

Cryogenic Mechanical Alloying of Poly (ether ether ketone) – Polycarbonate Composite Powders for Selective Laser Sintering

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Abstract

Mechanical alloying is a solid state processing technique traditionally used in the metallurgical industry to extend solubility limits in alloy systems. Mechanical alloying can also be used to blend polymer systems at ambient or cryogenic temperatures. In this work, cryogenic mechanical alloying was employed to create composite powders of Poly (ether ether ketone) (PEEK) – Polycarbonate (PC) for use in selective laser sintering applications. The microstructural development of the PEEK-PC system that occurs during laser sintering and the effects of this microstructure on mechanical properties of the laser sintered parts was investigated.

Key Words: Selective Laser Sintering (SLS), Mechanical Alloying, Poly (ether ether ketone) (PEEK), Polycarbonate (PC)

Introduction

Mechanical alloying (MA) was first developed at The International Nickel Company, Inc. as a means of producing oxide dispersion strengthened nickel-based superalloys. This process is now a widely used fabrication method in the metals industry. Mechanical alloying is employed to enhance microstructural control and extend solubility limits in metal alloys^[1]; however, since the late 1980s efforts have been made to apply this technology to the processing of polymer composites and blends. Research in mechanical processing of polymers has shown improved ultimate tensile strengths of mechanically processed polymers^[2] and the ability to blend immiscible polymers with no significant degradation^[3].

The device used for mechanical alloying in this study is the vibratory mill, which provides the highest energy collisions of any milling device available. Figure 4 shows a schematic representation of the motion of a vibratory mill; the arrows indicate the axis of motion of the milling vial (B). Motion of the milling vial results in collisions between the milling media (A).

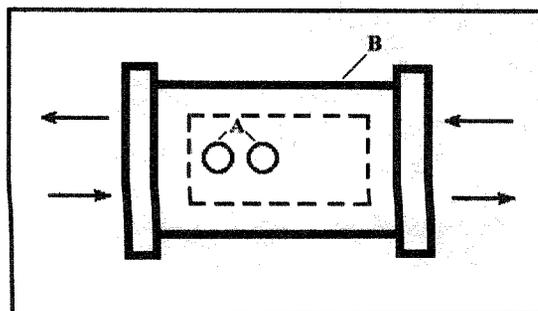


Figure 4: Schematic representation of a vibratory mill.^[1]

Typically, at least two balls (milling media) are used in this type of mill. Due to a decrease in the kinetic energy of the collisions with increasing number of collisions, there is a limit to the benefit of adding more balls. The vibratory mill can also be outfitted to operate at cryogenic temperatures, often required to mill polymers whose melting and glass transition temperature are near or below room temperature. Cryogenic mechanical alloying (CMA) also results in faster particle size reduction because of the increased brittleness of the polymer at low temperatures. Mixing of the polymers is done when powder particles are trapped between the balls during rapid high-energy collisions with each other and the container walls. The powders are repeatedly fractured and “welded” together by the collisions, which results in the mixing of the powders and refining of the particle microstructure^[4]. Figure 5 shows a schematic representation of the welding and fracture of particles. The particles in the *A* region are being welded together into a lamellar two-phase structure. The particles in region *B* are being fractured, thus reducing the particle size.

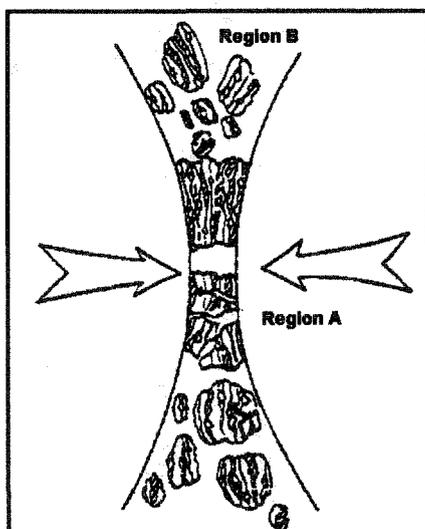


Figure 5: Schematic Representation of high-energy collision.^[1]

As the milling time increases, the number of fractures and welds per particle is increased. This results in increased refinement of the particle morphology. Figure 6 shows the progression of particle morphology refinement with increased milling time.

