the PET powder using Perkin Elmer Pyris Diamond DSC. The sample was stabilized at 25°C for 5 min and then heated to 300°C at rate of 5°C/min under nitrogen atmosphere.

RESULT AND DISCUSSION

THF–PET phase behavior

The initial task was to determine if PET could dissolve in saturated liquid solvents with relatively low-normal boiling points. PET pellets were combined (at 1 wt %) with organic solvents such as methanol, ethanol, ethyl acetate, acetone, toluene, and THF in the 4-L windowed phase behavior cell. The vessel was filled halfway with this PET-solvent mixture to ensure that there would be adequate space for an equilibrium vapor phase. PET was not soluble in any of these saturated liquid solvents at 200°C. Three-phase LLV equilibrium (polymer-rich liquid, THF-rich liquid, THF-rich vapor) was observed for these mixtures at elevated temperatures. Only in the case of THF, however, did the PET-rich liquid form droplets that were readily dispersed in the solvent upon mixing; all other solvents yielded a viscous PET-rich liquid that adhered to the sides and bottom of the windowed vessel. The PET-in-THF emulsion formed even though no surfactant had been introduced to the system. Although it will
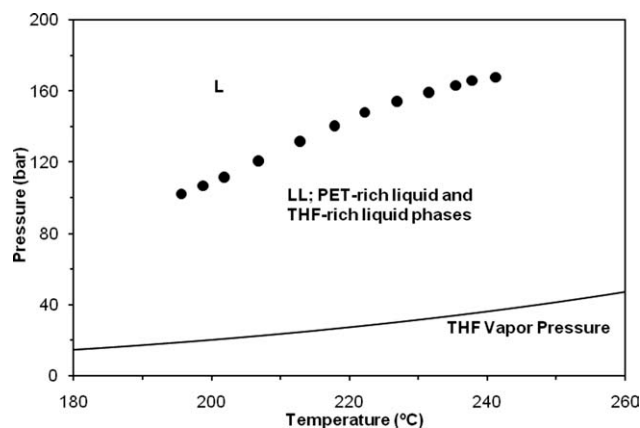
Figure 1 Cloud-point pressure curve for 1 wt % PET in THF from 200 to 240°C. A single phase exists above the curve, and a PET-rich liquid phase forms at pressures on and below the curve indicated by the data above. The vapor pressure curve of THF ($T_c = 267$°C, $P_c = 51.3$ bar) is also shown.

be shown that the molecular weight of the PET was reduced during this process, we do not believe that this degradation formed a surfactant with PET-philic and THF-philic segments. Therefore, it is likely that the emulsion formed because of a significant decrease in the interfacial tension (IFT) between the two liquid phases. Unfortunately, we did not have the capability to measure the high-temperature, high-pressure IFT between the two liquid phases.

It had been previously reported in the results from a study that used a windowless vessel that PET was soluble in saturated THF,[2,3] which contradicted our observations that PET was not soluble in saturated THF. Therefore, the cloud-point pressure of PET in THF (1 wt % concentration) was determined using the high-temperature, high-pressure, windowed, variable-volume vessel. A 1 wt % concentration was selected, because this concentration (or less) will typically lead to the formation of particles (rather than fibers) if the rapid expansion of a supercritical solution process is used to form PET particles from the homogenous single-phase solution of polymer in solvent.[11] The cloud-point results are illustrated in Figure 1. These cloud-point pressure values greatly exceed the vapor pressure of THF; thus, these results convincingly demonstrate that saturated liquid THF cannot dissolve 1 wt % or more of PET. We therefore believe that Naumann and Lynch[2,3] were flash-devolatilizing a PET-in-saturated liquid THF emulsion (rather than a single-phase solution) through the valve of their windowless vessel as they generated PET powder.

