

Powder Production From Waste Polyethylene Terephthalate (PET) Water Bottles

by Anit Giri, Frank Kellogg, Kyu Cho, and Marc Pepi

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**Anit Giri and Frank Kellogg
Bowhead Science and Technology**

**Kyu Cho and Marc Pepi
Weapons and Materials Research Directorate, ARL**

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14. ABSTRACT The ability to make powders from battlefield scrap and general waste materials in-situ on the battlefield forward operating base (FOB) is investigated. Three different techniques have been employed to grind mm-size small scrap pieces of water bottles, which are made of polyethylene terephthalate (PET). The particle size distribution of the milled powder obtained in each technique was measured. The results are presented in this report.					
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Contents

List of Figures	iv
List of Tables	iv
Acknowledgments	v
1. Introduction	1
2. Experimental	2
3. Results and Discussion	4
4. Conclusions and Future Research	8
5. References	10
List of Symbols, Abbreviations, and Acronyms	12
Distribution List	13

List of Figures

Figure 1. Shredded PET material.....	2
Figure 2. (a) A schematic of cryogenic attrition, (b) a cryogenic attrition mill in action, (c) and the cryogenic attrition mill at ARL.	3
Figure 3. Powder produced via ZM200 rotary mill.	4
Figure 4. PSD graphs for the four measurements made on the Retsch cryomilled material.	5
Figure 5. PSD graphs for the four measurements made on the ARL cryomilled material.	5
Figure 6. A comparison of typical large particles found in the Retsch material (a and b) and in the ARL material (c and d).	7
Figure 7. A comparison of the typical particles found in the Retsch material (a and b) and in the ARL material (c and d).	8

List of Tables

Table 1. Retsch cryomilled PET PSD averages.....	6
Table 2. ARL cryomilled PET PSD averages.....	6

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1. Introduction

The Army is researching processing science to enable adaptive mobile manufacturing of indigenous materials. Of particular focus, is the ability to make powders from battlefield scrap and general waste materials in-situ on the battlefield forward operating base (FOB). This study focused on polyethylene terephthalate (PET), the common material used to make the vast number of water bottles available as waste on an FOB. The hope is that this powder could then be used in manufacturing processes on FOBs, in order to create new materials and products of potential use to the Warfighter. This capability would reduce the logistics tail required to fortify these FOBs, thereby reducing the vulnerable convoys that deliver the materiel. One such example could be the formation of polymeric coatings (1) or perhaps for use in three-dimensional (3-D) printing applications. Among different techniques used to reduce the particle size of metals, ceramics, and polymers, ball milling is widely used (2, 3). However, for polymers, size reduction by milling is a challenge due to the difficulties with the repeated fracturing and cold welding of polymer particles. It has been demonstrated that if the milling was performed at relatively low-temperature (e.g., liquid nitrogen [LN₂] temperature [−196 °C]), in other words, cryomilling, it was possible to reduce the particle size of polymers (4, 5). Cryomilling has been employed to produce powders of many different polymers (6–15), to facilitate production of polymers in powder form, and to enable manufacturers to make parts in any shape from polymer powders while avoiding such difficulties as high viscosity and insolubility associated with conventional processing techniques (4). Cryomilling can also be performed by milling the starting powders within LN₂ with milling balls forming a slurry during milling (16). To distinguish it from conventional cryomilling, we will call the process of milling in an attritor—where the powder is in intimate contact with LN₂—“cryogenic attrition.” Recently it has been demonstrated at the U.S. Army Research Laboratory (ARL) that it was possible to reduce the particle size of a thermoplastic polymer by cryogenic attrition (16).

For this research herein, we have employed three different techniques to grind millimeter (mm)-size small scrap pieces of water bottles using (1) the Retsch Ultra Centrifugal Mill ZM 200 (ZM 200) with scooping LN₂, (2) the Retsch CryoMill (both were performed at Retsch), and (3) cryogenic attrition performed at ARL. Particle size of the ground powder obtained using the three aforementioned techniques was measured and the efficiency of the techniques was compared. The results are presented herein. Although cryomilling might not yet be able to be performed in an FOB environment, this study is considered a proof-of-concept to determine that usable powder could be produced from waste water bottles for further processing.

