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Enhancing Plastic Recycling Through Nano-Scale Structure Analysis in Custom Block Copolymer Filaments

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Abstract: As plastic production continues to increase, new methods to combat plastic waste are needed. This paper explores upcycling, a way to increase the utility or value of waste plastic. This can be done using block copolymers as compatibilizers. Block copolymers are made of two immiscible polymer blocks that phase separate on the nanoscale, forming small structures. The orientation of these nano-scale structures influences mechanical properties, and we show that orientation can be controlled by directional 3D (three dimensional) printing. Using small-angle X-ray scattering (SAXS), we analyze block copolymer filaments extruded at varying speeds. The SAXS data provide a baseline understanding of nano-scale structure in these unique filaments for future use in 3D printing experiments.

1. Introduction and Background

As plastic use continues to grow, global production is expected to accelerate. 42% of this plastic is used in packaging applications (single use) and will end up as waste [1]. Additionally, only 9% of plastic created has been recycled (600 million tons of the estimated 6.3 billion tons created) [1]. The other 91% enters waste streams (landfill or incinerator) causing environmental damage. Because of these concerning statistics, new alternatives for plastic recycling are needed. This project proposes the use of polymer upcycling via a compatibilizer for 3D printing applications as an alternative to conventionally recycling or disposing plastic.

1.1 Block Copolymers and Upcycling

To effectively handle mounting volumes of plastic, new capabilities for plastic waste disposal are necessary. This project aims to develop an alternate upcycling method by using block copolymers as compatibilizers for polyethylene (PE). Block copolymers contain two or more immiscible polymer blocks that undergo self-assembly processes to form nano-scale structures (see figure 1). Compatibilization refers to the process by which polymers that normally do not mix can be combined. In this case, PE will be combined with a custom block copolymer made of styrene and ethylene-propylene. This can be done because PE is made of long chains of CH_2, which should mix with the ethylene-propylene block of our block copolymers, generating the outlet for waste plastic. Figure 1 shows a visual description of the block copolymers used in this project.

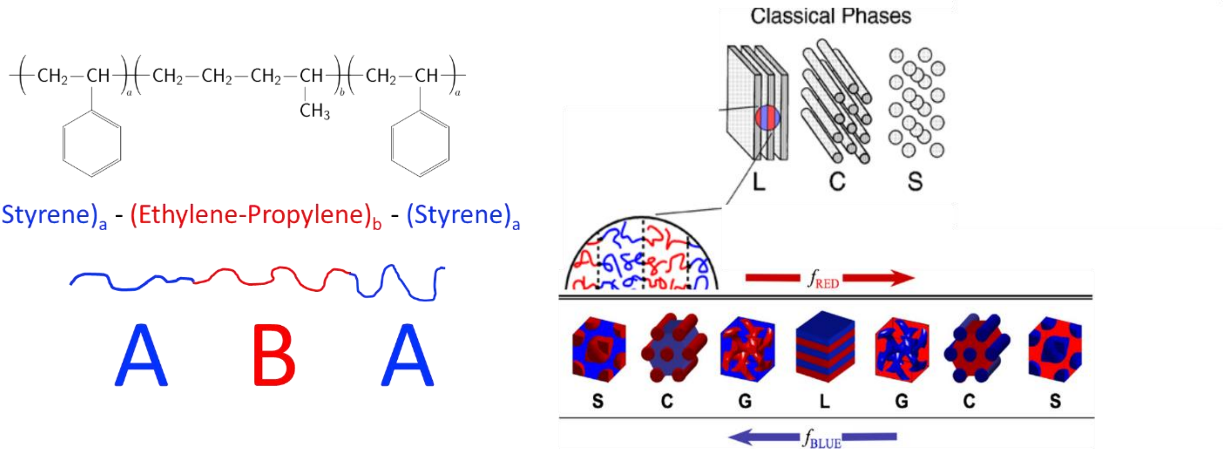
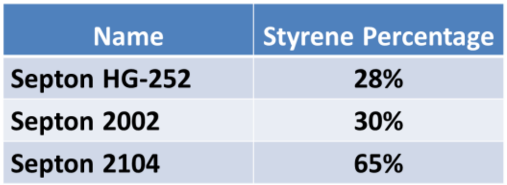


Figure 1. A visualization of the chemical structure of our block copolymers (left) and a description of lamellar (L), cylindrical (C), and spherical (S) crystalline morphologies (right). The red and blue depiction at bottom right shows different components of the block copolymers aligning in bulk to form nano-scale structures. This figure adapted from [2, 3] .