Micronization process

Having verified that a micronization process based on dissolution of PET in THF would require prohibi-

tively high pressures illustrated in Figure 1, we again turned our attention to a micronization process based on saturated THF at its (relatively low) vapor pressure. The windowed 4-L phase behavior cell was filled with liquid THF and PET particles, and the vapor space above was flushed with nitrogen gas at ambient temperature. The vessel was only filled about halfway with THF, because the saturated liquid THF would expand substantially as the system was heated, and it was desired to maintain the process pressure at approximately the vapor pressure of THF, rather than at the elevated pressure that would occur if the vessel became completely filled with compressed liquid THF. For example, a material balance on the system combined with a knowledge of the saturated liquid and vapor THF density values indicated that the vessel filled halfway at the beginning of the experiment would be 80% full at 220°C, while a vessel initially filled to a 60% level would be more than 95% full at 220°C. As the system was heated, the pressure of the system increased, following the vapor pressure curve of THF. At about 190°C and 17.1 bar, with the impeller spinning at 1200 rpm, the PET pellets softened and started to become transparent. The molten PET was readily dispersed in saturated liquid THF at ~ 200°C and 20.1 bar. Then, while the impeller was still stirring, the heater was turned off, and cooling water was delivered at ~ 100 psi through the cooling coil within the 4-L vessel in an attempt to solidify the droplets as quickly as possible. The dispersed PET droplets froze at ~ 190°C, and the system was further cooled and agitated until the temperature was ~ 150°C. Although the bulk of the PET particles was formed by the freezing of the emulsified PET droplets, a very small amount of the PET particles were formed by the traces of dissolved PET coming out of solution. This was qualitatively demonstrated by the THF-rich liquid phase becoming slightly cloudy as the vessel was cooled. The system was then cooled to ambient temperature at a low-impeller speed of ~ 500 rpm. The micronized PET and liquid THF were then drained from the microreactor. Although this procedure successfully generated PET particles, their size distribution was well above the targeted 1–100 μm range.

The micronization process was then conducted in the 50 mL, high-shear, nonwindowed, microreactor, with the close-clearance, high-speed, radial impeller spinning at 5000 rpm for 5 min at 200°C and 20.1 bar. The resultant particle sizes were much smaller than those attained using the 4-L vessel. About 100% of the PET particles made in the high-shear microreactor were less than 70 μm in size (as detailed in the subsequent section on particle size distribution). Therefore, this apparatus was used in all the subsequent particle generation experiments.
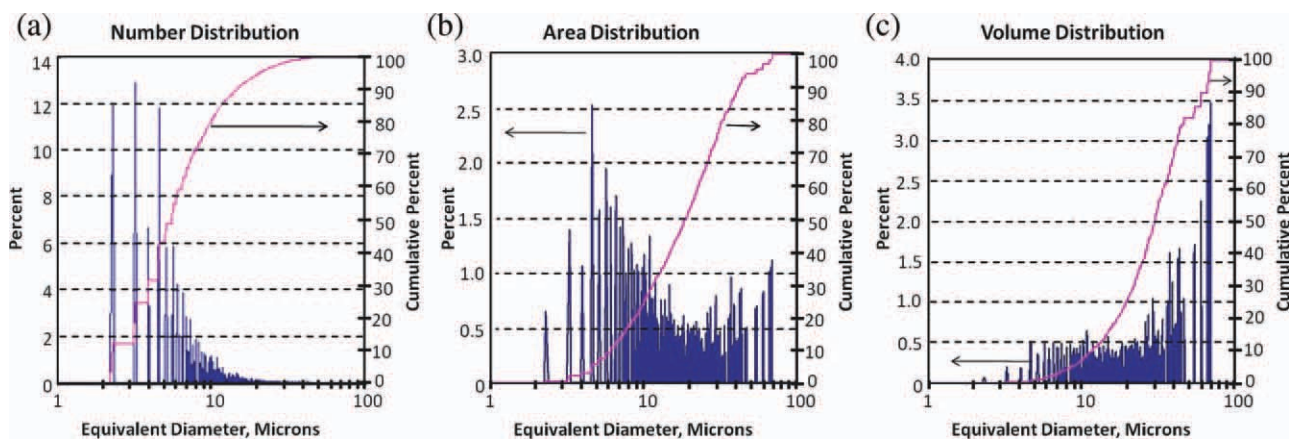
Figure 2 (a–c) Particle-size analysis for a 50 g PET powder sample prepared using the high-shear microreactor; number, area, and volume distributions, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Experiments were also conducted to maximize the loading of the PET in THF in each run of the 50-mL microreactor with the close-clearance impeller spinning at 5000 rpm. In particular, mixtures of PET and liquid THF (at ambient conditions) of 0.5–3.0 g PET/25 mL THF were studied in increments of 0.5 g PET. The highest loading that consistently produced a high-yield PET powder was 1.5 g PET/25 mL THF (7 wt %). Experiments containing 2.0 g PET/25 mL THF usually yielded PET powder at high yield, but on occasion, a significant portion of the PET was not emulsified. At a loading of 2.5 g PET/25 mL THF, the PET was micronized only occasionally. We were not able to produce a high yield of PET powder at a loading of 3.0 g of PET/25 mL THF.