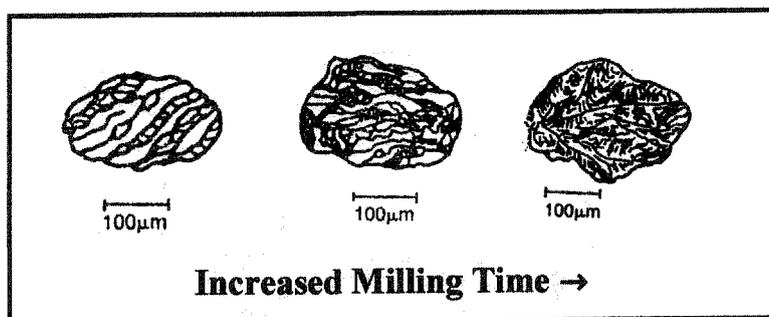


Figure 6: Particle Morphology Refinement.^[5]

The characteristic plate-like shape of mechanically alloyed polymers is also illustrated in Figure 6. The individual plates are made up of multiple lamellar structures of varying orientation. The

number of different lamellar orientations in a particle increases with time, but the spacing of the lamella decreases with time^[4], as shown in Figure 6.

The objective of the work presented here was to demonstrate the feasibility of using cryogenic mechanical alloying to produce micro-composite powders for use in selective laser sintering. The goal of using cryogenic mechanical alloying to produce powders for SLS application is to improve the mechanical properties of parts made by SLS. Therefore, parts produced by SLS could be used as fully functional parts. The material system chosen to be cryogenically mechanically alloyed is a polymer-polymer composite of polycarbonate and poly(ether ether ketone).

Experimental Equipment

Two pieces of equipment have been designed as a part of this research, a cryogenic vibratory ball mill and a laboratory scale selective laser sintering unit. The following two sections describe the operation of these two devices.

The Cryogenic Vibratory Ball Mill

Mechanical alloying of the composite blend for selective laser sintering was accomplished using a cryogenic vibratory ball mill (shown in Figure 7) designed to make polymeric composite powders. Figure 8 shows a schematic representation of the operation of the cryogenic vibratory ball mill.

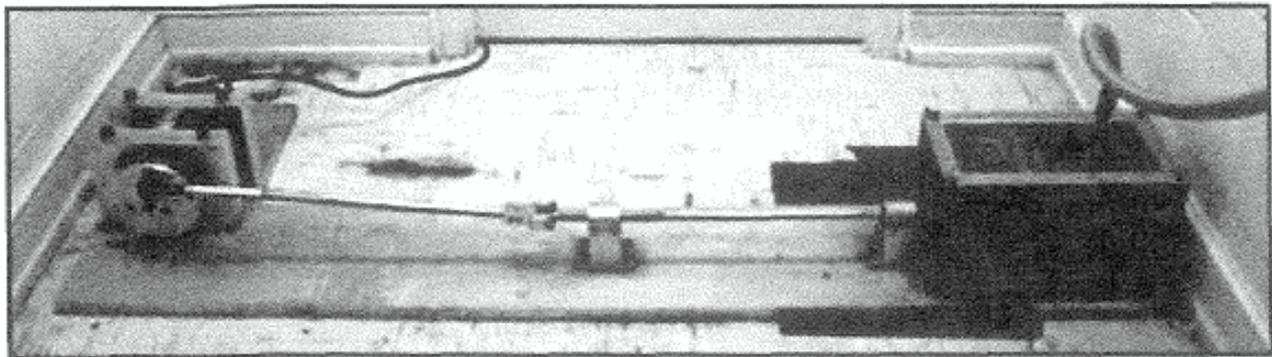


Figure 7: Cryogenic vibratory ball mill.