2. Experimental

PET water bottles were shredded using a commercial paper shredder. The size of the shredded pieces varied from 2–10 mm length and 1–3 mm width. The thickness of the shredded pieces was less than 1 mm thick (figure 1).

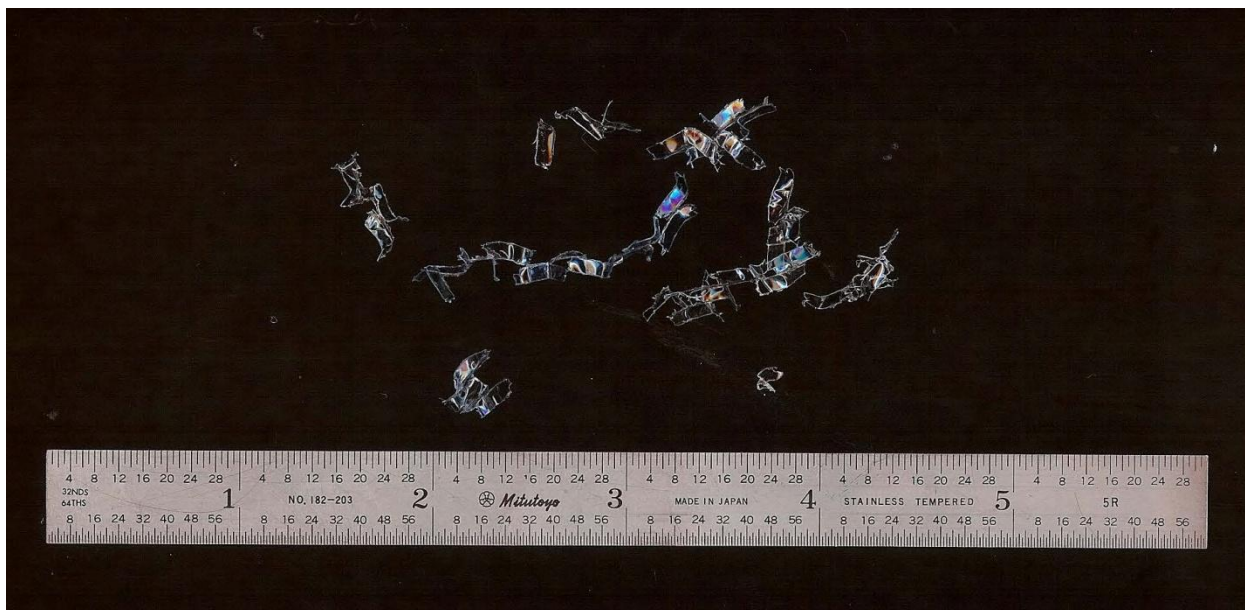


Figure 1. Shredded PET material.

A total of 9.5 g of the shredded scrap starter material was milled for 3 min in an Ultra Centrifugal Mill ZM 200 rotating at 18,000 rpm with scooping LN₂. In the ZM 200, the starting material was fed onto a rotor and size reduction took place via impact and shearing effects between the rotor and a fixed-ring sieve.

In the Retsch cryomill, 3 g of the scrap starter material were prechilled for 5 min at LN₂ temperature and then transferred to a 50-ml cylindrical grinding jar with one 1-in-diameter stainless steel grinding ball. The scrap starter material was milled by radial oscillations of the jar in a horizontal position where the inertia of the grinding ball caused them to impact with high energy on the sample material for subsequent grinding. The grinding jar was continually cooled with LN₂.

For cryogenic attrition at ARL, 100 g of shredded PET were milled in liquid nitrogen for 4 h in a 1S Szegvari attritor (Union Process, Akron, OH) modified to allow for continuous flow of LN₂ with 0.25-in-diameter stainless steel balls and a powder-to ball ratio of 1:64. Figure 2 shows a schematic design and photo of a typical cryogenic attritor along with that of the one available at ARL (18).