When a dry powder was the desired final product, the PET particles were permitted to settle in the THF overnight, and the excess THF was then decanted, and the PET-THF slurry was then filtered. The PET particles were then placed in a vacuum oven overnight at 65°C, yielding dry PET particles. A cumulative total of 100 g of dry micronized PET was generated in 74 runs, with a 1.5 g PET resin loading per run, representing an average yield of 90%.

If a dispersion of PET powder in a high-boiling point liquid carrier was desired, it proved difficult to disperse the dry powder in the liquid, because the PET particles agglomerated during the micronization process. Prolonged and intense agitation and sonication were required to disperse the PET in a liquid. Therefore, an alternative technique was used for preparing a liquid dispersion. Dispersions of micronized PET particles were easily prepared by mixing a high-boiling-point liquid (e.g., DMSO) with the THF–PET slurry (rather than dry PET powder) and then rotovaping the dispersion at ~ 65°C for an hour to drive off the THF.

Particle size distribution

The PET particle-size analysis was conducted using a Hockmeyer Particle Analysis System (HPAS-2000) with MicroPart (rel 2.0) Software. The PET particles sizes ranged between 2 and 70 μm. The number, area, and volume distributions are shown below in Figure 2(a–c), respectively. The average particle diameter values (i.e., the particle diameter that corresponds to 50% cumulative total on the right-hand side y-axis) for the PET powder are 6, 20, and 30 μm for the number, area, and volume distributions, respectively. This represents a significant size reduction from the original size of the PET pellets (~ 3000 μm).

TEM images (JEOL 200-CX) of some of the smallest PET particles are provided in Figure 3(a–c). These results indicate that the crystallization of the emulsified PET droplets during solidification resulted in the formation of irregularly shaped particles.

PET resin and PET powder melting point and glass transition temperature

Typical DSC results for the PET resin, shown in Figure 4(a,b), exhibit melting points at 250 and 242°C, with corresponding latent heats of 10.82 and 50.15 J/g, respectively. The PET powder exhibited two broad melting point peaks; a large peak at 251°C (a temperature comparable to that observed for the PET resin) and a very small peak at 167°C. The corresponding heats of fusion were 51.96 and 3.65 J/g, respectively. Based on a heat of fusion for pure crystalline PET of 140 J/g, the crystallinity of the PET resin was reduced from 43.6% (60.97/140) to 39.7% (55.61/140) as a result of the micronization.
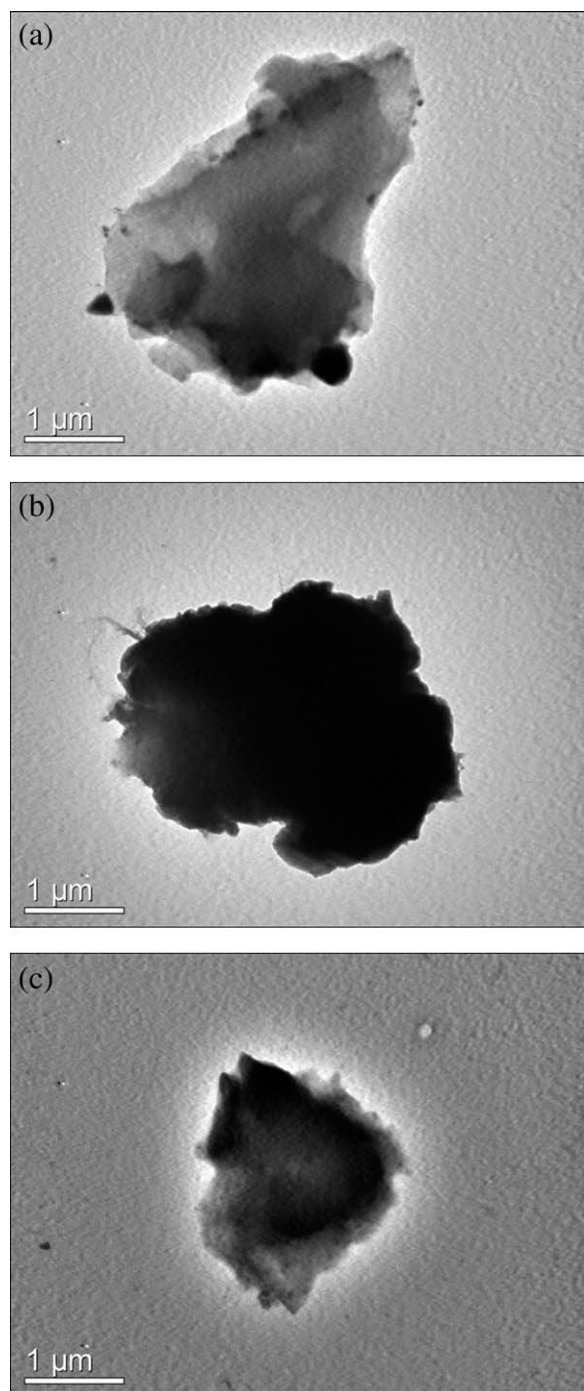
**Figure 3** (a–c) TEM images of some of the smallest PET particles.