For this project, three different block copolymers are used. They were obtained from Kuraray and came in pellet form, each with a different styrene content as shown in figure 2. The variation in styrene percentage will cause each block copolymer to form different nano-scale structures shown in figure 1.



Name	Styrene Percentage
Septon HG-252	**28%**
Septon 2002	**30%**
Septon 2104	**65%**

Figure 2. A description of the content of our block copolymers used in these experiments.

Adding PE will swell the ethylene-propylene domain, thus decreasing the styrene percentage in the block copolymers. This may change the type of nano-scale structure formed, but this is a problem to be addressed deeper into the project. The advantage of using block copolymers as compatibilizers is their unique ability to form nano-scale structures that influence mechanical properties. These properties can be manipulated by directional 3D printing, causing identical shapes to yield dissimilar properties. The process that enables a change in mechanical properties is shear alignment[4], a phenomenon that causes nano-scale structures to align along the axis of shear forces. Therefore, when block copolymer filaments are 3D printed, aligned nano-scale structures follow the print head's path. Consequently, we hypothesize by printing shapes in different ways (horizontal layers, alternating layer directions, vertical layers, etc.), we can affect the mechanical properties of a printed shape.

1.2 X-ray Scattering

SAXS is a powerful method used to measure orientation and domain structure as a function of extrusion conditions. Additionally, it can give information on geometry of crystal lattice structures in polymers [2]. Though structures formed in block copolymers will not be "crystalline," they are crystal-like meaning SAXS will be a valuable tool for determining type and orientation of nano-scale structures. SAXS requires a complex and expensive system, and there are a limited number of laboratory SAXS instruments in the United States. Conveniently, a Xenocs Xeuss 3.0 X-ray instrument is present at the Los Alamos National Laboratory (LANL) and is the instrument used to collect data in this paper. An example SAXS setup is shown in figure 1.

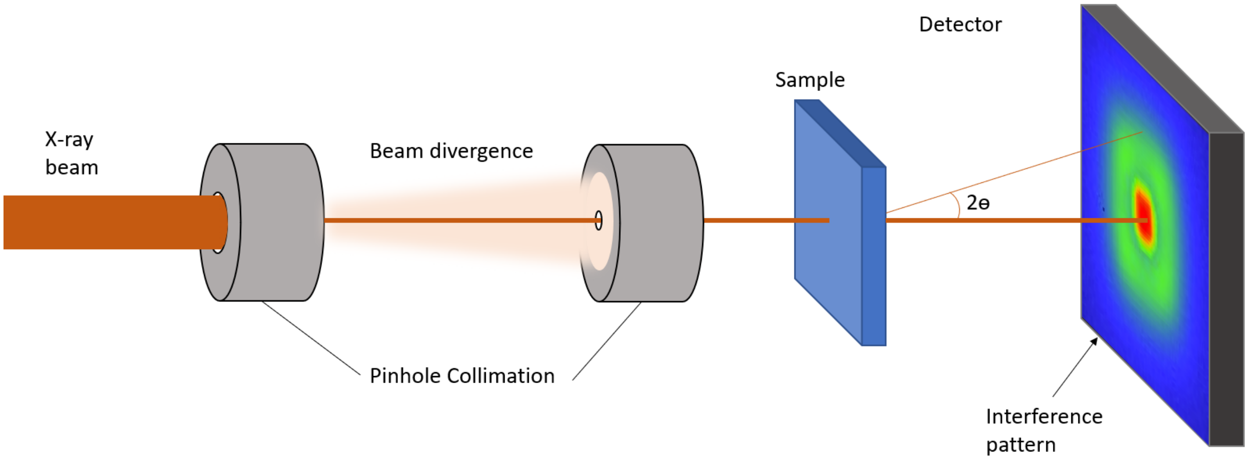


Figure 3. A common setup for SAXS measurements. The initial X-ray beam is monochromatic and collimated via pinholes. The beam is passed through the sample and scattered X-rays are picked up on a detector.

In a SAXS system, a beam of hard X-rays is prepared via an X-ray source and sent through a mirror or crystal monochromator. Next, the beam of X-rays passes through a series of pinholes for collimation. At this point, the beam is ready for interaction with a sample. As the beam enters the sample, X-rays exhibit elastic scattering behavior and are deflected off path by the sample's internal structures. Additionally, X-rays can exhibit diffraction behavior as they interact with the sample. The scattered photons then interact with a detector at the end of the system, and the scattering or diffraction pattern is recorded [3]. From there, an experimentalist can use a variety models and techniques to analyze the scattering data.