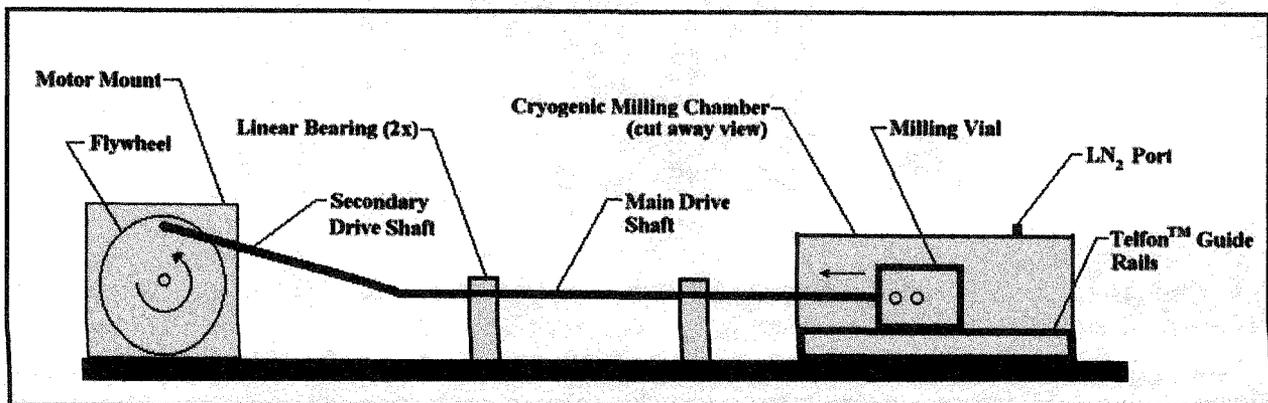


Figure 8: Schematic of the operation of the cryogenic vibratory ball mill.

A one half horsepower motor drives the cryogenic vibratory ball mill. The rotational motion of the motor is converted into linear motion by a flywheel and a wishbone linkage that connects the primary and secondary drive shafts. The milling vial, which rides on three Teflon™ guide rails, is connected to the opposite end of the main drive shaft. As the motor rotates, the milling vial and its contents (powdered material and the mixing media) are oscillated at approximately 10 Hz through a 4.2 inch linear range of motion. During operation, the bottom inch of the cryogenic milling chamber is filled with liquid nitrogen which is continuously fed through the port in the acrylic lid. The steady-state temperature in the cryogenic mill approaches that of liquid nitrogen, -196°C. Exact measurement of the temperature inside the milling vial is not possible because of the vigorous motion imparted to it. Stainless steel was chosen as the material for the milling vial and balls because its fracture toughness at cryogenic temperatures is such that the impacting surfaces do not erode and contaminate the samples. Each run of the cryogenic vibratory ball mill produces approximately 40mL of mechanically alloyed powder.

2.2 Laboratory Scale Selective Laser Sintering Unit

The selective laser sintering unit, shown in Figure 9 is a laboratory scale machine which can be used to test the applicability of a material to SLS processing using only small amounts of the material. Design and development of the lab-scale SLS unit was necessitated by the fact that only 40 ml of composite powder are produced for every run of the cryogenic vibratory ball mill. In the lab-scale SLS unit's present configuration, part geometries are limited to plaques and other flat test specimens.

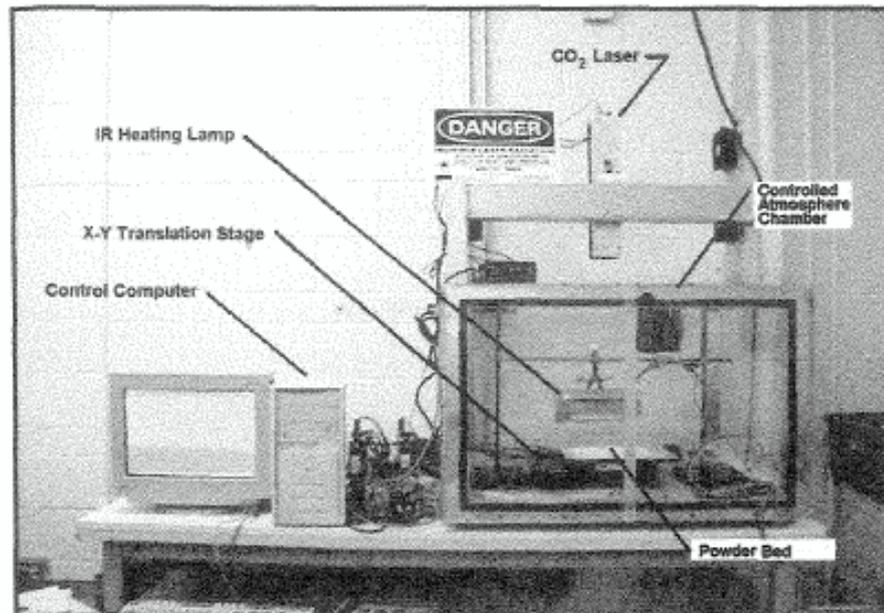


Figure 9: Laboratory scale selective laser sintering unit.