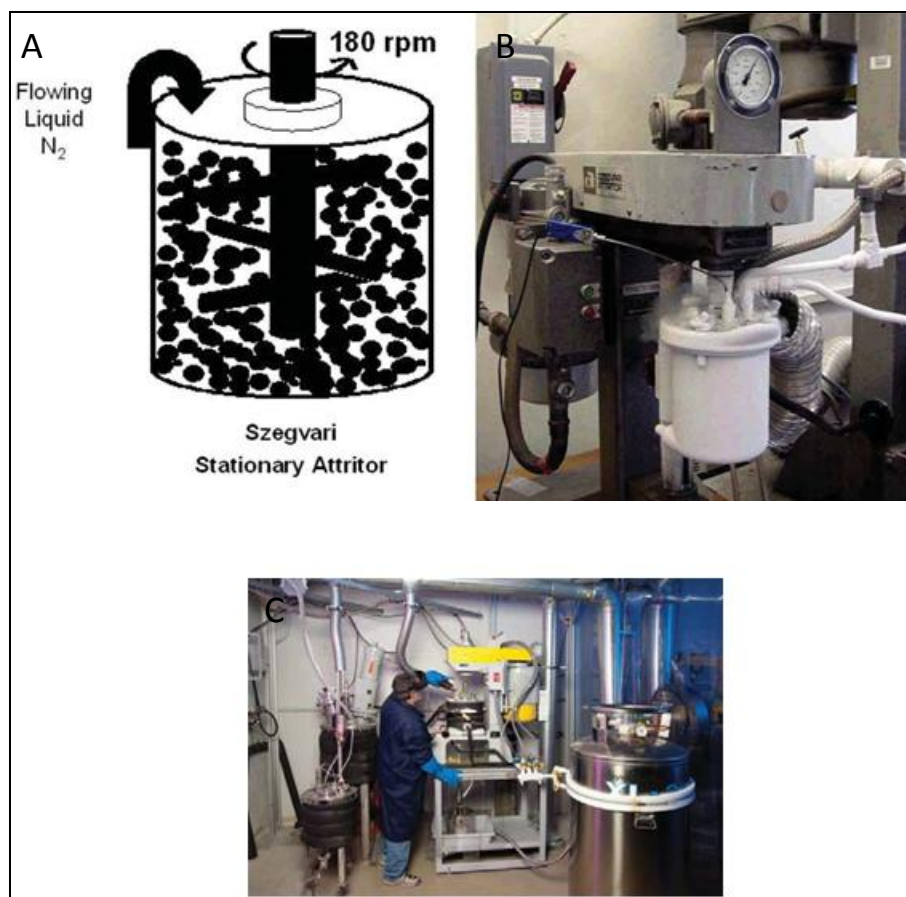


Figure 2. (a) A schematic of cryogenic attrition, (b) a cryogenic attrition mill in action, (c) and the cryogenic attrition mill at ARL.

After 4 h of cryogenic attrition, a slurry containing the milled product and LN₂ was collected. After the LN₂ boiled off, it was found that the discharged product contained about 40 g of milled powder mixed with some large (lengths greater than 1 mm), unmilled flakes. Those large flakes were sieved and separated from the powder.

Particle size distribution (PSD) measurements were carried out using a Horiba LA-910 Laser Light Scattering Particle Size Analyzer. This instrument measures particle size by shining a laser through sample particles that have been suspended in a small liquid bath; any clear liquid that the particles will be suspended in (they cannot sink or float) can be used. For the milled PET powders, ethanol was found to be a suitable suspending agent. Images of the powders were taken via scanning electron microscopy (SEM). A Hitachi S-4700 field emission scanning electron microscope (FESEM) was used to examine the morphology of the three milled powder samples.

3. Results and Discussion

The material that was produced by the Retsch ZM200 mill was “huge” compared to the two cryomilled (Retsch and ARL) powders; individual particles could be easily discerned by the eye (figure 3). As a result, the powder produced via the ZM200 was not examined further.