1.3 Modeling and Interpretation

To identify structures present in block copolymers, a technique known as Bragg Scattering Analysis will be used. This technique uses the distance between peaks in a 1D (one-dimensional) scattering curve to identify nano-scale structure via the “decoupling approximation” [5] where the scattered intensity I is given by

$$I(\boldsymbol{Q}) = (b_1 - b_2)^2 \rho_N P(\boldsymbol{Q})[1 + \beta(\boldsymbol{Q})(Z(\boldsymbol{Q}) - 1)G(\boldsymbol{Q})]$$

Where **Q** is the scattering vector, a reciprocal space measure quantifying locations of electrons picked up on a system’s detector. b_1 & b_2 are the scattering cross-sections of the matrix and the particle, ρ_N is the particle number density, $P(\boldsymbol{Q})$ is the particle form factor, $\beta(\boldsymbol{Q})$ is the fluctuation term related to particle polydispersity, $Z(\boldsymbol{Q})$ is the lattice factor, and $G(\boldsymbol{Q})$ is the Debye-Waller factor. [5]

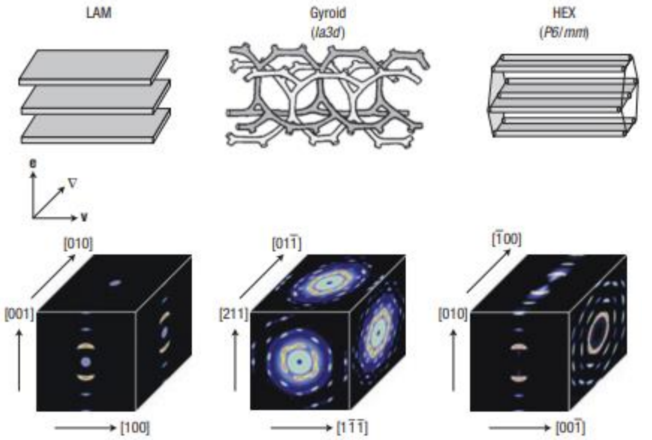


Figure 4. An example of regular, oriented structures and their corresponding calculated scattering patterns. Some structures shown in figure 1 are shown here along with their calculated scattering patterns. Figure from [5].

The decoupling approximation enables us to use positional ratios of peaks in a 1D scattering graph to identify structures formed by each block copolymer. This technique is used on filaments and 3D printed shapes to identify nano-scale structures and pinpoint their orientations (see figure 4 for an example of regular orientations and their corresponding calculated scattering patterns). The data give us a baseline for further investigation into how adding PE will change the block copolymers and affect their ability to 3D print.

2. Method development

To establish groundwork for the upcycling effort, experiments are conducted on the raw block copolymers to understand their characteristics before PE is added. These experiments include extruding filaments at different speeds and attempting to 3D print different shapes with the filaments.

2.1 Extruding

To start, each block copolymer is extruded at six different speeds through a FilaBot EX2 extruder visualized in figure 5.

Figure 5. A visualization of the filament extrusion process. First, polymer pellets are loaded into the extruder. The extruder melts the polymer and extrudes it at a controlled diameter to make 3D printable filament. Photos adapted from [6-8].

The extruding is done at a temperature of 200C, which gives good, consistent melting of pellets without degrading them as confirmed by TGA (thermogravimetric analysis) seen in figure 6.