The laser, mounted vertically, in the SLS unit is a CO₂ laser with a nominal power of 10W. The translation of the system, mounted in the bottom of the enclosure, has a travel of 152mm x 152mm. The powder bed was made by smoothing the powder between two gage blocks with a doctor blade. Additional layers were added by placing shim stock on the gage blocks and smoothing the new layer of powder with the doctor blade. DTM Polycarbonate was laser sintered in the lab-scale unit to provide a benchmark for the capabilities of the unit and guide the design improvements. The benchmark tests were done on ASTM D 638 Type M-II⁽⁶⁾ tensile

specimens. Five tensile specimens, each consisting of five 0.25mm thick layers, were laser sintered at the following conditions: 2.6 W laser power, 66 mm/s scan speed, 0.2 mm scan spacing, 115°C bed temperature (obtained using an IR lamp), 3mm spot size. The average ultimate tensile strength (UTS), strain to failure, and elastic modulus of the specimens were 3.0 ± 0.6 MPa, 5.8 ± 0.5 % and 71.8 ± 16.8 MPa. DTM reports a UTS of 23 MPa^[7], a strain to failure of 5%^[7], and an elastic modulus of 1220 MPa^[7] for samples produced in a Sinterstation® under standard operating conditions. The porosity of each of the tensile specimens was also determined using ASTM C 373-88^[8] and the average porosity was calculated to 59 ± 2.1 %. The high porosity and low UTS relative to DTM's published value result from the fact that the lab-scale SLS unit is still in the developmental stages.

Procedure

PEEK-PC sample production

Composite powders of 50vol% Victrex™ PEEK and 50vol% DTM Polycarbonate were made using the cryogenic vibratory ball mill. The samples were milled for one hour and the charge ratio (mass of powder/ mass of milling media) used was 0.45. Each one-hour run produced 25.6 grams of the PEEK-PC composite powder. After milling, the PEEK-PC composite powder was laser sintered into ASTM D 638 Type M-II^[6] tensile specimens. Each specimen was 4 layers thick and was produced using the following conditions: 6 W laser power, 66 mm/s scan speed, 0.2 mm scan spacing, 125°C bed temperature, 3mm spot size, 0.25mm layer thickness.

Mechanical testing

Five PEEK-PC laser sintered tensile specimens, made using the aforementioned conditions, were tested at 0.2 mm/s using a Texture Technologies Texture Analyzer load frame. Stress-strain curves as well as the UTS, elastic modulus, and strain to failure were recorded for each specimen. The average and standard deviation of the UTS, strain to failure and elastic modulus for the five specimens was calculated.

Porosity testing

After mechanical testing, a 25x10 mm strip was cut from each of the tensile specimens and porosity testing was performed using the Archimedes method, based on ASTM C378-88^[8] with ethanol as the submersion liquid. The porosity of each specimen (the percentage of sample volume occupied by pores), was calculated along with the average and standard deviation for the five samples.

Scanning electron microscopy

Scanning electron micrographs of the as received DTM Polycarbonate, cryogenically mechanically alloyed PEEK-PC composite powder, and laser sintered PEEK-PC (same sintering conditions as above), were taken using an International Scientific Instruments SX-40 with an accelerating voltage of 20kV.

Results and Discussion

Figure 10 shows a PEEK-PC tensile specimen laser sintered with the lab-scale SLS unit. No gross distortion or geometric inaccuracies are visible from the photo. The tensile specimen does, however, exhibit a large number of relatively large pores throughout the surface of the specimen.

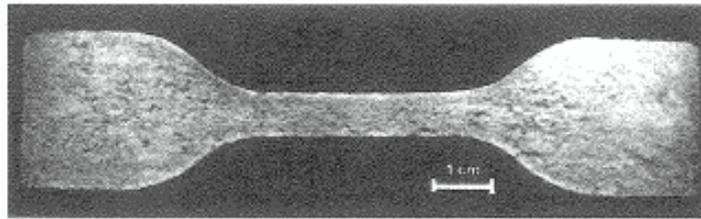


Figure 10: PEEK-PC tensile specimen made with the lab-scale SLS unit.