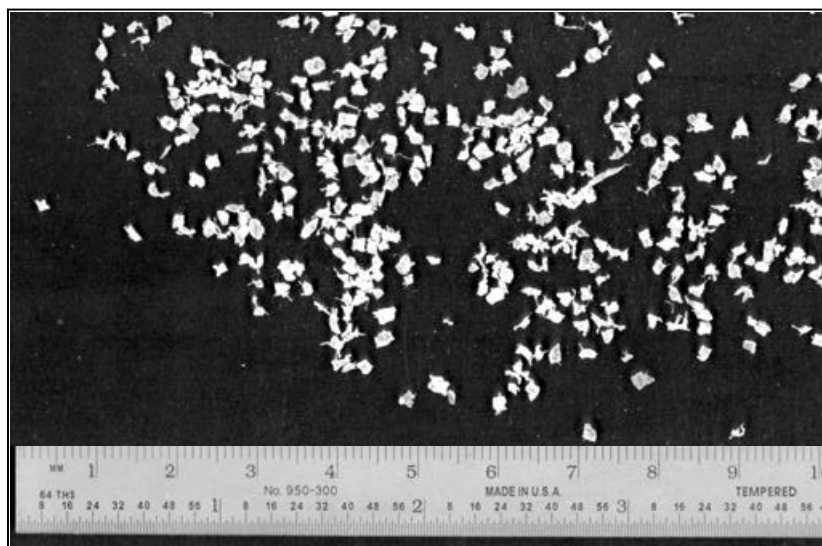


Figure 3. Powder produced via ZM200 rotary mill.

For data reproducibility, four Horiba measurements were made for each cryomilled powder. The PSD graphs of all four measurements for the Retsch and ARL cryomilled powders are collected in figures 4 and 5. The average particle size diameters for each run are collected in tables 1 and 2.

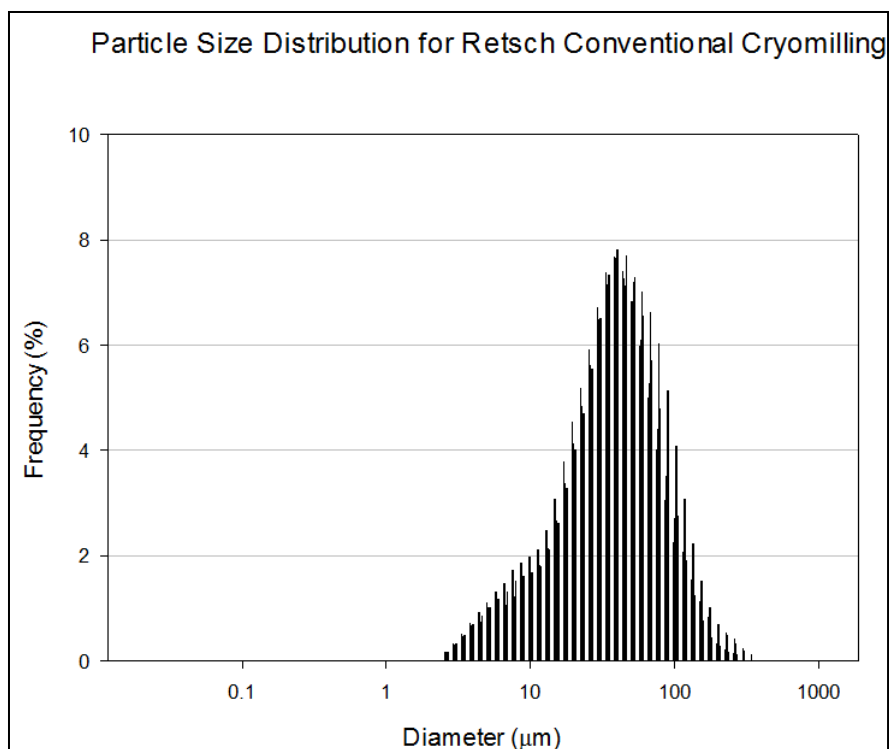


Figure 4. PSD graphs for the four measurements made on the Retsch cryomilled material.