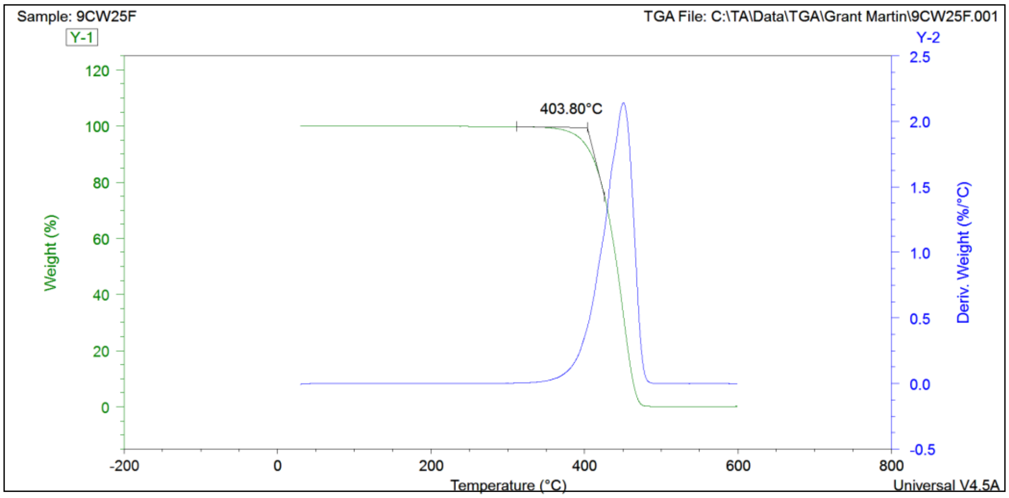
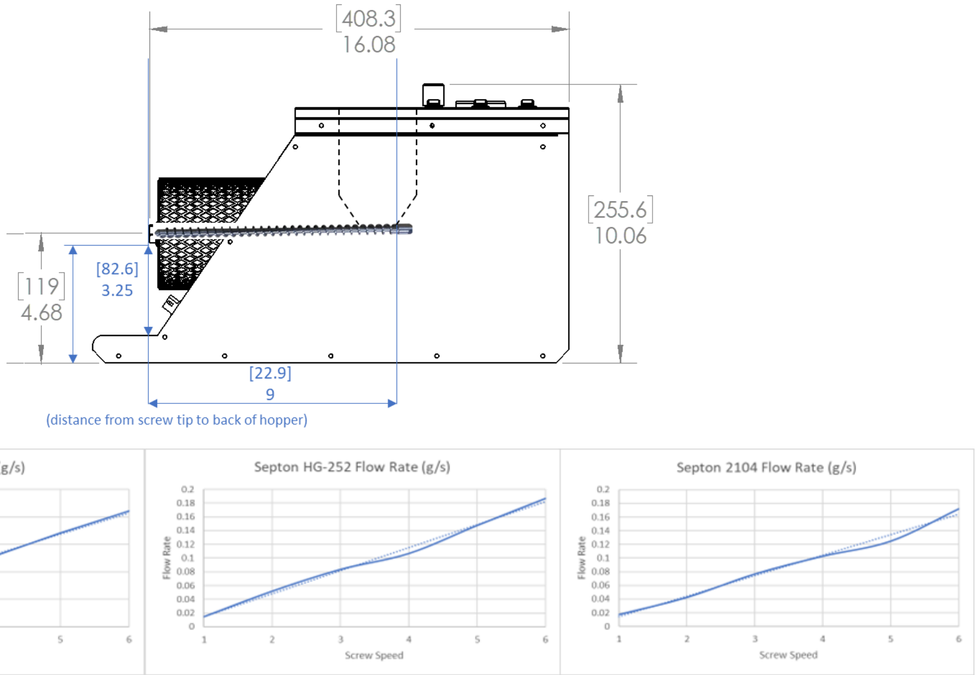


Figure 6. A TGA graph showing the degradation onset point of Septon HG-252. In this experiment, extrusion is done at 200C, well below the degradation temperature.

The block copolymer pellets are poured into the extruder's hopper, the temperature raised to 200C, and the extruder screw turned on. When activated, the screw pushes melted filament out of the nozzle at a specified speed (See figure 7).



Screw Speed	Length (in)	Time (s)
1	54	327
2	52	154
3	53	106
4	54.5	71
5	57	54
6	53	41

Screw Speed	Length (in)	Time (s)
1	51	474
2	52.5	158
3	52	106
4	51.5	80
5	53.5	61
6	51	44

Screw Speed	Length (in)	Time (s)
1	51	437
2	53	174
3	51	93
4	52	72
5	51.5	56
6	52	42

Figure 7. A schematic of the FilaBot EX2 extruder (top). The dotted lines represent the hopper's location. The screw at the base of the hopper drives melted polymer out the nozzle, producing filament. The graphs (bottom) show filament flow rates as a function of screw speed along with tables showing the time it took to extrude a given length of filament.

The screw generates shear flow which drives orientation of domains in the polymer during its time in the extruder. Once pushed out, the filament is cooled by passing over a series of fans and wrapped on a spool to be used in a LulzBot Mini 2 3D printer.

2.2 3D Printing

FDM (fused deposition modeling) 3D printing is a cost-effective and versatile way to 3D print commercial and self-made filaments. Producing good quality prints while being affordable has led FDM printers to become popular among hobbyists and scientists alike.