Mechanical testing

Figure 11 shows the stress strain curves for the PEEK-PC tensile specimens that were laser sintered using the lab scale SLS unit. The average elastic modulus, UTS and strain to failure were calculated to be 103.2 ± 12.1 MPa, 2.8 ± 0.4 MPa and $2.7 \pm 0.3\%$. The authors believe that these low UTS and strain to failure values are a result of the large porosity observed in the laser sintered tensile specimens that results from the difficulty in achieving a smooth uniformly dense powder bed with the PEEK-PC powders. The elastic modulus of the PEEK-PC laser sintered using the lab-scale SLS is 43% higher than the elastic modulus of the DTM PC laser sintered using the lab-scale SLS unit.

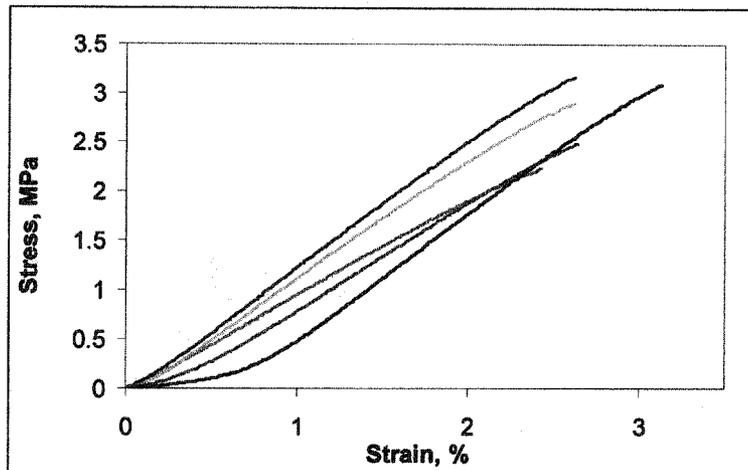


Figure 11: Stress-strain curves for laser sintered PEEK-PC tensile specimens.

Porosity testing

The porosity of the PEEK-PC samples was quantified through porosity testing and was determined to be $54.9 \pm 2.3\%$. The high degree of porosity is attributed to the aforementioned difficulties in achieving a uniform dense packing of the powder bed. The porous surface of a laser sintered PEEK-PC sample is shown in Figure 12.

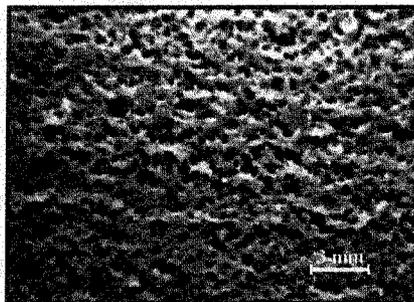


Figure 12: Laser sintered PEEK-PC surface.

Scanning electron microscopy

Figures 13 and 14 are scanning electron micrographs of the as-received DTM Polycarbonate and the PEEK-PC composite powders that resulted from 1 hour of cryogenic mechanical alloying.

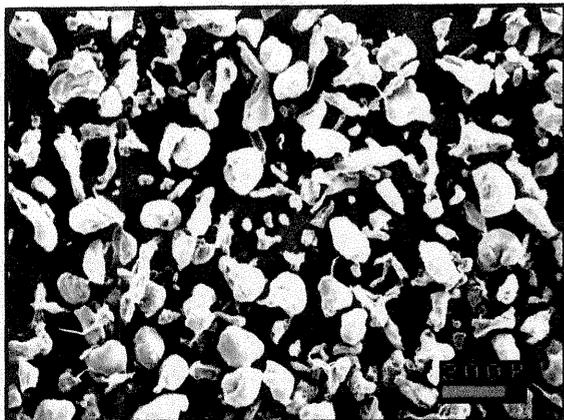


Figure 13: SEM micrograph of DTM Polycarbonate powder.