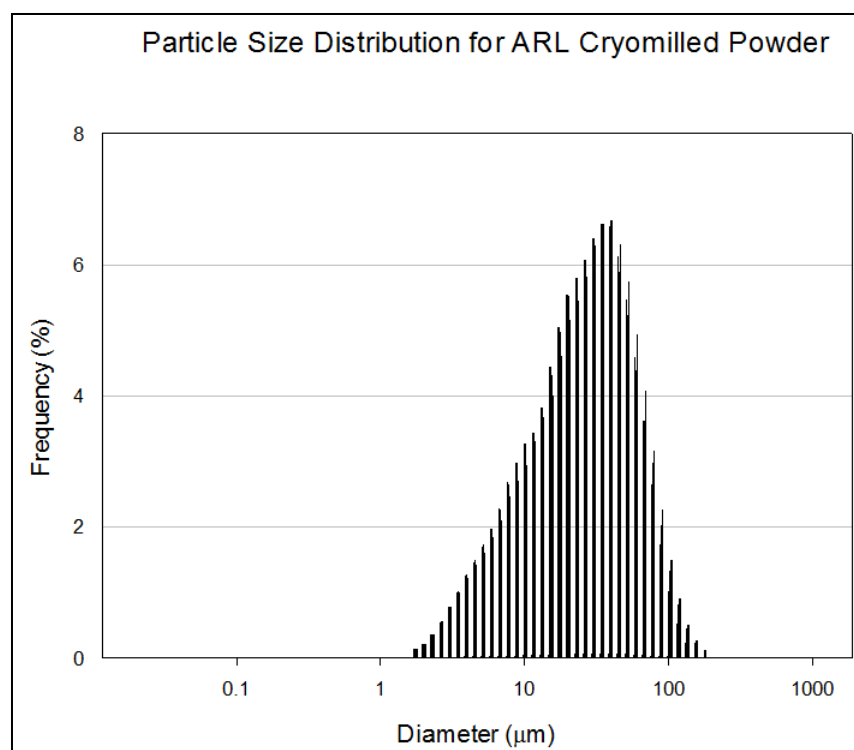


Figure 5. PSD graphs for the four measurements made on the ARL cryomilled material.

Table 1. Retsch cryomilled PET PSD averages.

	M1	M2	M3	M4	Average
Mean (um)	39.60	45.23	50.74	41.91	44.37
Medium (um)	32.31	34.91	41.28	35.04	35.885
Mode (um)	36.67	36.70	48.04	36.77	39.545

Table 2. ARL cryomilled PET PSD averages.

	M1	M2	M3	M4	Average
Mean (um)	29.96	45.23	29.79	31.47	29.98
Medium (um)	23.87	34.91	23.91	25.67	24.26
Mode (um)	32.02	32.08	32.02	36.54	33.17

The PSD data show that the ARL cryomilled material is finer than the Retsch cryomilled material; the PSD graph shows a higher percentage of very small particles in the ARL material, a smaller percentage of very large particles, and smaller average (mean, median, and mode) diameter values. SEM micrographs also show that the large particles in the Retsch material are larger than the large particles in the ARL material (figure 6) and that the average particles are also larger in the Retsch material (figure 7).