The presence of the two melting peaks is not atypical for polymers rapidly quenched from a purely liquid (amorphous) to a solid state. Crystals produced during the rapid quenching would be small and imperfect, leading to the relatively low-melting temperature observed in the DSC (at 167°C). These small crystallites would be subject to annealing during the DSC scan, leading to the generation of a peak at the conventional melting temperature in the

vicinity of 250°C. Again, given the rapid quench, it is not surprising that the powder exhibits a lower extent of crystallization, despite the annealing—it is likely that the actual degree of crystallization in the powder (before DSC) is even lower.

The glass transition temperature of the PET resin was 74°C. The T_g of the PET powder could not be detected, however, even though the powder had a significant amorphous content. The absence of a detectable T_g for the micronized PET may be attributable to the rapid quenching of the molten PET droplets, which may have yielded a powder whose morphology was kinetically far from equilibrium, and hence where the difference between the heat capacities of the glassy and liquid phases was not nearly as large as would be expected from an aged material. This could lead to a very small or nonexistent T_g peak.

PET resin and PET powder molecular weight

The molecular weight of the PET was reduced by the micronization process. PET molecular weight before and after micronization was determined by
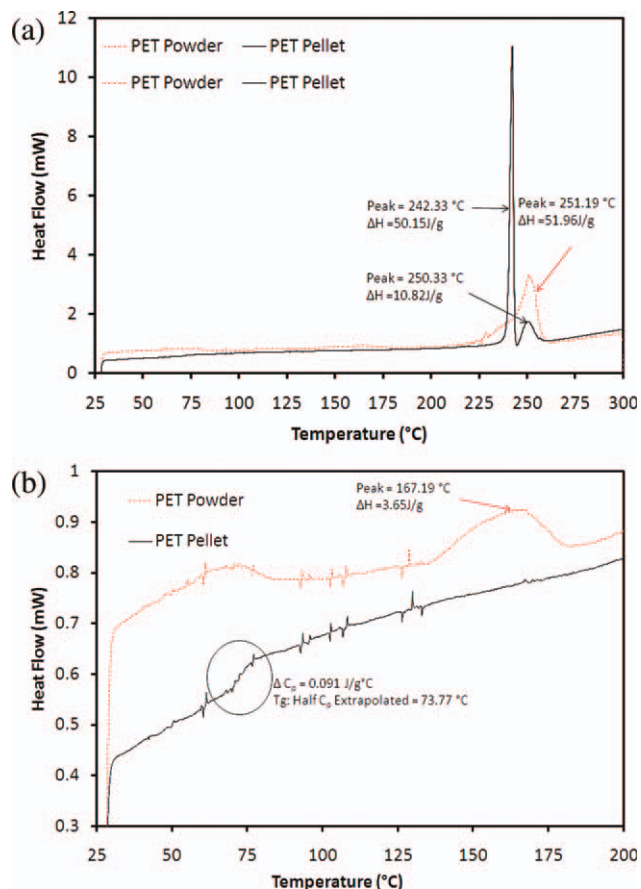
Figure 4 DSC of PET pellets and powder. (a) Melting point range; (b) T_g temperature range. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
PET Molecular Weight by Intrinsic Viscosity