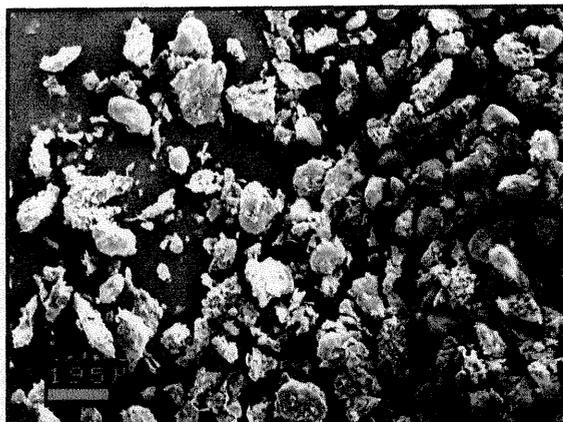


Figure 14: SEM micrograph PEEK-PC composite powder.

No drastic size differences are observed between the PC and PEEK-PC particles but the latter particles appear to be much rougher and more plate-like. The authors attribute the difficulty in obtaining a smooth powder bed to the surface roughness and plate-like shape of the powder particles since the rough plate-like particles do not roll over one another as well as particles with smooth surfaces.

Figure 15 shows a scanning electron micrograph of a cross sectioned surface of a PEEK-PC laser sintered sample. Unsintered particles are visible between the dense sintered layers shown in Figure 15. The presence of these unsintered particles suggests the laser sintering parameters employed in producing this sample were inadequate in sintering through the interlayer. Insufficient interlayer sintering could result from using a scan speed that is too high, laser power that is too low, layer thickness that is too large, or a combination of these.

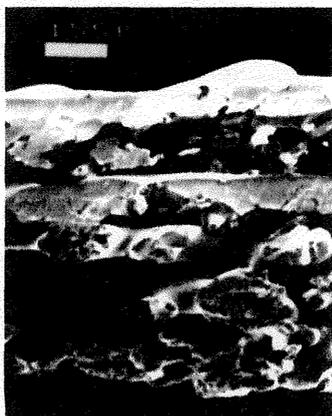


Figure 15: SEM micrograph of PEEK-PC laser sintered sample.

Conclusion

The low UTS and strain to failure values measured and high porosity of the PEEK-PC samples laser sintered with the lab-scale SLS unit were attributed to difficulty in achieving a smooth, uniformly dense powder bed and inadequate laser sintering parameters which resulted in large porosity and insufficient interlayer sintering. The problem obtaining a smooth uniformly dense powder bed were attributed to the surface roughness of the PEEK-PC powder particles. It was determined from the SEM micrograph of the laser sintered PEEK-PC cross-section that the laser sintering parameters used to produce the current samples results in insufficient interlayer sintering.

Future Work

Continued development of the lab-scale SLS unit will improve the quality the samples; areas of concentration include reduction of beam spot size and improved powder delivery. These improvements are expected to result in improved mechanical properties of laser sintered samples. Investigation into methods of smoothing the rough surfaces of the PEEK-PC will also be undertaken. Investigation into the formation of other SLS material systems formed by cryogenic mechanical alloying will be ongoing.

Acknowledgements

The authors would like to thank DTM Corporation for supplying the DTM Polycarbonate. The authors would also like to thank Dr. Alex Aning for his continued support and input into our mechanical alloying research. Additional thanks goes to Julie Martin for performing the microscopy.

References

- [1] D. R. Maurice & T. H. Courtney, *Metall. Trans.*, 21, 289, 1990.
- [2] J. Pan, W. J. D. Shaw. "Effects of Processing Parameters on Material Properties of Mechanically Processed Polyamide." *Journal of Applied Polymer Science*, Vol. 56, John Wiley & Sons, 1995.
- [3] T. Ishida. Mechanical Alloying of Polytetrafluorethylene with Polyethylene." *Journal of Materials Science Letters*, 13, 1994.
- [4] Farrell, M. P., R. G. Kander, and A. O. Aning, "Polymer Blends Formed by Solid State Mechanical Alloying", *Journal of Materials Synthesis and Processing*, 4, pp 151-161, 1996.
- [5] R. Sundaresan and F. H. Froes, *J. Metals*, 39, 22, 1987.
- [6] ASTM Standard D638M-93, "Standard Test Method for Tensile Properties of Plastics (Metric)".
- [7] <http://www.dtm-corp.com/Technology/Materials/polycarb.htm>
- [8] ASTM Standard C373-88, "Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products".