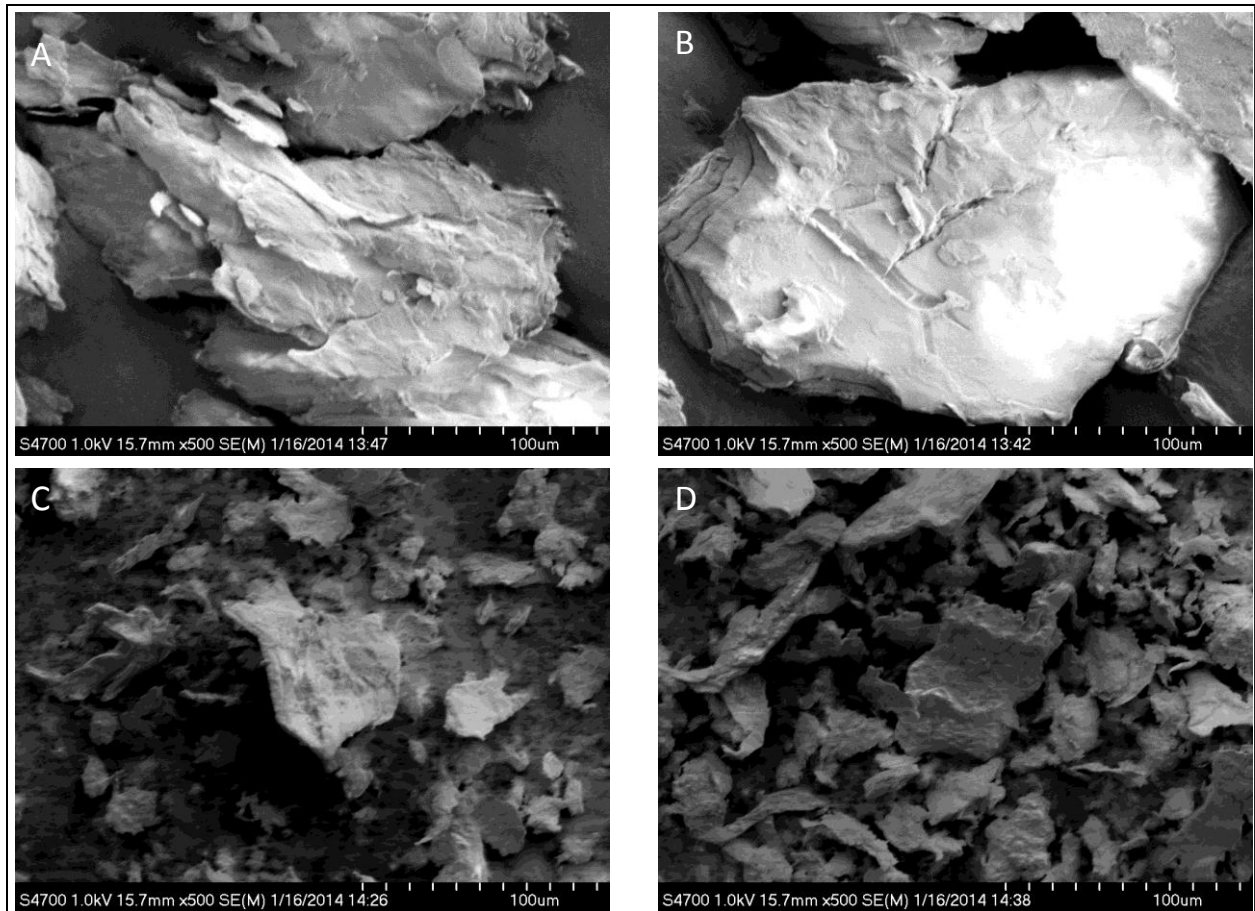


Figure 6. A comparison of typical large particles found in the Retsch material (a and b) and in the ARL material (c and d).