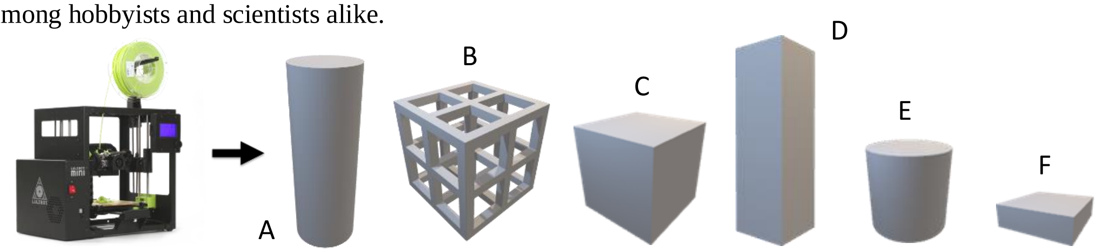


Figure 8. The LulzBot Mini 2 and shapes used for prints during this project. The Lulzbot Mini 2 printer is shown on the left (image from [9]). The large cylinder (A) and rectangular prism (D) are shapes made for mechanical testing. The lattice (B), cube (C), and short cylinder (E) are test shapes used to optimize settings. The small rectangle (F) is the shape used for SAXS measurements.

The LulzBot Mini 2 uses a direct drive extruder to push filament out of its hot end. This is problematic for soft filaments such as commercially available TPU (thermoplastic polyurethane). While easy to extrude, Septon 2002 and Septon HG-252 both have a low styrene percentage meaning they are soft and rubbery, making them harder to 3D print. Septon 2104, while still easy to extrude, is similar in stiffness to common filaments such as PLA (polylactic acid) or ABS (acrylonitrile butadiene styrene). This allows the printer to easily drive the filament through its hot end. Unfortunately, there are additional challenges with Septon 2104, namely build plate adhesion. To solve this problem, a thin compression molded sheet was made in the shape of the build plate. Once attached via tape, the thin sheet made the block copolymer stick very well, as similar polymers are more likely to bond with each other [10]. Now that the filament can stick to the build plate, the challenges are not over. The LulzBot Mini 2 runs on Cura, a software package containing hundreds of settings. Optimizing print settings requires trial and error: Many settings have been tested over the course of this project, and more are currently being tested. For an example, see figure 9.

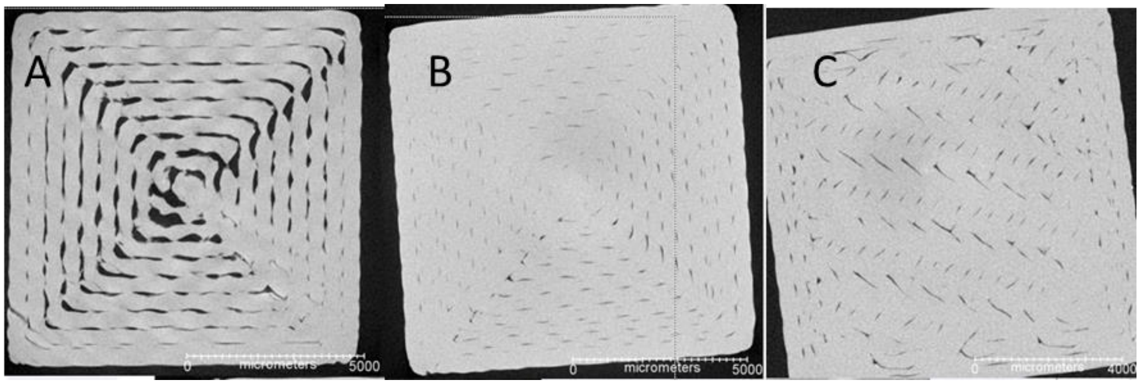


Figure 9. CT (computed tomography) images showing changes in 3D printed shapes as a result of different settings in Cura.

Figure 9A shows a concentric infill pattern with an infill distance of 0.5 mm. This results in air gaps (the black regions). The same concentric pattern is shown in figure 9B but with a smaller infill distance of 0.4 mm. This results in less airgaps present in the sample, shown by the absence of dark spots. Figure 9C shows a pattern called “lines,” yielding a different infill pattern. Finding ideal settings is still a work in progress, but most of the groundwork has been done at this point.

3. Results

The block copolymer SAXS experiment looked to identify and examine changes in nano-scale structure as a function of extruder screw speed (see figure 7). This experiment was done on the same block copolymers shown in figure 2. The data from the Xeuss instrument initially looks like the plot shown in figure 10 or the 2D (two dimensional) scattering pattern shown below in figure 11.

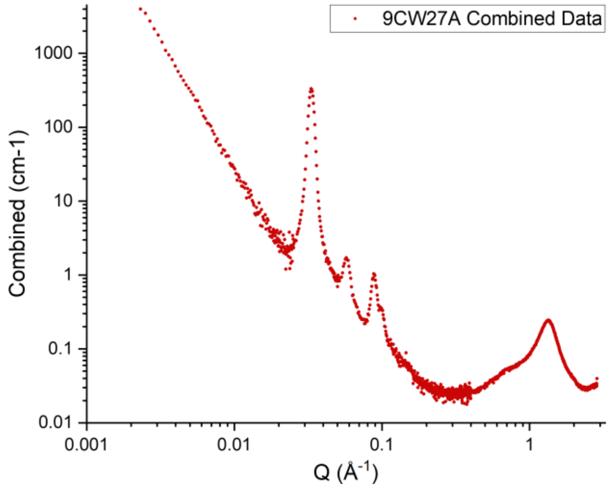


Figure 10. An example of raw data plotted before any extra analysis is conducted. This data is on a Septon 2104 sample extruded at its slowest speed.