	Concentration (g/dL)	Inherent viscosity (dL/g)	Intrinsic viscosity (dL/g)	Relative viscosity	M_n	M_w	PDI
PET pellets	0.4996	0.533	0.55	1.305	21990	32725	1.488
PET powder	0.4998	0.418	0.43	1.2321	15696	22787	1.452

ASTM D4603 method for intrinsic viscosity. As shown in Table I, the M_n and M_w of the PET were 21,990 M_n and 32,715 M_w for the as-received Eastman pellets and 15,969 M_n and 22787 M_w for the PET micronized powder. This decrease in molecular weight is probably attributable to the hydrolysis of the PET due to the presence of small amounts of water in the THF. Alternately, the initial molecular weight of the PET may have been abnormally high, because it was kinetically trapped, that is, the equilibrium molecular weight of the PET was lower than the actual molecular weight of the PET resin but could not attain the lower value because of the polymer resin being in the solid state and at low temperature when first produced.

CONCLUSIONS

A new method for micronizing PET pellets has been developed. PET exhibited melting-point depression from 250 to 190°C in saturated liquid THF. At about 200°C and 20.1 bar, emulsions of PET in saturated liquid THF, with loadings as great as 7 wt % PET, were formed via intense agitation. No surfactant was added to this system; therefore, it appears that a very low IFT between THF-rich and PET-rich liquid phases was responsible for the formation of the emulsion. Micronized PET particles were formed as the PET-in-THF emulsion was rapidly cooled to temperatures below 190°C while agitation continued. The PET droplets solidified, and the removal of the PET from the THF was accomplished easily via settling, decanting of the excess THF, and drying of the PET powder in a vacuum oven. The PET yield was $\sim$ 90%, with most of the lost 10% forming a layer of PET particles on the inner surfaces of the high-pres-sure vessel. PET particle sizes ranged from 2 to 70 μm, with number-, area-, and volume–average particle sizes of 6, 20, and 30 μm, respectively. The melting point of the PET powder decreased only slightly from 250 to 247°C, but the number–average molecular weight of the PET was reduced from 21,990 to 15,969 by this process. DSC results suggest that the rapid quench of the small particles leads to a morphology relatively far from equilibrium, with a reduced extent of crystallinity, relatively small, imperfect crystallite that are subject to annealing during DSC scans, and a suppressed delta-Cp at the glass transition.

References

1. Yu, Y.; Yu, Y.; Jin, M.; Li, G.; Bu, H. Macromol Chem Phys 2001, 202, 139.
2. Dimer, T.; Tinçer, T. J Appl Polym Sci 2000, 79, 827.
3. Naumann, E. B.; Lynch, J. C. U.S. Pat. 5,198,471 (1993).
4. Naumann, E. B.; Lynch, J. C. U.S. Pat. 5,278,282 (1994).
5. Sane, A.; Thies, M. J Supercrit Fluids 2007, 40, 134.
6. Hasch, B. M.; Lee, S.-H.; McHugh, M. Fluid Phase Equilibr 1993, 83, 341.
7. Tekie, Z.; Li, J.; Morsi, B.; Chang, M.-Y. Chem Eng Sci 1997, 52, 1541.
8. Lemoine, R.; Fillion, B.; Morsi, B. Int J Chem Reactor Eng 2004, 2, A29.
9. Heintz, Y.; Lemoine, R.; Sehabiague, L.; Morsi, B.; Jones, K.; Pennline, H. Proceedings of the 22nd Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 12-15, 2005; pp 34.5/1–34.5/40.
10. Sanches, N.; Dias, M.; Pacheco, E. Polym Test 2005, 24, 688.
11. Blasig, A.; Shi, C.; Enick, R.; Thies, M. Ind Eng Chem Res 2002, 41, 4976.