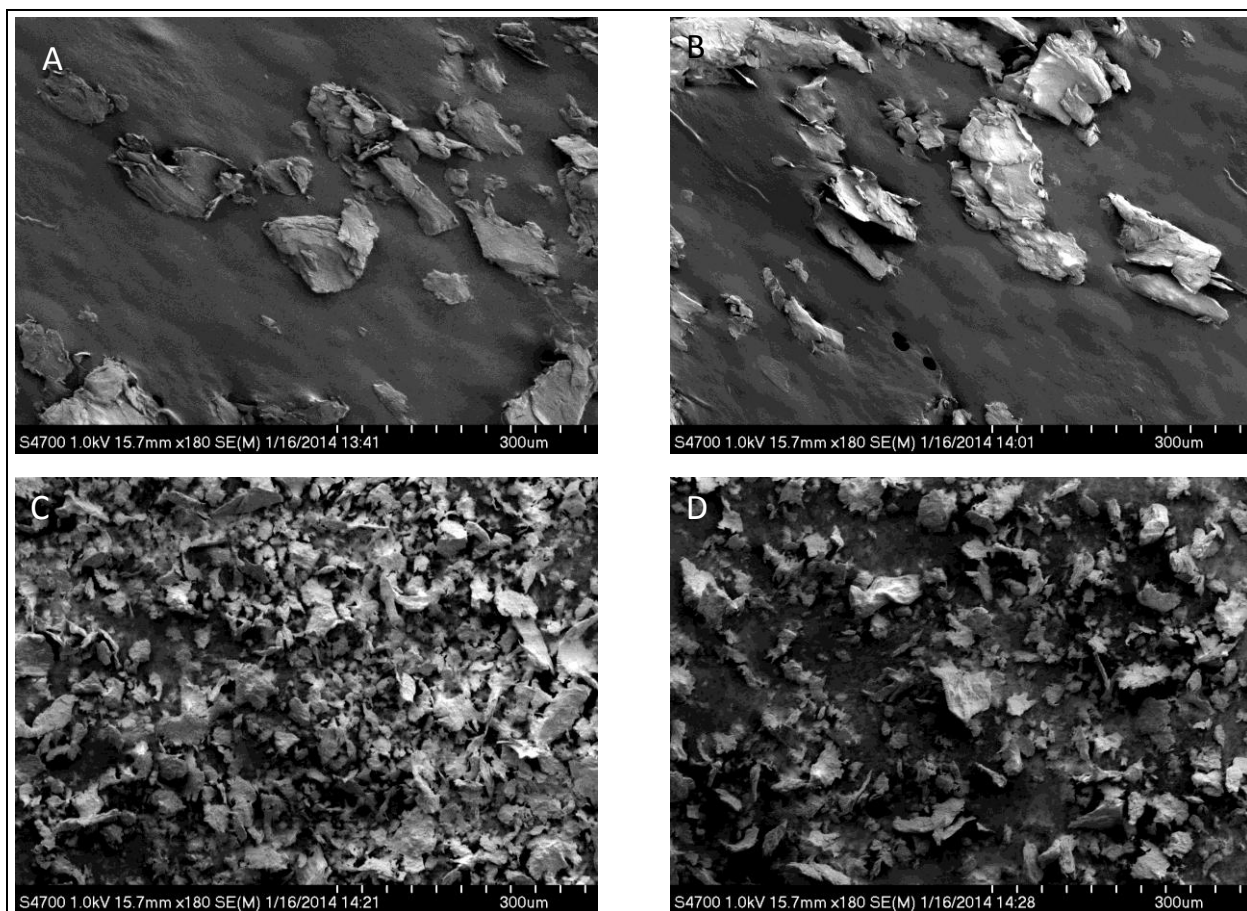


Figure 7. A comparison of the typical particles found in the Retsch material (a and b) and in the ARL material (c and d).

4. Conclusions and Future Research

To grind mm-size small scrap pieces of water bottles into powder form, three different techniques have been employed: (1) the Retsch Ultra Centrifugal Mill ZM 200 (ZM 200) with scooping LN₂, (2) the Retsch CryoMill (both were performed at Retsch), and (3) cryogenic attrition performed at ARL. The particle size distribution of the milled powder obtained from each cryogenic technique was measured. The ARL cryogenic attrition produced the smallest particles, in both size and distribution. Longer milling times and different material to ball ratios could be used to produce smaller particles. The milling parameters could be tailored to make particles in a specific size range. This technique is scalable and potentially kilogram quantities of materials could be efficiently ground into powder form once the milling parameters are optimized.

The challenge presented here is to recycle a commonly available material (in this case, PET) into an acceptable starter material in the field for use in further processing. It is recognized that the methods and equipment used herein to transform water bottles into powder form are not expected to be easily translated onto the battlefield, but the intent here is to produce enough powder to show viability as a “proof-of-concept.”