The 2D scattering patterns recorded on the detector of the Xeuss instrument are Septon 2002 extruded at its slowest (left image) and fastest speeds (right image) respectively. The X-axis is notated as **Q**, a representative inverse length scale which is a product of the Fourier transform done to produce each image. Each 2D scattering pattern is a Fourier transform of the 3D structure in the filaments. Because the sample is not rotated, information in one dimension is lost, giving the 2D scattering pattern. For these experiments, a 2D pattern provides enough information to perform our analysis.

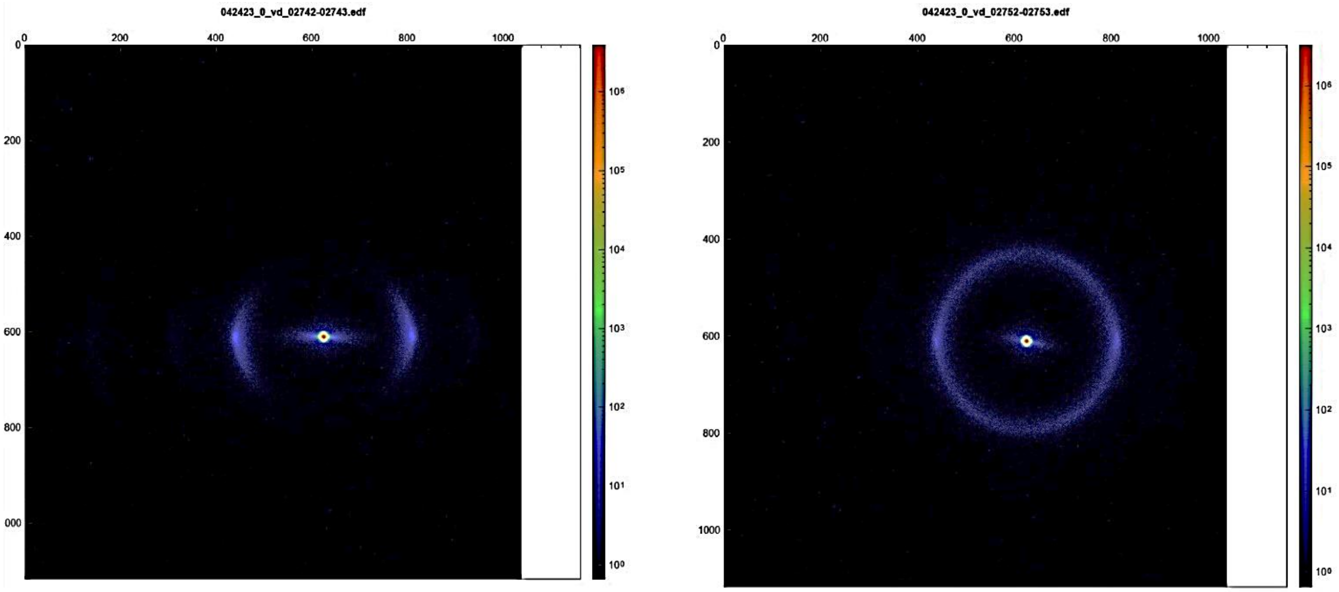
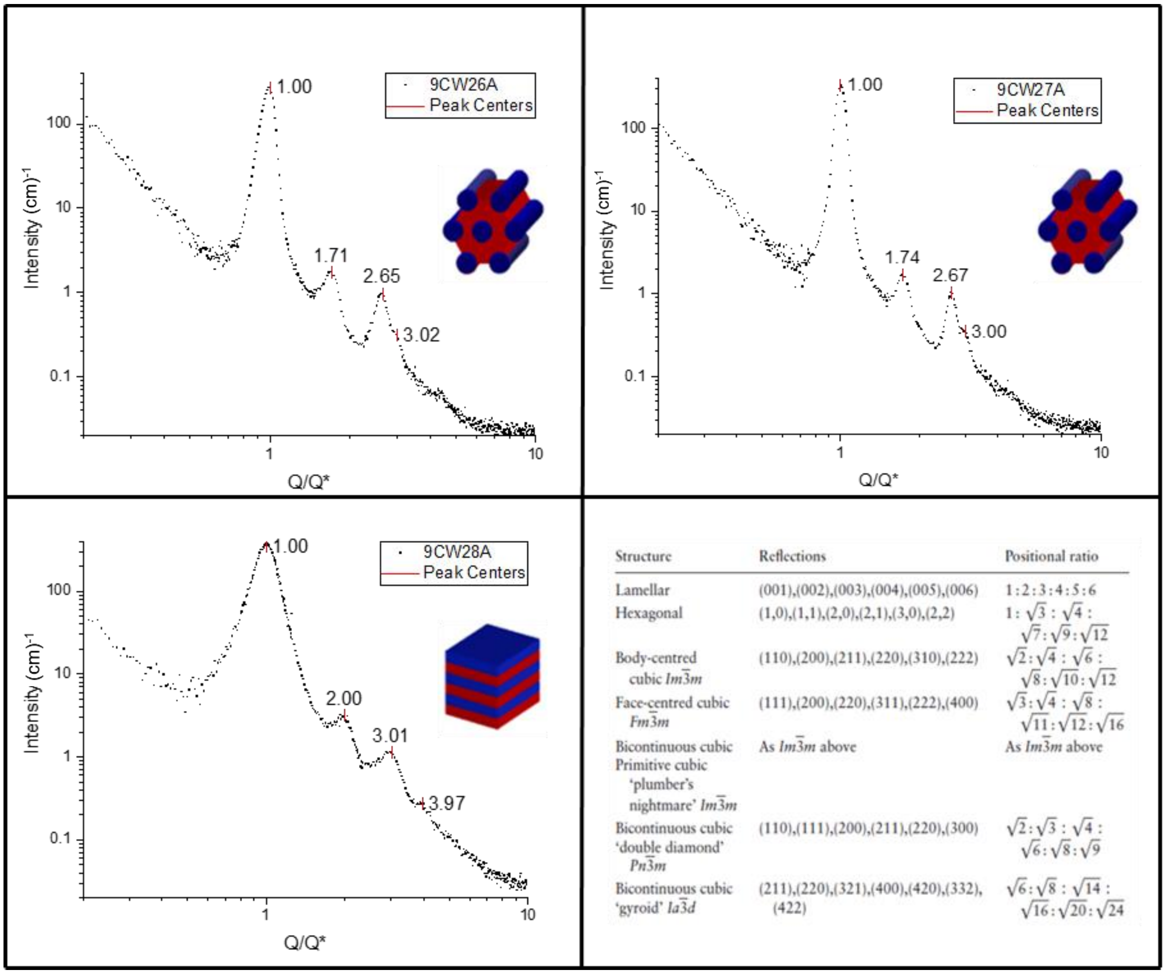