5. References

1. Van Brederode, R. A.; Steinkamp, R. A. Crosslinkable Polymer Powder and Laminate. U.S. Patent 42256560A, 1980, <http://www.google.com/patents/US4225650>.
2. Suryanarayana, C. Mechanical Alloying and Milling. *Prog. Mater. Sci.* **2001**, *46*, 1.
3. Zhang, D. L. Processing of Advanced Materials Using High-Energy Mechanical Milling. *Prog. Mater. Sci.* **2004**, *49*, 537.
4. Shaw, W. J. D.; Pan, J. Effects of Processing Parameters on Material Properties of Mechanically Processed Polyamide. *J. Appl. Polym. Sci.* **1995**, *56*, 557.
5. Zhu, Y. G.; Li, Z. Q.; Zhang, D.; Tanimoto, T. Effect of Cryomilling on the Thermal Behaviors of Poly(ethylene terephthalate). *J. Appl. Polym. Sci.* **2006**, *99*, 2868.
6. Smith, A. P.; Shay, J. S.; Spontak, R. J.; Balic, C. M.; Ade, H.; Smith, S. D.; Koch, C. C. High-Energy Mechanical Milling of Poly(methyl methacrylate), Polyisoprene and Poly(ethylene-alt-propylene). *Polymer* **2000**, *41*, 6271.
7. Cavalieri, F.; Padella, F.; Bourbonneux, S. High-Energy Mechanical Alloying of Thermoplastic Polymers in Carbon Dioxide. *Polymer* **2002**, *43*, 1155.
8. Furgiuele, N.; Lebovitz, A. H.; Khait, K.; Torkelson, J. M. Novel Strategy for Polymer Blend Compatibilization: Solid-State Shear Pulverization. *Macromolecules* **2000**, *33*, 225.
9. Smith, A. P.; Spontak, R. J.; Balic, C. M.; Koch, C. C.; Smith, S. D.; Ade, H. Cryogenic Mechanical Alloying of Poly(methyl methacrylate) With Polyisoprene and Poly(ethylene-altpropylene). *Macromolecules* **2000**, *33*, 2595.
10. Smith, A. P.; Ade, H.; Smith, S. D.; Koch, C. C.; Spontak, R. J. Anomalous Phase Inversion in Polymer Blends Prepared by Cryogenic Mechanical Alloying. *Macromolecules* **2001**, *34*, 1536.
11. Castricum, H. L.; Yang, H.; Bakker, H.; Van Deursen, J. H. A Study of Milling of Pure Polymers and a Structural Transformation of Polyethylene. *Mater. Sci. Forum* **1997**, *211*, 235.
12. Zhu, Y. G.; Li, Z. Q.; Zhang, D.; Tanimoto, T. ABS/Iron Nanocomposites Prepared by Cryomilling. *J. Appl. Polym. Sci.* **2006**, *99*, 501.
13. Zhu, Y.; Li, Z.; Zhang, D. Electromagnetic Nanocomposites Prepared by Cryomilling of Polyaniline and Fe Nanoparticles. *J. Polymer Sci.* **2008**, *46*, 1571.

14. Lim, J.; Chong, M.; Chan, J.; Teoh, S. Polymer Powder Processing of Cryomilled Polycaprolactone for Solvent-Free Generation of homogeneous Bioactive Tissue Engineering Scaffolds. *Small*, **2014** (DOI: 10.1002/sml.201302389).
15. Witkin, D. B.; Lavernia, E. J. Synthesis and Mechanical Behavior of Nanostructured Materials via Cryomilling. *Prog. Mater. Sci.* **2006**, *51*, 1.
16. Parquette, B.; Giri, A.; Daniel, J.; O'Brien, D. J.; Brennan, S.; Cho, K.; Tzeng, J. *Cryomilling of Thermoplastic Powder for Prepreg Applications*; ARL-TR-6591; U.S. Army Research Laboratory: Aberdeen Proving Ground, MD, 2013.

List of Symbols, Abbreviations, and Acronyms

3-D	three-dimensional
ARL	U.S. Army Research Laboratory
FESEM	field emission scanning electron microscope
FOB	forward operating base
LN ₂	liquid nitrogen
mm	millimeter
PET	polyethylene terephthalate
PSD	particle size distribution
SEM	scanning electron microscopy

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J SANDS
J TZENG
E WETZEL
RDRL WMM B
T BOGETTI
B CHEESEMAN
C FOUNTZOULAS
G GAZONAS
D HOPKINS
T JENKINS
B LOVE
P MOY
B POWERS
C RANDOW
T SANO
R WILDMAN
C YEN
RDRL WMM C
J LA SCALA
RDRL WMM D
R CARTER
K CHO
A GIRI
F KELLOGG
M PEPI
S WALSH
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M COLE
J SWAB
J ADAMS
RDRL WMM F
H MAUPIN
S GREND AHL
L KECSKES
E KLIER
RDRL WMM G
A RAWLETT

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D LYON
S SCHOENFELD
RDRL WMP A
R MUDD
RDRL WMP B
C HOPPEL
RDRL WMP C
T BJERKE
RDRL WMP D
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