Figure 11. Two-dimensional scattering patterns imaged by the detector in the Xeuss 3.0 for the 9CW26A(left) and 9CW26F (right) samples.

The slower extrusion speed makes a scattering pattern that displays less of a ring (left) than the faster extrusion speed (right). Therefore, we infer that internal structures are less aligned in the sample that was extruded faster. Less order causes the scattered X-rays to travel in a wider range of angles relative to the slower extrusion speed. These patterns provided a source of confusion initially, as the filament extruded at slower speeds will experience less shear force as it passes through the extruder. However, slower extrusion speeds mean the filament has a long residence time. Even though the slowly extruded filament experiences less shear force as it exits the extruder, the structures inside the filament have more time to move and align, analogous to slowly cooled glass having less internal stress than rapidly cooled glass.

To make sure each sample has the morphology advertised by Kuraray, the 2D scattering patterns in figure 6 are used to develop the 1D scattering curves seen in table 1. These graphs are plots of intensity starting at the center of the 2D pattern and extending in a straight line to an edge. The average of intensities is taken across the whole image, meaning images displaying less order (right image of figure 6) will form wider peaks. This happens because X-ray intensity is distributed across a larger area of the detector. Highly ordered patterns such as the left image in figure 6 will have localized areas where the scattered light is directed. Therefore, regions of the 2D pattern will have very high or low intensity, causing peaks to be much narrower relative to the ring image, where photons are distributed across a larger area. This series of experiments looked at many different extrusion speeds. To understand the internal structure, Bragg Scattering Analysis was used [11]. This technique uses Bragg peak positional ratios to identify a sample's crystalline or crystal-like morphology [5, 11]. Table 1 shows the peak locations and their corresponding morphology that they display.



Structure	Reflections	Positional ratio
Lamellar	(001),(002),(003),(004),(005),(006)	1 : 2 : 3 : 4 : 5 : 6
Hexagonal	(1,0),(1,1),(2,0),(2,1),(3,0),(2,2)	$1 : \sqrt{3} : \sqrt{4} : \sqrt{7} : \sqrt{9} : \sqrt{12}$
Body-centred cubic *Im*$\bar{3}$*m*	(110),(200),(211),(220),(310),(222)	$\sqrt{2} : \sqrt{4} : \sqrt{6} : \sqrt{8} : \sqrt{10} : \sqrt{12}$
Face-centred cubic *Fm*$\bar{3}$*m*	(111),(200),(220),(311),(222),(400)	$\sqrt{3} : \sqrt{4} : \sqrt{8} : \sqrt{11} : \sqrt{12} : \sqrt{16}$
Bicontinuous cubic Primitive cubic 'plumber's nightmare' *Im*$\bar{3}$*m*	As *Im*$\bar{3}$*m* above	As *Im*$\bar{3}$*m* above
Bicontinuous cubic 'double diamond' *Pn*$\bar{3}$*m*	(110),(111),(200),(211),(220),(300)	$\sqrt{2} : \sqrt{3} : \sqrt{4} : \sqrt{6} : \sqrt{8} : \sqrt{9}$
Bicontinuous cubic 'gyroid' *Ia*$\bar{3}$*d*	(211),(220),(321),(400),(420),(332), (422)	$\sqrt{6} : \sqrt{8} : \sqrt{14} : \sqrt{16} : \sqrt{20} : \sqrt{24}$

Table 1. 1D scattering curves of Septon 2002 (top left), Septon HG-252 (top right), and Septon 2104 (bottom left) and their corresponding nano-scale structures. For ease of identifying peaks, $\sqrt{3} = 1.73$, and $\sqrt{7} = 2.65$ The table in the bottom right shows positional ratios and their corresponding structures. Adapted from [11]

These results confirm that each block copolymer's internal structure is the same as advertised. For these graphs, the "A" sample (the sample that was extruded the slowest) was used to plot each curve. This meant that each curve is showing the block copolymers at their highest degree of alignment, making the graphs as accurate as possible. Each graph is made by finding the X-axis location of the first peak and normalizing all Q values to that location. The subsequent peaks are then located and compared with the table of positional ratios in the bottom of Table 1.

The first graph of 9CW26 shows only the $\sqrt{12}$ peak missing in the hexagonal cylinder section. This peak may exist as the small bump on the outside of the $\sqrt{9}$ peak, but there is not a significant difference from the background to definitively call it a Bragg peak. Another small feature can be seen in a "shoulder" located after the $\sqrt{7}$ peak, which is labeled as $\sqrt{9}$. While being a small feature, we determine that there is enough of a "shoulder" to justify marking it as a peak. 9CW27 lines up very well with expected values for hexagonal cylinders although it is missing the $\sqrt{4}$ peak. There may be a feature at a Q/Q* value of 2, but it does not exhibit peak behavior as strong as others, so it is excluded. The same idea holds for the $\sqrt{12}$ peak. Lastly, 9CW28 lines up well with lamellar peak locations shown in Table 1. The "4" peak is slightly off, but it is broad and likely includes that value. The Bragg peaks line up well with the values specified in Table 1; however not all peaks are included. This reduction in peak intensity can be caused by destructive interference between X-ray photons. As photons scatter off nano-scale structures separated by just the right distance, the X-rays end up out of phase with one other and the waves cancel out [11]. Omitting the peaks does not change the results however, as it is not required to have every peak specified in Table 1 to make a conclusion about a sample's structure. Overall, peaks lined up with their specified values, clearly showing an accurate morphology for all three samples.

4. Conclusion and Future Work

Polymer upcycling is a challenging task. This paper discusses the groundwork completed to start adding PE to block copolymers for 3D printing applications. Currently, each block copolymer has been extruded at varying speeds, and some of those filaments 3D printed into basic shapes. These filaments have been analyzed using SAXS to verify their internal nano-scale structures. Now, Septon 2002 and HG-252 need to be 3D printed which will be challenging because of their softness. It is important that these block copolymers are printed because their hexagonal structure can lead to printed shapes with unique properties. Additionally, SAXS experiments need to be done on the pellets and 3D printed structures to make sure no changes are taking place during the first extrusion step as the pellets are heated to 200ºC, or the printer's extrusion step when the filament is heated to 210ºC. Lastly, PE needs to be added to the samples. First pure PE will be used, and kinks with extruding and printing worked out. After that, waste PE can be substituted in, and the upcycling process completed.

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